GEMADRAS

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PROCEEDINGS OF THE

# Nuclear Physics And Solid State Physics Symposium

# 1968

SOLID STATE PHYSICS

vol. 2

M A D R A S February 27 – March 1, 1968

ORGANISED BY PHYSICS COMMITTEE DEPARTMENT OF ATOMIC ENERGY GOVERNMENT OF INDIA 45 ° 1 ° 1

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#### PROCEEDINGS OF THE

# NUCLEAR PHYSICS AND SOLID STATE PHYSICS SYMPOSIUM

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# GOVERNMENT OF INDIA

# SYMPOSIUM COMMITTEE

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| BARC | : Bhabha Atomic Research Centre, Trombay, Bombay.        |
|------|--|
| tifr | : Tata Institute of Fundamental Research, Colaba, Bombay |
| SINP | : Saha Institute of Nuclear Physics, Calcutta.           |
| IIT  | : Indian Institute of Technology, Guindy, Madras.        |
| NAL  | National Aeronautical Laboratory, Bangalore.             |
| DAE  | : Department of Atomic Energy, Bombay.                   |

# FOREWORD

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The twelfth annual Nuclear Physics and Solid State Physics Symposium sponsored by the Physics Committee of the Department of Atomic Energy was held at the Indian Institute of Technology, Guindy, Madras during February 27 - March 1, 1968. The Symposium was inaugurated by Dr. A. Ramachandran, Director, Indian Institute of Technology, Guindy, Madras and Dr. B.D. Nagchaudhuri, Member, Planning Commission and Chairman, Physics Committee, Department of Atomic Energy presided.

The scientific sessions covered all the four days of the Symposium. There were 13 invited talks and 162 contributed papers, 75 being in Nuclear Physics and 87 in Solid State Physics. Subjectwise distribution of the contributed papers is given in Table I.

#### TABLE I.

# Distribution of Contributed Papers

|            | Subject                  | No. of papers |
|------------|--------------------------|---------------|
| A.         | Nuclear Physics:         |               |
|            | Nuclear Reactions        | 33            |
|            | Nuclear Structure Theory | 27            |
| ·          | Nuclear Spectroscopy     | 15            |
| •          | Total                    | 75            |
|            |                          |               |
|            | Subject                  | No. of papers |
| <b>B</b> . | Solid State Physics:     |               |
|            | Magnetic Properties      | 39            |
|            | Defects                  | 32            |
|            | Lattics Dynamics         | 11            |
|            | Low Temperature Physics  | 5             |
|            | Total                    | 87            |

We have been faced with the problem of keeping the size of the Symposium Proceedings within manageable limits and we have attempted this time to reduce the physical size by resorting to xerographic reduction. It is felt by the Symposium Committee that the xerographic process should be utilized more fully to keep the size of the Proceedings reasonable as well as to expedite the publication date. If the papers received from the authors conform strictly to the format laid down by the Symposium Committee, they can be xerographed directly and considerable saving of time can be effected. This year's experience shows that all the papers were not with the Symposium Committee by the time of the Symposium and extra time had to be allowed, which has resulted in a certain delay in publishing the Proceedings. We propose to adopt stricter deadlines in future and insist on all the papers being received in final form by the time of the Symposium.

The Symposium Committee wishes to thank the Indian Institute of Technology, Guindy, Madras for the hospitality and the excellent arrangements made during the Symposium. The cooperation of our colleagues in the editorial work is appreciated.

Ochratia

(A.S. Divatia) Convener, Nuclear Physics & Solid State Physics Symposium Committee

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# PROGRAMME

# SOLID STATE PHYSICS

# TUESDAY, FEBRUARY 27, 1968

Inauguration: A. Ramachandran Chairman: B.D. Magchaudhuri

## SESSION - 1

Invited Talk

## Chairman: R. Remanna

I1. Muclear Structure Calculations with Realistic Two-Mucleon Page Potentials: M.K. Pal.

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SESSION - 2

#### Invited Talk

#### Chairman: C. Ramasastry

I2. The Problem of Lambda Transitions in Solids: 97 E.S. Raja Gopal. 97

# LOW TEMPERATURE PHYSICS Chairman: P.T. Narasimhan

U.N. Upadhyaya<sup>+</sup> and K.P. Sinha.

| <sup>+</sup> S1. | Cocurrence of Superconductivity in Elements: J.S. Rajput and A.K. Gupta.  | 185 |
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| S2.              | Lattice Thermal Conductivities of Alloys at low Temperatures:<br>B.N. Srivastava, S. Chatterjee and S.K. Sen <sup>4</sup> .   | 186 |
| 53.              | Withdrawn.  |     |
| 54.              | Magnetic Hyperfine Interactions of <sup>119</sup> Sn in GdSn <sub>3</sub> and CeSn <sub>3</sub> at 4.2 <sup>0</sup> K: C.R. Kanekar, K.R.P. Mallikarjuna Rao <sup>+</sup> and V. Udaya Shankar Rao. | 190 |
| 55.              | Tow Temperature Anomalous Properties of Dilute Megnetic Allows:   | AOF |

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|-------|--|----|---|
| 13.   | Nuclear Structure Calculations:<br>R.D. Lawson.          | 1  | 7 |
| 14.   | High Frequency Ultrasonic Waves in Solids:<br>B.K. Basu. | 10 | 3 |

\* Paper not presented and printed as abstract only.

Author presenting paper.

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| 86.           | Mossbauer Effect for <sup>57</sup> Fe in Single Crystal of Nickel:<br>Girish Chandra and T.S. Radhakrishnan <sup>+</sup> .  | 199 |  |  |
| 87.           | On the Direction of Magnetization in KFeF3: R. Fatehally,<br>N.P. Sastry and R. Nagarajan <sup>+</sup> .  | 203 |  |  |
| 58.           | Relaxation and Magnetic Structure Studies of Cr <sub>2</sub> O <sub>3</sub> -Fe <sub>2</sub> O <sub>3</sub> System:<br>J.K. Srivastava and R.P. Sharma <sup>+</sup> .                         | 207 |  |  |
| <b>59.</b>    | Internal Magnetic Field on <sup>143</sup> Pr in Gadolinium Metal:<br>P.N. Tandon, S.H. Devare and H.G. Devare <sup>+</sup> .  | 210 |  |  |
| S10.          | The Magnetic Hyperfine Field at the Palladium Nuclei in Iron: P.N. Tandon, H.C. Jain <sup>+</sup> and K. Johansson, E.Karlsson and L.O. Norlin.   | 214 |  |  |
| 511.          | No cear Quadrupole Moment of 14.4 KeV Level of <sup>57</sup> Fe from<br>Mogsbauer Data in Trivalent Iron Salts: Deo Raj <sup>+</sup> and S.P. Puri.   | 218 |  |  |
| 812.          | Mossbauer Spectra of Anhydrous Ferrocyanic Acid: A.N. Garg <sup>+</sup><br>and P.S. Goel.   | 222 |  |  |
| <b>*</b> 813. | Nuclear Electric Field Gradient Determination in Single Crystals of Fe( $NH_4SO_4$ ) <sub>2</sub> .6H <sub>2</sub> O and FeSO <sub>4</sub> .7H <sub>2</sub> O: Kailash Chandra and S.P. Puri. | 225 |  |  |
| *S14.         | Internal Quadrupole Field in HfQCl2: Vikram Singh and I.M.Govil.  | 225 |  |  |

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Chairman: W. Koch

| 15. | Superconducting Materials:<br>M.F. Merriam. | 104 |
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| 16. | Flementary Farticles and Muclear Structure: | 30  |

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\*\* Submitted as abstract only.

Invited Talks

B. Banerjee.

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# Chairman: B.V. Thosar

| [7. | Phonons in Metals:<br>S.K. Joshi.                               | 119 |
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| 18. | Iso-Spin Impurities of Low-lying Nuclear States;<br>S.K. Mitra. | 42  |

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| S24.         | Phonon Conductivity and Acoustic Attenuation in Si: R.P. Singh<br>and G.S. Verma <sup>+</sup> .  | 250                    |
| S25。         | Attenuation of Ultrasound in Ferromagnetic Nickel: B.K. Basu<br>and P.P. Sethna <sup>+</sup> .   | 252                    |
| *926.        | Lettice Dynamics and Hand Structure of Beryllium Using Pseudc-<br>potential Approach: V.C. Sahni and G. Venkataraman.                      | 256                    |
| 527 <b>.</b> | Study of the Fermi Surface of Noble Metals: S. Chatterjee <sup>+</sup><br>and S.K. Sen.  | 257                    |
| 528.         | Hole Bands in Bismuth: V.K. Chopra <sup>+</sup> and R.K. Ray.  | 260                    |
| 529 <b>.</b> | Dynamics of Water Molecules in Crystals: A.S. Sequeira, C.L.<br>Thaper <sup>+</sup> , R. Chidambaram, B.A. Dasannacharya and P.K. Iyengar. | 265 Y auter on cuttine |
| * \$30 .     | Exchange Charge Model for the Third Order Elastic Constants of Germanium and Silicon: R. Srinivasan <sup>+</sup> .                         | 268                    |
| <b>531.</b>  | The Greenian Method for Energy Bands in Disordered Alloys:<br>M.M. Pant <sup>+</sup> and S.K. Joshi.                                       | 269                    |
| *586.        | The Anharmonic Constants of Silicon and Germanium: K.K. Mani.  | 272                    |
| 587.         | Slow Neutron Scattering by Liquids: S.C. Jain <sup>+</sup> and R.C. Bhandari.  | 273 Y lutered          |
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Molecular Forces in Physics and Biology:

G.N. Ramachandran.

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# THURSDAY, FEBRUARY 29, 1968

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| DEFEC             | TS I Chairman: C. Ambasankaran   |      |
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| 833.              | Effect of Li Impurity on the Long Lifetime of Positronium:<br>N.G. Huide <sup>+</sup> .  | 277  |
| *834 .            | Positron Annihilation in Rhodium and Niobium: N.K. Dave,<br>Y.S. Shishodia and B.L. Saraf.   | 282  |
| 535.              | Positron Annibilation in Metals: J.C. Garg <sup>+</sup> and B.L. Saraf.  | 283  |
| <sup>b</sup> S36. | Positron Aunihilation in Oxides of Antimony and Arsenic:<br>Girish Chandra, V.G. Kulkarni, R.G. Lagu <sup>+</sup> and B.V. Thosar.         | 287  |
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| <b>5</b> 38.      | Oxygen Quenching of Positron Lifetimes in Silicon Fluids: P. Sen <sup>+</sup><br>and A.P. Patro.   | 296  |
| <b>8</b> 39.      | Positron Annihilation in Monomer and Polymer Phases of Trioxane:<br>Girish Chandra, V.G. Kulkarni, R.G. Iagu <sup>+</sup> and B.V. Thosar. | .287 |

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| <b>\$40</b> .    | Electronic Band Structure of InBi Intermetallic Compound:<br>B.D. Mungurwadi <sup>+</sup> and D.L.R. Setty.  | 299 |
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| 542 <sub>+</sub> | Nuclear Magnetic Resonance in Antiferromagnetically Ordered<br>Rb2MnCl4.2H2O and CB2MnCl4.2H2O: V. Nagarajan <sup>+</sup> , R.D. Spence and<br>J.A. Casey.           | 310 |
| S43.             | Determination of Crystal Farameters from an Analysis of Zeeman<br>Split NQR Spectra: A.K. Saha, S. Sengupta <sup>+</sup> and R. Roy.                                 | 312 |
| 544 <b>.</b>     | Some Remarks Concerning the Powder Method for the Determination of Asymmetry Farameters for $I = 3/2$ Nuclei from NQR Zeeman Spectra: P.T. Narasimhan <sup>+</sup> . | 317 |
| S45.             | ESR of Transition Metal Ion Impurities in Ferroelectric Crystals:<br>C.K. Subramanian and J. Ramakrishna <sup>+</sup> .  | 322 |
| S46.             | Relaxation Effects in the Double Resonance Spectrum of a Symmetri-<br>cal Three-Spin System $(AB_2)$ : A. Kumar <sup>+</sup> and B.D. Nageswara Rao.                 | 326 |
| <b>547</b> .     | Electronic Absorption Spectrum of NaMnF3: J.P. Srivastava <sup>+</sup> ,<br>A. Mehra and P. Venkateswarlu.   | 329 |
| 548.             | Double Bond Character of C-Br Bond in Multibromobenzenes from<br>Nuclear Quadrupole Resonance: K. Kameswara Rao <sup>+</sup> and C.R.K.Murty.                        | 332 |
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a Combined with S33.

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# SESSION - 11

# Invited Talks

# Chairman: R.M. Singru

- 19. Recent Advances in Muclear Pission Studies: S.S. Kapoor.
- 110. Radiation Damage in Solids Some New Trends: A.V. Patankar.

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## DEFECTS II

# Chairman: R. Srinivasan

| *549。             | Optical Absorption of Co <sup>2+</sup> -Doped NH4C1: Phase Transformation<br>Studies: P.A. Narayana, A.K. Mehra and P. Venkateswarlu. | 335  |
|-------------------|---|------|
| #850 .            | Analysis of the Absorption Spectrum of $Mn^{2+}$ in ZnS: A. Mehra.  | 335  |
| S51.              | Colour Centres in X-Irradiated WCl Doped with Cobalt:<br>E.V.R. Sastry <sup>+</sup> and T.M. Srinivasan.                              | 336  |
| S52.              | Fundamental Band Edge Absorption of NaClO3: C. Ramasastry,<br>S.B.S. Sastry <sup>+</sup> and R. Ramesh Murthy.                        | .340 |
| 553.              | Luminescence Mechanism of the CaS (Zr) Phosphor: M.S. Tomar <sup>+</sup><br>and J.D. Ranade.  | 345  |
| <sup>0</sup> S54∙ | Photoluminescence Spectra of Heavily Doped Single Crystals of KCl with TlCl: D.N. Srivastava and S.C. Sen.                            | 349  |
| *855.             | On the Recombination Lifetime of an Electron in a Photo-Conductor:<br>V.K. Mathur.  | 353  |
| *856 <b>.</b>     | Red Fluorescence of Thallium Salts: C. Ramasastry and B.S.V.S.R. Acharyalu.   | 353  |
| *S57∙             | Thermoluminescence of CaF2: (Ce+Mn) System: S.C. Sen.   | 354  |

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| 111.          | Molecular Motions in Flu<br>B.A. Desannacharya. | lide:        | •  |            |        | 144 | Y | 15/5cg1 170 |
| I12.          | Non-Resonant Coherent Sc<br>A.M. Chose.         | eattering of | Ga | mma Rays:  |        | 85  |   |             |
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858. Neutron Diffraction Studies of Zinc-Nickel Ferrites: M.G. Natera<sup>+</sup>, R.J. Begum, S.I. Youssef, C.S. Somanathan, B.S. Srinivasan and N.S. Satya Murthy.
859. Sublattice Magnetization in Mixed Magnesium-Manganese Ferrites: R.J. Begum<sup>+</sup>, S.I. Youssef, M.G. Natera, C.S. Somanathan,

Presented by M.S. Tomar.

B.S. Srinivasan and N.S. Satya Murthy.

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| 560.           | Measurement of Exchange Integral in CrF <sub>2</sub> by Faramagnetic Neutron<br>Scattering: L. Madhav Rao <sup>+</sup> , M.G. Natera, N.S. Satya Murthy,<br>B.A. Dasannacharya and P.K. Iyengar. | 365 <sup>v</sup> |
|----------------|--|------------------|
| <b>S</b> 61.   | Electron Paramagnetic Resonance of Cu <sup>2+</sup> Ion in Rb <sub>2</sub> SO <sub>4</sub> Single<br>Crystals: S.K. Banerjee, B.V.R. Chowdari <sup>+</sup> and P. Venkateswarlu.                 | 369              |
| 862.           | Electron Paramagnetic Resonance of Mn <sup>2+</sup> in Rb <sub>2</sub> SO <sub>4</sub> Single Crystal:<br>B.V.R. Chowdari <sup>+</sup> and P. Venkateswarlu.                                     | 372              |
| *863.          | Electron Paramagnetic Resonance Studies of Mn <sup>2+</sup> in WH <sub>4</sub> Br:<br>M.D. Sastry and P. Venkateswarlu.  | 376              |
| *S <b>64</b> ₀ | Electron Paramagnetic Resonance Studies of VO <sup>2+</sup> Ion Doped in<br>Potash Alum Single Crystals: K.V.S. Rao and P. Venkateswarlu.  | 376              |
| *865.          | Electron Spin Resonance Studies of VO <sup>2+</sup> in Alkali Chlorides:<br>A.V. Jagannadham.  | 377              |

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| MAGNE         | TIC PROPERTIES V AND DEFECTS III Chairman: R. Roy.   |                  |
|---------------|--|------------------|
| *S66.         | The Effect of an External Uniform Field on a Single<br>(Ferromagnetic) Crystal Containing 180° Domains: V.B. Kelkar.                     | 377              |
| <b>S67.</b>   | Exchange Constants in Nickel-Zinc Ferrite Systems:<br>C.M. Srivastava <sup>+</sup> .   | 378 <sup>V</sup> |
| 868.          | Magnetization of Ferro- and Ferrimagnetic Substances Near the<br>Curie Temperatures C. Srinivasan <sup>+</sup> .                         | 382              |
| 569.          | Spin-Ordering in Dilute Magnetic Alloys: S.K. Dutta Roy <sup>+</sup> and<br>A.V. Subrahmanyam.   | 385              |
| \$70.         | Electron Spin Resonance in Irradiated Li <sub>2</sub> SO <sub>4</sub> .H <sub>2</sub> O: N. Hariharan <sup>+</sup><br>and J. Sobhanadri. | 389              |
| *S71.         | EFR Spectra of CCl Produced by 1 MeV Electrons at 77 <sup>0</sup> K -<br>Evidence for Trapped Chlorine Atom: P.S. Rao.                   | 394              |
| <b>87</b> 2 • | Electron Microscopy of Radiation Damage in PbI2 at Low<br>Temperature: A.V. Patankar <sup>+</sup> , E.E. Schneider and J. Congleton.     | 395              |
| S73.          | Ion Induced Damages in a Silver Monocrystal: S.D. Dey <sup>+</sup> and S.B. Karmohapatro.  | 399              |
| S74.          | Radiation Damage in Calcite Single Crystals: A.R. Patel <sup>+</sup> and C.C. Desai.   | 402              |

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| S75.               | "Cooled Electrons" in Semiconductors: P. Singh <sup>+</sup>   | 407 |
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| 578.          | Determination of Particle Size and Strain in Cold Worked Cadmium<br>by Single Reflection Technique: N.K. Misra <sup>+</sup> .                                   | 420 |
| 879.          | Dislocation Etch Pits in Single Crystals of NCl: S. Keerti <sup>+</sup> and T.S. Murty.   | 423 |
| **880.        | Association of Point Defects in NaNO3 Crystals: C. Ramasastry<br>and Y.V.G.S. Murti <sup>+</sup> .  | 428 |
| 881.          | Studies on the Preparation and Properties of Thallous Sulphide<br>Cells: M.J. Mangalam, K. Nagaraja Rao <sup>+</sup> , N. Rangarajan and<br>C.V. Suryanarayana. | 429 |
| <b>5</b> 82 . | Thermoelectric Power of Thallium Selenide: P.S. Nayar <sup>+</sup> , J.K.D.<br>Verma and B.D. Nagchaudhuri.   | 432 |
| 583.          | Dislocations in Natural Diamonds: A.R. Patel <sup>4</sup> and S.M. Fatel.   | 436 |
| <b>S84</b> .  | Temperature Dependence of the Relaxation Time of the "Fast"<br>Surface States of Germanium: C. Ramasastry and J. Majhi <sup>+</sup> .                           | 441 |
| **S85.        | Miscibility of MaClO3 and MaBrO3 in the Solid State:<br>K.S. Chandrasekaran <sup>+</sup> and S.K. Mohanlal.   | 444 |

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# VITED TALKS

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### NUCLEAR STRUCTURE CALCULATION WITH REALISTIC TWO-NUCLEON POTENTIAL

M.K. Pal Saha Institute of Nuclear Physics Calcutta.

One of the most interesting problems of nuclear structure theory, in recent years, has centred around the use of realistic two-nucleon potentials via a Brueckner-Bethe-Goldstone (1) type reaction matrix theory.

Realistic potentials are obtained directly from an analysis of the deuteron, and two-nucleon scattering data. In their most general form they consist of central, tensor, spin-orbit coupling (L.S) and the quadratic spin-orbit coupling  $(L.S)^2$ , together with various types of exchange-dependence. In this form the potential is state-dependent, that is it depends on the spin, isospin singlet or triplet character of the two-body state, and also on their odd and even characteristic with respect to orbital angular momentum. The tensor potential produces a coupling between states of same parity, spin, and total angular momentum. As far as low-energy structural properties are concerened, the potential in a few low angular momentum states produces the major contribution. Usually all the S, P, D states are considered of which  ${}^{3}S_{1} + {}^{3}D_{1}$  are coupled.

The radial shape of the potential is usually taken to have forms derived from the exchange of mesons. In the latest attempt of this kind by Feshbach and Lomon (2) the exchange of one and two  $\mathbf{M}$ -mesons, and the exchange of one  $\mathbf{P}, \boldsymbol{\omega}$  and m mesons have been considered. In some emperical potentials these shapes are taken with adjustable, depth and range parameters. Normally the latter is related to the inverse of the mass of the excannged particles, and hence at very small separation distance between the nucleons the effect of exchanging several mesons at the same time becomes very important. Such potentials are difficult to derive from meson theory, and only sketchy arguments based on the dispersion theory are available which tend to show that the effect of many-boson exchange at very short distances can be roughly simulated by a suitably chosen boundary condition on the wave function on an inner surface. In the Feshbach-Lomon model this boundary condition is prescribed in terms of an energy-independent value of the logarithmic derivative of the wave function of each state. In the earlier and more popular approach the boundary condition is imposed by taking the potential up to a distance r = c to be a repulsive core of infinite magnitude - the so-called hard core. The core has the effect of producing a wave function that is zero everywhere inside it, and on its surface. Historically, however, the repulsive core of the potential was directly established from two-nucleon scattering data through the change in the sign of the 'S - state phaseshift from its low-energy positive sign (attractive potential) to a negative sign characteristic of a repulsive potential above 200 MeV. The infinite repulsive core is a feature of two of the most widely used realistic potentials.

that of Hamada and Johnston (3) (HJ) and of the Yale group of Breit and collaborators (4) (Yale). In another recent potential, set up at MIT by Bressel, Kerman and Lomon (5) (BKL) the idealized infinite core is replaced by a softer repulsive core, which is quite strong but not infinitely large. The behaviour of the wave function inside and outside the core region for the hard and soft-core potentials is shown in Fig. 1. Since the wave function  $\Psi$  (r) is zero everywhere inside and on the surface of the core, the product  $\Psi$  is still a finite quantity, even though  $\Psi \to \infty$  for the hard core potential. For the soft core potential, the wave function inside the core is very small, and the kink in the wave function at r = c disappears. Nevertheless in both cases, the short range strong repulsion builds up very large Fourier components in the wave function. This fact is some - times expressed by saying that the repulsive core of a realistic potential builds up very strong short-range correlation in the motion of a nucleon pair, characterised by large off-energy shell matrix elements.

I would like to mention here another potential, due to Tabakin (6), which consists of two separable non-local terms in each two-body state:

 $\langle x_1 v_1 x_2' \rangle = f(x_2) f(x_2') + g(x_2) g(x_2')$ 

The momentum transform of the factors f and g were chosen deliberately to give small off-energy shell matrix elements. Therefore, this potential does not produce the strong short-range correlation, of which there is experimental evidence. In that sense the Tabakin potential is not a very realistic two-body potential. The type of fit to the two-body phase-shift data, produced by this potential, is, according to expectation, not as spectacular as the more realistic HJ or Yale potentials. As a matter of fact, in his original paper Tabakin called his potential an effective potential, a fact which will be worth while to bear in mind. The usefulness of this potential in nuclear structural work stems from the case with which its matrix elements can be calculated (due to the factorability), and the possibility of applying a straightforward Rayleigh-Schrodinger perturbation theory to this potential while making many-body calculations.

Let me proceed now to describe what happens in the case of a repulsive core potential. In nuclear structure problems we have at our disposal many more than two nucleons. In the lowest order their motion is described by a one-body Hamiltonian A

$$H_{o} = \sum_{i=1}^{A} (\tau_{i} + \tilde{V}_{i})$$

where V is a suitably defined one-body potential. It is actually the shell-model potential, and is usually approximated by the harmonic oscillator potential plus the Mayer-Jensen spin-orbit coupling. In principle, however, it should be determined by a Hartree-Fock type procedure from the given two-body realistic potential between all the pairs, a problem to which we shall come back later in this lecture.

The wave function of any two nucleons is an antisymmetrized product of the single-particle wave functions,  $\overline{\Phi}_{\chi}$  and  $\overline{\Phi}_{\beta}$ , let us say. This unperturbed wave function can be transformed to centre-of-mass wave functions and wave functions



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describing the relative motion of the pair. If  $\ll, \beta$  are harmonic oscillator wave functions, for example, then the centre-of-mass and relative wave functions are also harmonic oscillator functions, and one knows that such a relative wave function has no reason to vanish for r = c. Thus the unperturbed relative wave function,  $\phi$  say, completely lacks the short-range correlation which is so essential for producing a finite value when multiplied by the repulsive core potential. In the case of the hard-core potential  $\odot \phi$  will diverge, while for a softer core it produces a very large number, although not infinite. We, however, know that the way to rectify the situation is to calculate the correlated exact wave function

from the unperturbed relative wave function  $\Phi(A)$ . But how do we do it?  $\Psi(\mathcal{L})$ Since the pair of nucleons, being considered now, are surrounded by many other nucleons, an equation for  $\Psi(\Lambda)$  which is identical with the deuteron equation, say, will be clearly wrong. In reality the motion of any pair is actually coupled to that of other nucleons through the two-body potential. Therefore, if the compilcations of an exact mathematical treatment is to be avoided, one will have to use physical intuition. For example, the nature of approximation that succeeds in the electron gas will not succeed in the many-nucleon system. The actual nature of the two-body interaction and the density of the many-body system under consideration can only determine the nature of approximation to be used. Because of the strong short-range correlations generated by the two-nucleon potential, it is assumed that the motion of a pair will not be affected by the other nucleons through any multi-particle clustering; the other nucleons will only modify the energics of the interacting nucleons through the Hartree-Fock potential, and because of the Pauli principle, they will prevent the test nucleons to scatter to states that they themselves are occupying. In other words, if we call the set of single-particle states occupied by all the nucleons to be the Fermi-sea, then the interacting pair can only go outside this sea. The consequent equation for  $\Psi$  is called the Brueckner, Bethe, Goldstone equation (1), and the physical approximation mentioned above, is usually called 'independent pair approximation', a term first used by Weisskopt (7). When a solution  $\Psi(\Lambda)$  of this equation has been obtained,  $\sqrt{\psi}$  will be a finite quantity and hence a matrix element of the type  $(\chi | \psi | \psi)$ where  $\chi$  is any unperturbed relative wave function, can be easily evaluated. This matrix element is called the reaction matrix element, or the matrix element of the effective potential t. That is to say, t is defined by

$$( + |v| + ) = ( + |t| + )$$
 .... (1)

The equation for  $\psi$ , which I have avoided writing so far, can now be equivalently written in terms of t, by using the definition (1),

$$t = v - v \frac{Q}{e} t \qquad \dots (2)$$

This equation, I am sure, is familiar to almost every nuclear physicist by now. Q here is the Pauli operator that takes us out of the Fermi-sea. The energy denominator  $\mathcal{C}$  is given by  $k_0 - E_0$  where  $k_0$  is the Hamiltonian of the unperturbed pair,

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and  $E_0$  is their unperturbed inital energy. For a given centre-of-mass state, the centre-of-mass part of  $h_0$  reduces to a number, and hence the energy denominator gives rise to a dependence of the t-matrix on the centre-of-mass states of the pair. Furthermore, through the operator Q the calculated t-matrix becomes dependent, in an indirect way, on the occupied states of all other nucleons. These two complications are usually called the state-dependence of the t-matrix, and gives rise difficulties in Hartree-Fock type work, to be discussed later.

A very convenient method of calculating t in two steps was suggested by Bethe, Brandow and Petscheck (8) (BBP) in the case of infinite nuclear matter, where the single-particle states are plane-waves. The success of this procedure led to a major break through in the theory of finite nuclei, and accounts for the recent spurt of calculations on the effective matrix elements of finite nuclei. The BBP equation, I referred to, relates the actual t matrix elements of eq. (2) with that of a modified t-matrix, let us say t', calculated with potential V'and the operator  $\frac{Q'}{T}$ . t' satisfies the equation:

$$t' = v' - v' \frac{Q'}{e'} t' \qquad \dots (3)$$

and the final equation connecting t and t' is given by

$$t = t' + n'^{\dagger} (v - v') n + t' (\frac{Q}{e} - \frac{Q}{e}) t \qquad \dots (4)$$

This equation really serves as the 'open sesame' magic words for entering any of the different approaches made recently, in the t-matrix theory. The trick is to use Q' = 1 and reasonably approximate values of the energies contained in e'. Such a reaction matrix t' is Hermitean, a fact that has been already utilised in writing eq. (4). The operators  $\Re$   $\Re'$  appearing here are defined by

$$t = \vartheta \Omega$$
;  $t' = \vartheta \varkappa'$  (5a)

or in other words

 $\psi = s.\phi$ ;  $\psi' = s.\phi$  .... (5b)

Since Q' = 1, the equation (3) for t', or equivalently the corresponding Brueckner-Bether-Goldstone equation:

 $\vartheta \psi' = e' (\phi - \psi')$  .... (6)

is quite straightforward to solve. If the full potential thas been used for the interpretation of the second term in eq. (4) is zero, and the only correction to be calculated is the third term:  $t'\left(\frac{Q'}{q'}-\frac{Q}{e}\right)$  to the expression  $\left(\frac{1}{e_{i}}-\frac{Q}{e}\right)$  can be written as  $\left(\frac{1}{e'}-\frac{1}{e}\right)+\frac{1}{e}\left(1-Q\right)$ . The first part gives the so-called dispersion correction, and the second the Pauli correction. The last t is substituted by t' in evaluating these corrections. Since the operator (1-Q) keeps one confined within the Fermi-sea, a direct method of evaluating this Pauli correction is to introduce all the occupied pair states of the Fermi-sea as intermediate states in  $t'\frac{1}{e}(1-Q)+t'$ . This is the so-called "global approximation" of Brandow (8) and of Wong (9), which has also been used independently by Grillot and McManus (13).

Another simpler way has also been used (10) where the intermediate states above the Fermi-sea are taken to be plane waves, and Q is replaced by an angle averaged approximation of the corresponding Fermi-gas expression. The Fermi-momentum appearing in such an expression is related in the usual way to the density of the nucleus. In the approximation used by Kuo and Brown (10) one average value of the density, and hence ke was used, while in a later calculation by Wong (9) a point-by-point calculation has been dome inside the nucleus using the local density of each point. This procedure is specially relevant for the surface region of a finite nucleus where the density falls off rapidly.

If, however, a full v is not used in the calculation of t' then according to eq. (4), the difference of the two potentials gives a further nonvanishing correction  $\mathfrak{A}'^{\dagger}(v \cdot v') \mathfrak{A}$ . In particular if the potential v is written as the sum of a short-range part  $\mathfrak{I}_{S}$  plus the outer potential (long-range)  $\mathcal{V}_{L}$  and t' is calculated only with  $\mathcal{V}_{S}$  then  $\mathbf{U}_{-}v'_{-}v_{L}$ , and hence in the matrix elements of t, this correction term corresponds to matrix elements of  $\mathcal{V}_{L}$  between the correlated states. The  $\mathfrak{A}$  on the right is replaced by  $\mathfrak{A}'_{1}$  and then  $\mathfrak{A}'_{2}$  on the left and  $\mathfrak{R}'$  on the right bring in the correlated wavefunctions in the matrix elements.

Similarly, in the calculation of t', the energies in have also been prescribed by various authors in several different ways. The one-body potential contained in e' has also been handled differently by different authors. Sometimes its effect is put into the energy as a number from some physical intuition and the modified energies are then called the "reference spectrum", and the method of calculation the reference spectrum method. At other times the harmonic oscillator potential has been used explicitly as the unperturbed potential.

The equation of Shakin et al (11) also follow from this general equation, as has been shown by Stamp and myself (12). These authors (11), instead of using the entire tensor potential in their short and long range separation, use only the part of it that is diagonal in orbital angular momentum. This has the obvious effect that at the stage of calculating t' their  ${}^{3}S_{1}$  and  ${}^{3}D_{1}$  states are uncoupled. I mention this fact because the work with the Yale potential of these authors has been presented from a radically different point of view using a unitary operator to transform the unperturbed  $\phi$  to the correlated  $\psi$ . Since this operator is not required explicitly in their work, the question that is genuinely asked is: are they really doing something new? The answer to this question is no, because the final equations, used by them, are derivable from the t-matrix equation of BEP in a more satisfactory way and one knows that the operator  $\mathcal{R}$  of the t-matrix theory that generates  $\psi$  from  $\phi$  is not unitary.

I shall now describe some structural work that has been done with these reaction matrix elements. First there is the calculation on the binding energy of  ${}^{16}$ O and  ${}^{40}$ Ca by several authors (13); then the calculation on the shell-model spectrum of  ${}^{18}$ O and  ${}^{18}$ F by Kuo and Brown (10) and also by Kuo (14); the Hartree-

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Fock calculations done by Stamp and myslef (12) on the shapes of deformed N = Zeven nuclei starting from <sup>8</sup>Be and ending with <sup>36</sup>A; finally the calculations of Kuo (15) on the effective matrix elements in the Ni-region and the spectral calculation of Ni-isotopes by Lawson, Kuo and others (15); perhaps a few more structural calculations may also have been done, but unfortunately any such work has escaped my attention.

The situation on the binding energy is very conclusive now. In spite of the early spectacular success of Becker and Mckellar (16) and Shakin et al (11) in producing the right binding energy, it is now agreed that HJ or Yale potential misses the binding energy per nucleon by 4-5 MeV. Various sources of error have been attributed to the earlier work, mentioned above.

The 18 and 18 work has revealed a very important phenomenon. Let us have a quick look at a few figures at this point. In Fig. 2 the left hand diagram shows the effective interaction t between the two particles outside the <sup>10</sup>0 core. The right hand diagram shows the possibility of exciting a hole and a particle out of the core, by one of the extra-core particles and their reabsorption by the other extra-core particle. This second-order effect in t can be thought of as an effective renormalisation of the t-matrix between the extra-core particles. This core-pole arization effect in modifying t has been found to be very important by KB. In the next figure, Fig. 3, we see the same ideas working on a slightly more complicated scale. Instead of letting the core polarization effect be confined to just onehole one particle states the excitation of the core is allowd to multiply itself by producing more and more hole-particle pairs. The entire complicated excitation process can be viewed as the excitation of a collective vibrational state of the core. The renormalizations of t due to a single hole particle excitation, and the excitation of the full collective state have both been worked out by Kuo (14). The agreement with the spectra of  ${}^{18}$  o and  ${}^{18}$  F are shows in the next two figures, Fig. 4 and Fig. 5. Needless to mention that without the core-polarization correction to t, the agreement is hopless. We shall, however, come back to a discussion of the core-polarization effect from another angle very soon.

Next our own work on the Hartree-Fock calculations (12). The HF potential V is obtained by summing the effective pair interaction t over all the occupied states of one of the nucleons. Thus

$$(i|V/i) = \sum_{k}^{\infty} (ik|i|jk) \dots (7)$$

I mentioned earlier the state-dependence of the relative t-matrix elements. Actually this is a great handicap in even trying to define, according to the above equation, a Hartree-Fock potential from the t-matrix elements. Some of these difficulties and way out were discussed in my work with Stamp (12). In more recent publications Brandow (8) and also Wong (9) have carried on the discussion still further. According to the present-day view point, the only practicable procedure appears to use the matrix elements of t', using average energy values in e', in the



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first definition of the Hartree-Fock potential. Then allow for the state-dependence, and also some higher-order effects, to be discussed soon, empirically in the form of certain functions of nuclear density.

The higher order processes will be represented by diagrams. The t-interaction between two Fermi-sea particles is represented by the diagram (a) of Fig. 6. The Fermi-sea particles are shown as circles and the effective potential t as a wavy line. There is no diagram involving two successive t-interactions between a pair of particles because the t-matrix itself corresponds to the effects of successive interactions between such a pair to all orders. In the third order one can have the diagrams (b) and (c) of Fig. 6. In both these diagrams each lens-shaped object corresponds to the excitation of a hole-particle pair from the Fermi-sea. In diagram (b) one member of such a pair is shown to be interacting with a typical Fermi-sea particle. The sum over the latter, according to eq. (7), corresponds to the interaction of the said member with the Hartree-Fock field. Thus the effect of the higher-order process represented by diagram (b) can be included through the definition of the Hartree-Fock potential itself. An alternative third-order diagram, called the ring diagram, is shown in diagram (c). This diagram represents a genuine correlation amongst three Fermi-sea particles and forms the subject matter of several fundamental papers by Rajaraman (17) and Bethe (18) in the case of infinite nuclear matter. In the case of finite nuclei nobody has done any detailed calculation on these diagrams, but the general conclusions of Rajaraman and Bethe are taken to be valid. Actually these authors have taken the thirds order ring diagram and shown that the effect of this diagram, through the long-range part of the interaction, can once again be taken into the definition of the Hartree-Fock potential. For the short-range part of the interaction, on the other hand, this ring diagram, together with all higher-order diagrams containing three hole lines can be summed together by the Faddeev (19) technique, and their effect has been demonstrated to be small by Bethe (18) and also by Moszkowski (20).

The forms suggested by Brandow (8) and Wong (9) as the modification of the HF potential, due to these higher order processes and the state-dependence, are normalized where near the final words on the Hartree-Fock potential. Moreover, it appears that Wong did not actually use these extra bits in his HF-calculation of <sup>16</sup>O and <sup>40</sup>Ca.

In our work on the deformed nuclei also we used the same approach, namely used the t'-matrix elements of the Yale potential as calculated by Shakin et al (11). Our results on the shapes of nuclei, using the first and second set of matrix elements of these authors, are very similar. This leads us to believe that, at least up to  $^{40}$ Ca, the shapes do not very sensitively depend on the precise values of the t'-matrix elements. The binding energies, however, do. With the first set we obtained values close to 6 MeV, while with the second set we get values between 4-5 MeV. Fig. 7 shows our calculated shapes. It is clear that the calculated deformation in all cases is somewhat smaller than the observed deformation. We shall discuss this point soon.

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In our calculations we used all the single-particle harmonic oscillator states up to 2s-1d to diagonalise the HF matrix. As a result our 1s wavefunctions of the core get mixed with 2s and id functions. However, the 1p-function do not get the scope of mixing with the 2p, 1f-states. If we do include the latter states then the 1p-states will also get the opportunity of polarisation. Thus in such an extended HF calculation the core-polarisation effect is fully built in. The Kuo-Brown diagram of Fig. 2 has now to be looked upon as the process represented by Fig. 8. The straight lines of Fig. 2 which represented the two particles outside the <sup>10</sup>O core get replaced by circles because these two states also are occupied states in the Fermi-sea in our way of tackling the problem. However, if the correct HF potential is used them the matrix element at each vertex is the same as that of  $\sqrt{}$  between the states h and p. Since the residual interaction is  $(V - \sqrt{})$  this diagram will exactly cancel out. Thus what KB calculate by a very involved method is exactly zero in a more careful theory. The correct way to put the core-polarisation into the <sup>18</sup>F, <sup>18</sup>O theory will be to do the extended HF calculation, mentioned above, and then from the two-particle HF wavefunctions project out the states of appropriate angular momentum. This work is now in progress. In the meantime, we have observed a very simple fact from our numbers in the HF calculations restricted up to the 2s-id shell. The core-polarization effect of the is-particles can be produced by a very simple one-body potential of the form

# $a_0 + a_2 \beta \gamma_0^2$

where  $\beta$  is the deformation parameter of a nucleus having a spheroidal shape. Further evidence will be obtained on this simple view-point once the full HF calculation is completed. This simple fact, if found to be true, brings the core-polarization theory into conformity with Bohr-Mottelson ideas on the subject.

Fig. 9 shows the complete results of my HF calculation with Stamp (12) on a single nucleus. 28 Si. What is shown here is the plot of the ground-state energy as a function of the deformation parameter  $oldsymbol{eta}$  . Similar studies were made near each minimum as a function of the asymmetry parameter Y of a tri-axial nucleus. It is believed that the lowest minimum will correspond to the actual ground state and in the case of this particular nucleus it is found to be an oblate shape. The single-particle energy levels which result from the diagonalization of each HF-matrix were also calculated. In general, the gap in the single-particle spectrum between occupied and unoccupied states is larger for the lowest minimum. As a matter of fact this gap is a measure of the stability of the HF state against depletion into hole-particle pairs. If the HF potential is correctly determined, the lowestorder processes correspond to two-hole two-particle excitations, and naturally across a smaller gap the probability of such excitations is more pronounced. It may be expected that these pair excitations from the HF state may tend to mix with the latter and produce a ground state that is lower in energy than the HF-state itself. We shall refer to this process as the pairing correction of the HF-state. In the case of <sup>20</sup>Ne Stamp and I (21) calculated the pairing effect for the lowest HF state and found it to be rather unimportant. A later calculation by Grillot

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and myself (22) led to the same conclusion in <sup>28</sup>Si. However, I now draw your attention to some of the other minima present in Fig. 9. These minima are somewhat higher compared to the lowest one. The gap in the spectrum for some of this minima was found to be small in our calculations, and hence the question can be asked: can some of these other minima, through the pairing effect, come down below the lowest one. If it does then what is known about the shape from the HF calculation so far, may be compeltely wrong. This point has been recently explored by Goswami and collaborators (23) for the deformed nucleus 24Mg. For this nucleus the HF calculation gives an asymmetric deformed shape of positive eta and  $m{
u}$ around 23°. There is a neighbouring higher minimum with nearly equal  $\beta$  but  $\gamma = 0$ (i.e. spheroidal). In the calculation of Goswami et al this shape is found to be pushed by pairing effects below the asymmetric shape by about 0.5 MeV. There are several points about this work for which the whole problem needs further careful examination. In the first place, 0.5 MeV is too small an amount to be conclusive; secondly the quasi-particle theory used by them does not conserve the number of particles and they do not use correct projected wave functions which, if used, can very easily cause changes 0.0.5 MeV in the results; thirdly for the lowest HF state they do not calculated the pairing effects at all (this may very well be  $\approx 0.5$  MeV); fourthly what one should compare is the energy obtained from the intrinsic HF-state for the projected ground state of angular momentum zero; finally, the quasi-particle formalism using the special T = 0 pairing for N = 2 nuclei is not conceptually in a very healthy state. In view of these shortcomings of the work of Goswami et al we have undertaken a systematic programme of doing the pairing correction to HFstates, following my paper with Stamp (21), for the other HF minima near the groundstate one. Our conclusions on the final shapes will be based on the energies of J = 0 projected states out of all such intrinsic states, calculated with pairing correction. Simultaneously with Goswami et al, Grillot and I (22) calculated the effect of pairing corrections on the two lowermost minima of <sup>28</sup>Si and found that the HF lowest minimum still remains the lowest. We have not published these results yet because, as I mentioned, one should compare the energies of the J = 0 projected states, rather than that of the HF intrinsic states. Such projection work (13) is now under progress at the University of Oregon.

I shall conclude by making a final remark on the inadequacy of the calculated binding energy of nuclei based on the HP or the Yale potential. Some authors have expressed the feeling that perhaps replacement of these hard-core potentials by softer core ones will improve the situation. At the same time one may also look for missing physical effects in the present calculations. It seems to me that, at least in finite nuclei upto<sup>40</sup>Ca, the known four-particle correlation amongst two neutrons and two protons, has not been properly treated in the method for calculating the binding energy. Such correlation is quite difficult to include, but one must work it out explicitly before drawing any final conlusions on the existing twonucleon potentials.

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#### DISCUSSION:

C.S. Warke: Should one go ahead and calculate the higher order correlations or should one try to improve the approach of calculating two body interaction? M.K. Pal: One should specially keep in mind the large off-diagonal matrix elements that the present t-matrix calculations of Kuo-Brown or Shakin-Waghmare give.

According to the basic philosophy of the t-matrix calculation, one should not even use the solution of the Bethe-Goldstone equation in calculating offenergy shell matrix elements connecting states very widely separated in energy. Moreover, the shortcoming of the ground-state energy result is unaffected by the values of the off-energy shell matrix elements of t that KB or Shakin-Waghmare quote. I do not find anything wrong with the present definition of the two-body t-matrix, and the amount of careful work that various authors have put into their numerical - evaluation perhaps does not leave much scope of improvement. Even though a doubly self-consistent calculation has not been done, the dispersion and Pauli corrections have been quite carefully studied. I shall be quite happy if some basic physical ideas are shown to be missing in the two-body effective potential. My suggestion about the two-neutron two-proton quadrupling effects for the finite nuclei upto  $^{40}$ Ca was also in the spirit of a search for missing physical facts. To summarise, the missing binding energy may be partly obtained from alterations of the potential, and partly from new physical effects either in two-body process, as you suggest, or in four-body processes; as I suggest. But we are both equally making a guess.

S.C.K. Nair: (Comment)

If what Dr. Warke has said is really the trouble then one would not expect to get for such "simple" nuclei like <sup>18</sup>O and <sup>18</sup>F good agreement for the spectra. Since it is in the total binding energy calculation we find it difficult toget good agreement with the experimental number, as Prof. Pal observed it may be that it is the neglect of some real physics such as four body correlation which is at the root of the trouble.

B. Banerjee: The latest calculations show that none of the potentials you have mentioned saturate the nuclear matter. Would you like to comment on the utility of using these potentials for calculations of nuclear (finite) binding energies? M.K. Fal: It is true, with the exception of the Tabakin potential, the other two potentials mentioned by me, namely Hamada Johnston and Yale, do not produce enough binding energy. The Bressol, Kreman, Lomon potential is still being looked at; specially attempts are being made to introduce a nonlocal periodic potential in the core region. Wong mentions in his paper on <sup>16</sup>0 and <sup>40</sup>Ca that perhaps the soft core potential will provide the extra energy that is still missing. However, I have my doubts; if the soft core potential has to fit the two-body data as well, it may produce results not very much different from the HJ of Yale results. At least in the finite nuclei, it seems to me, that the quadrupling effect of two neutrons and two protons into of -particle type structures, has not been dequately treated in the t-matrix type theory. In infinite nuclear matter Bethe and also Moszkowski have shown that the three-body clustering effect is small. By an extension of that work Sprung and collaborators have shown that the four-body clustering effect is still smaller. But what is not clear to me is whether these four-body diagrams take care of the type of four-body correlations, I have mentioned. Someone has to look at it. and at least in finite nuclei up to <sup>40</sup>Ca, where this quadrupling effect is expected to be very important, there is scope of detailed work.

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# NUCLEAR STRUCTURE CALCULATIONS

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If one attempts to make nuclear structure calculations on the basis of the Nuclear Shell Model one rapidly becomes aware of the fact that even when all the approximations that go into the Shell Model are made the problem is still so large that it is beyond the bounds of present day computers. Thus one must look for approximate ways of making Nuclear Structure Studies and the BCS wave function, which was originally introduced as a calculational tool in the theory of super-conductivity, provides one way of approximating the nuclear problem. In this paper I would <u>first</u> like to illustrate the particular qualities of nuclear states that make them amenable to the BCS approximation and <u>second</u> to discuss to what accuracy the nuclear ECS calculations reproduce the results of certain exact calculations that have been made.

The exact calculations that I would like to discuss are those concerning the Nickel isotopes (1). The Nickel isotopes are nuclei with 28 protons and anywhere from 28 to 38 neutrons. According to the shell model the 28 protons and first 28 neutrons from an inert closed shell -- that is they provide the average shell model potential in which the valence nucleons move. Thus the nucleus  $\frac{57}{28}$ Ni, which has one neutron outside the doubly magic core, should exhibit a single particle spectrum. The experimental level scheme of this nucleus is shown in Figure 1 and it is seen that below 2 MeV only three levels are observed. This is much less than normally seen -- for most odd A nuclei in this region something of the order of ten levels are observed below 2 MeV. This result, therefore, tells us first that our assumption that  $\frac{56}{28}$ Ni form an inert core is reasonable and second it provides us with the single particle levels and their energies that should be taken into account in discussing the structure of the low-lying states of the Nickel nuclei. Thus the model we will take is one in which the N = Z = 28core is inert and neutrons are filling the  $2p_{3/2}$ ,  $1f_{5/2}$  and  $2p_{1/2}$  single particle levels whose experimental energies are taken to be 0, 0.78 MeV and 1.08 MeV respectively (2). At about 2.5 MeV in  $\frac{57}{28}$ Ni a state with spin 7/2 is seen in pickup experiments (3). This is interpreted as corresponding to an excitation out of the closed  $f_{7/2}$  shell and immediately tells us that our simple model, in which we assume the core is inert, should not be taken seriously in odd A nuclei for states above 2.5 MeV excitation.

Using these single particle basis states one must now diagonalize the nuclear Hamiltonian

 $H = H_0 + V \qquad \dots \qquad (1)$ 

where  $H_0$  is the independent particle Hamiltonian which should give rise to single particle states with energies similar to those observed in  $\frac{57}{28}$ Ni and V is the re-

<sup>+</sup> Work performed under the auspices of the U.S. Atomic Energy Commission.

<sup>\*</sup> Senior Weizmann Fellow 1967 - 68.







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sidual two-body interaction between the valence nucleons. In view of the violent truncation that has been made it is not likely that V can be taken as the free nucleon-nuclon interaction. An attempt to derive the effective interaction needed in the truncated  $(2p_{3/2}, 1f_{5/2}, 2p_{1/2})$  configuration space from the free nucleonnucleon interaction led to results qualitatively similar to those presented here (4). However, the actual calculations I will discuss at this time are those in which the nuclear wave functions were taken to be those of a harmonic oscillator and V was assumed to have a simple Gaussian dependence with a central, tensor and two-body spin orbit part. To obtain agreement with the experimental spectrum, the interaction energies when the two interacting neutrons were in relative s-states had to be taken as parameters also (1). The range of the interaction was fixed to be similar to that of the free nucleon-nucleon force and then the eight remaining parameters characterizing the potential were varied until a best fit to the data on all the Nickel isotopes was obtained (approximately 40 energy levels were fitted in the way). A typical example of the quality of agreement between theory and experiment is shown in figure 2 for  $\frac{58}{28}$ Ni.

Let us now turn our attention to the structure of the wave functions that describe these nuclear states. It is important to note that the lowest state of the system is a level with angular momentum J = 0. This corresponds to the case where the spins of the two nucleons are paired off. Such a state, in which there are no unpaired particles, is said to be a seniority zero state\* and can be pictorially represented as

This state lies approximately 1.5-MeV below all other states in the  $\frac{58}{28}$ Ni nucleus. Thus when the nuclear spins pair off one gets a bonus of about 1.5 MeV. The other states are those in which the spins do not pair off, that is, do not have J = 0, and these are called seniority two states corresponding to the fact that they contain two unpaired nucleons. Again pictorially they can be represented as

 $J \neq 0, v = 2.$ 

J=0, v=0.

If we now turn to the multi-particle system with an even number of particles it is logical to expect that the lowest state of the nucleus will be the one in which all possible spins are paired off. Pictorially one would expect the lowest state to be of the form

 $\uparrow \downarrow T \downarrow \qquad \qquad J = 0, \quad v = 0.$ 

TJ-

\* Throughout this discussion we shall define the seniority of the multi-level system as the sum of the seniorities of the individual configurations. That is, if the seniorities of the three configurations  $(f_{5/2})^{n_1}$ ,  $(p_{3/2})^{n_2}$  and  $(p_{1/2})^{n_3}$  are  $v_1$ ,  $v_2$ and  $v_3$  respectively, then the seniority of the N particle basis state  $(f_{5/2})^{n_1} (p_{3/2})^{n_2} (p_{1/2})^{n_3}$  where N =  $n_1 + n_2 + n_3$ , is  $v = v_1 + v_2 + v_3$ .

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The low-lying states in such a nucleus should be those in which only one pair is broken, that is the seniority two levels. Diagramatically these would be represented by

 $\uparrow \uparrow \uparrow \downarrow - - - - \uparrow \downarrow \qquad J \neq 0, \ \forall = 2$ 

and these should lie at excitation energies between 1.5 and 2.5 MeV. In a similar manner the next group of states should be the seniority four levels corresponding to four unpaired particles

↑↑↑↑↑↓---**↑↓** J, v=4

and these should describe states whose excitation energies are of the order of 3 MeV or greater. Thus one would expect that states below about 2.5 MeV in an even-even nucleus should have wave functions that are dominantly either seniority zero or two. Table I shows the seniority decomposition of the low-lying states in the 6 particle nucleus  $\frac{62}{28}$ Ni and from this table it is apparent that the above surmise is true for the states of even angular momentum.

| TABLE I. | , |
|----------|---|
|----------|---|

| 62.<br>28 <sup>N1</sup><br>state | Lowest<br>seniority | Percentage   |
|----------------------------------|---------------------|--------------|
| 0 <sup>+</sup><br>1              | 0                   | 99 <b>.7</b> |
| 0 <sup>+</sup> 2                 | 0                   | 87.3         |
| 2 <mark>1</mark>                 | 2                   | 99.5         |
| 22                               | 2                   | 89.0         |
| 4 <sup>+</sup> <sub>1</sub>      | 2                   | 92.9         |
| 11                               | 2                   | 23.7         |
| 31                               | 2                   | 40.6         |

Seniority decomposition of the low-lying state in  $\frac{62}{28}$ Ni. The lowest state of given spin has a subscript 1 and the second state of that spin has a subscript 2. The lowest possible seniority for the various states is either zero or two and this is listed in column 2. The percentage of the state with this seniority is listed in column 3.

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In view of this one would expect that if one made a seniority truncation and considered only the states of lowest seniority in carrying out the shell model calculation for even J states the energy predictions emerging from this should be close to those that arise from the exact diagonalization. That this is so is illustrated in Table 2 where the results of the two calculations are compared.

| TABLE | II: |
|-------|-----|
|       |     |

|                     |                               | •                                 |
|---------------------|-------------------------------|-----------------------------------|
| J                   | Exact<br>Calculation<br>(MeV) | Lowest<br>Seniority only<br>(MeV) |
| 0 <sup>+</sup> 1    | (0.448)                       | (0.463)                           |
| 2 <sup>+</sup><br>1 | 1,533                         | 1.534                             |
| 0 <sup>+</sup> 2    | 2.013                         | 2.130                             |
| 4 <sup>+</sup> 1    | 2.201                         | 2.278                             |
| 2 <sup>+</sup> 2    | 2.253                         | 2.358                             |
|                     | ,                             |                                   |

Energies of the various states in  $\frac{62}{28}$ Ni arising when all states of the  $(2p_{3/2}, 1f_{5/2}, 2p_{1/2})$  configuration are used and those arising when only seniority zero eignenfunctions are used for the J = 0 states and seniority two wave functions are used for the J  $\neq$  0 states. The tabulated ground state energy is the total interaction energy of the six extra core nucleons, whereas the other energies tabulated are excitation emergies relative to the ground state.

Thus if one wants to describe even angular momentum states with excitation energies below about 3 MeV a suitable way of cutting down the size of the energy matrices that must be constructed and diagonalized is to use only seniority zero eigenfunctions for the low-lying J = 0 states and only seniority two wave functions for the remaining even J states. In the case of  $\frac{62}{28}$ Ni the saving is quite considerable. For example, there are 14 possible J = 0 states only 6 of which have seniority zero. In the case of J = 2 there are 33 states that can be constructed from the entire  $(2p_{3/2}, 1f_{5/2}, 2p_{1/2})$  configuration whereas there are only 15 states if we limit ourselves to seniority two. The saving is, therefore, appreciable, but still not enough. To illustrate the inadequacy, consider the case of  $\frac{116}{50}$ Sn. To describe this nucleus we would have to consider 16 neutrons outside the closed N = Z = 50 shell and these neutrons would have to be distributed over the five single particle levels  $2d_{5/2}, 1g_{7/2}, 1h_{11/2}, 2d_{3/2}$  and  $3s_{1/2}$ . Even if we consider only the lowest seniority there are 110 J = 0 states and approximately 1,000 J = 2 basis states. Thus even though the seniority truncation provides an appreciable saying it is not enough and hence additional approximations have to be introduced.

To see how the BCS approximation can be used in nuclear structure calculations (5), let us define the Fermion creation operator  $a_{jm}^+$  and the destruction operator  $a_{jm}$  which create and destroy, respectively, a particle with angular momentum j and z - component of angular momentum m. Since these are Fermion operators they obey the anticommutation relationship

$$\left\{a_{jm}^{+}, a_{j'm'}\right\} = \delta_{jj'} \delta_{mm'}.$$

In terms of these operators the J = 0 seniority zero state of two particles can easily be written as

where the phase factor  $(-1)^{j-m}$  is proportional to the Clebsch-Gordan coefficient which ensures that the two particles couple their angular momentum to zero and  $|0\rangle$ is the vacuum. For the N particle system the seniority zero state is simply written as

$$\begin{array}{c} \uparrow \downarrow \uparrow \downarrow --- \uparrow \downarrow \qquad \longrightarrow \qquad ( \underbrace{\{ \{ (-1) \} }_{jm} A^+_{jm} A^+_{j-m} )^{N/2} | \circ \rangle \\ m > 0 \end{array}$$

One can now easily see that the BCS wave function

$$\Psi = \frac{\pi}{j,m} > 0 \left( u_{j} + (-1)^{j-m} v_{j} a_{jm}^{+} a_{j-m}^{+} \right) \left( 0 \right) \qquad \dots (2)$$

describes a system in which pairs of particles always couple their spins to zero. For example, if we consider the simple case where the only j of interest is j = 3/2 the BCS eigenfunction can be expanded and written as

$$\begin{split} \Psi &= (\mathbf{u} + \mathbf{v} \, \mathbf{a}_{3/2}^{+} \, _{3/2}^{-} \, _{3/2}^{-} \, _{3/2}^{-}) \, (\mathbf{u} - \mathbf{v} \mathbf{a}_{3/2}^{+} \, _{1/2}^{-} \, \mathbf{a}_{3/2 - 1/2}^{+}) \, | \, 0 \, \rangle \\ &= \left\{ \mathbf{u}^{2} + \mathbf{u} \mathbf{v} (\mathbf{a}_{3/2 \, 3/2}^{+} \, \mathbf{a}_{3/2 - 3/2}^{+} - \mathbf{a}_{3/2 \, 1/2}^{+} \, \mathbf{a}_{3/2 - 1/2}^{+}) \right. \\ &- \mathbf{v}^{2} \, \mathbf{a}_{3/2 \, 3/2}^{+} \, \mathbf{a}_{3/2 - 3/2}^{+} \, \mathbf{a}_{3/2 \, 1/2}^{+} \, \mathbf{a}_{3/2 - 1/2}^{+} \, | \, 0 \, \rangle \\ &= \left\{ \mathbf{u}^{2} + \mathbf{u} \mathbf{v} \, \mathbf{z}_{m \, 70}^{-} \, (-1)^{3/2 - m} \, \mathbf{a}_{3/2 \, m}^{+} \, \mathbf{a}_{3/2 - m}^{+} \right. \\ &+ \frac{\mathbf{v}^{2}}{2} \left( \, \mathbf{z}_{m \, 70}^{-} \, (-1)^{3/2 - m} \, \mathbf{a}_{3/2 \, m}^{+} \, \mathbf{a}_{3/2 \, m}^{-} \, \mathbf{a}_{3/2 - m}^{-} \, \mathbf{a}_{3/2 \, m}^{-} \, \mathbf{a$$

Inspection of equation (3) shows that each term in the expanded wave function describes zero coupled pairs and consequently the BCS wave function is a linear combination of seniority zero eigenfunctions. This wave function is automatically normalized provided

$$u_j^2 + v_j^2 = 1$$
 .... (4)

and  $v_1^2$  respresents the probability that the state (jm) is occupied.

The BCS wave function obviously does not describe a system with a fixed number of particles. For the simple case described by Eq. (3) there is a finite probability,  $u^4$ , that the wave function describes a state with no particles, a probability  $2u^2v^2$  that there are two particles and a probability  $v^4$  that the wave functions corresponds to a system with four particles. Thus one cannot use to minimize the Hamiltonian of Eq. (1) directly. One must minimize H subject to the constraint that the expectation value of the number operator

$$N = \sum_{jm} a_{jm}^{\dagger} a_{jm} \qquad \dots \qquad (5)$$

corresponds to the number of particles,  $\overline{N}$ , that are actually in the physical system we wish to describe. That is the quantity

$$\mathbf{A} = \langle \mathbf{\Psi} | \mathbf{H} - \mathbf{\lambda} \mathbf{N} | \mathbf{\Psi} \rangle \qquad \dots \quad (6)$$

where  $\lambda$  is a Lagrange multiplier, is minimized as a function of the  $v_j$ 's. Therefore, the equations that replace the diagonalization of the sehll model energy matrix are

$$\frac{\partial A}{\partial v_{j}} = 0 \qquad \dots (7)$$

and the constraint equation

$$\langle \psi | \mathbb{N} | \psi \rangle = \langle \psi | \underset{jm}{\not =} a_{jm}^{\dagger} a_{jm} | \psi \rangle = \underset{j}{\not =} (2j+1) v_{j}^{2} = \mathbb{N}.$$
 (8)

To illustrate the calculational simplicity that the BCS approximation introduces consider the example of  $\frac{116}{50}$ Sn discussed previously. Equations (7) and (8) with  $N = \frac{16}{10}$  provide six equations for the six unknowns (five  $v_j$ 's corresponding to the five single particle levels used in the calculation and the multiplier  $\lambda$ ). These six equations replace the 110 x 110 energy matrix that would have to be constructed and diagonalized if all possible seniority zero eigenfunctions were used. The BCS approximation attains this simplicity by imposing a relationship between the probability that the configuration  $(j_1)^{n_1}(j_2)^{n_2}\cdots(j_m)^{n_m}$  and the configuration  $(j_1)^{n_1}(j_2)^{n_2}\cdots(j_m)^{n_m}$  occup in the wave function. Therefore, the BCS wave function provides a particular linear combination of seniority zero wave functions that can be used to make the variational calculation. As stated before,  $v_j^2$  represents the probability that the state (jm) is occupied. A plot of this quantity as a function of the single particle energy is shown in Fig. 3. For states well within the Fermi sea the state is definitely occupied and  $v_j^2$  is certainly unity, for states far above the Fermi sea there is zero probability of occupation and for states near the Fermi surface the probability of occupation is somewhere between zero and one.

Since the BCS eigenfunction represents the lowest state of the system one can considere it to be a vacuum state. Let us, therefore, look for an operator which when acting on the BCS wave function gives zero. If one finds such an operator one can say that the BCS state represents the vacuum state for entities created by this operator. It is apparent that

when applied to the BCS wave function gives zero. This follows because  $\propto_{jm}$  commutes with all terms in the product wave function except the term in  $\pi$  in which  $(jm) = (j_1m_1)$ .

where the prime on  $\pi$  means that the term in the product in which  $(j_1m_1) = (jm)$  is left out. The Hermitian adjoint of  $\mathcal{A}_{im}$  is

$$\alpha_{jm}^{+} = u_{j} a_{jm}^{+} - (-1)^{j-m} v_{j} a_{j-m}$$
 .... (11)

and since  $u_j^2 + v_j^2 = 1$  it follows that

$$\left\{ \boldsymbol{\alpha}_{jm}^{*}, \boldsymbol{\alpha}_{j',m'} \right\} = \boldsymbol{\delta}_{jj}, \boldsymbol{\delta}_{mm'}, \qquad \dots \qquad (12)$$

Thus the operators  $\mathbf{a}_{jm}^+$  and  $\mathbf{a}_{jm}$  act like Fermion creation and annihilation operators respectively. The entities that they create and destroy are called quasi-particles and the BCS state is the state in which there are no quasi-particles present. If the level (jm) is far inside the Fermi sea, then it is apparent from Fig. 3 that  $\mathbf{v}_j^2 = 1$  and the quasi-particle creation operator creates a hole in the sea. For (jm) considerably above the Fermi surface  $\mathbf{u}_j^2 = 1$  and  $\mathbf{a}_{jm}^+$  produces an ordinary particle. Near the Fermi surface the quasi-particle is partly particle and partly hole.

If we now look at the form of the one quasi-particle state it is easy to show that it is identical to an ordinary seniority one shell model wave function.



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This follows because

where the ( ) immediately after  $\pi$ ' stands for that part of the product BCS wave function in which  $(j_{j}m_{j}) \neq (jm)$ . Thus the one quasi-particle state is related to the situation in which all particles are paired to angular momentum zero expect one and this is precisely the definition of a seniority one level. In a similar way the two quasi-particle states can be shown to be equivalent to seniority two eigenfunctions

$$\begin{aligned}
\varphi(\mathbf{J}) &= \left(\alpha_{\mathbf{j}_{1}\mathbf{m}_{1}}^{+} \mathbf{X} \alpha_{\mathbf{j}_{2}\mathbf{m}_{2}}^{+}\right) \mathbf{M} \prod_{\mathbf{j} \neq \mathbf{v}_{0}} \left(\mathbf{u}_{\mathbf{j}} + \mathbf{v}_{\mathbf{j}}^{(-1)\mathbf{j}-\mathbf{m}} \mathbf{a}_{\mathbf{j}-\mathbf{m}}^{+}\right) & | \mathbf{0} \\
&= \frac{1}{\mathbf{u}_{\mathbf{j}_{1}}\mathbf{u}_{\mathbf{j}_{2}}} \left[ \prod_{\mathbf{j} \neq \mathbf{w} > \mathbf{0}} \left(\mathbf{u}_{\mathbf{j}} + (-1)^{\mathbf{j}-\mathbf{m}} \mathbf{v}_{\mathbf{j}} \mathbf{a}_{\mathbf{j}\mathbf{m}}^{+} \mathbf{a}_{\mathbf{j}-\mathbf{m}}^{+}\right) \right] \left(\mathbf{a}_{\mathbf{j}_{1}\mathbf{m}_{1}}^{+} \mathbf{X} \mathbf{a}_{\mathbf{j}_{2}\mathbf{m}_{2}}^{+}\right) \mathbf{M} \left| \mathbf{0} \right\rangle (14)
\end{aligned}$$

where  $(X)_{JM}$  stands for the coupling of the two particles or quasi-particles to angular momentum J with z-component M.

To cut down the size of the shell model calculation it is now clear what should be done. For even-even single closed shell nuclei one should determine  $v_j$ and  $\lambda$  from the variational calculation described by Eqs. (6), (7) and (8). The ground state energy of the nucleus can then be computed from

 $\mathbf{E}_{o} = \langle \Psi | H | \Psi \rangle \qquad \dots \dots (15)$ 

The values of  $v_j$  and  $\lambda$  are thus fixed by this calculation. One then constructs all possible two quasi-particle states,  $\phi$ , of the form given by Eq. (14) and diagonalizes the shell model Hamiltonian using these as basis states. The labor saved by this approximation is immense. For example in  $\frac{116}{50}$ Sn we would have had to construct and diagonalize a matrix whose size was of the order of 1,000 x 1,000 if we did the seniority two calculation for J = 2. On the other hand, the number of two quasi-particle states with J = 2 and positive parity is only nine.

Although this approximation saves a large emount of labor the ultimate test of its usefulness is whether or not it yields results in reasonable agreement with exact calculations. To this end we have listed in Table 3 the results that the BCS and two quasi-particle approximations give for the case of  $\frac{62}{28}$ Ni . A comparison of columns

| J              | Exact<br>Energy<br>(MeV) | BCS or two<br>quasi-particle<br>Energy (MeV) | Projected BCS or<br>two quasi-particle<br>Energy (MeV) |
|----------------|--------------------------|--|--|
| 0 <sub>1</sub> | (0.448)                  | (1.932)                                      | (0.567)  |
| 2,             | 1.533                    | 1.066  | 1.455  |
| 22             | 2.253                    | 1.860  | 2.265  |
| 41             | 2.201                    | 1.830  | 2.226  |

TABLE III

Energies of the various states  $in_{28}^{62}$ Ni. The results of the exact calculation are given in column 2. The tabulated ground state energy is the total interaction energy of the six extra core neutrons. Other energies tabulated are excitation energies relative to the ground state. In column 3 the results of the ECS calculation are tabulated and in column 4 the results using projected ECS wave functions as described by Eq. (16) are tabulated.

two and three of the table immediately shows that the BCS and two quasi-particle approximations are not valid for this case. The reason may be understood as follows: If we examine the probability distribution for the number of particles in the BCS wave function we find that the maximum probability is for the state with  $N = \overline{N}$ (where  $\overline{N}$  is the number of particles in the state of physical interest). However, this part comparises only about 40% of the wave function. The remaining 60% describes a system with N different than  $\overline{N}$ . A plot of this distribution, given in Fig.4, shows that the distribution is more or less symmetric about  $\overline{N} = \overline{N}$ . Thus if we calculate the expectation value of any quantity that is symmetric about  $\overline{N}$  the errors introduced by particle number non-conservation in the BCS wave function will cancel out. In the case of the Nickel isotopes the curve for the binding energy of the extra core nucleons is illustrated in Fig. 5. This curve is clearly not symmetric about  $\overline{N} = 6$ , the number of valence nucleons in  $\frac{62}{26}Ni$ , and this explains why the approximation is so bad in this case.

However, if one projects out of  $\Psi$  the part that describes N particles and normalizes this projected wave function, then the energy

 $\mathbf{E}_{\text{proj}} = \langle \mathbf{P} \boldsymbol{\Psi} | \mathbf{E} | \mathbf{P} \boldsymbol{\Psi} \rangle \qquad \dots \qquad (16)$ 

agrees extremely well with the results of the exact calculation. In the above equation the notation P  $\Psi$  stands for the normalized N particle part of  $\Psi$ . The



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diagonalization of H using the two quasi-particle wave functions,  $\phi$ , of Eq. (14) leads to eigenfunctions

$$\mathcal{Y}_{\mathbf{k}}(\mathbf{J}) = \mathcal{E}_{\mathbf{I}} \mathcal{B}_{\mathbf{i}\mathbf{k}} \mathcal{P}_{\mathbf{i}}(\mathbf{J}) \qquad \dots \qquad (17)$$

where J denotes the angular momentum of the state and k labels which s tate with angular momentum J we are considering. In a similar way the energies

$$\mathbb{E}_{\text{proj}}(J,k) \triangleq \langle \mathbb{P} \chi_{k}(J) | H | \mathbb{P} \chi_{k}(J) \rangle \qquad \dots (18)$$

agree closely with the exact calculations. This is seen from a comparison of columns 2 and 4 of Table 3.

A second quantity that is of interest in an even-even nucleus is the value of B(E2) between the various nuclear states. In Table 4 we list the values of this quantity for  $\frac{62}{28}$ Ni. The results shown compare the exact  $(2p_{3/2}, if_{5/2}, 2p_{1/2})$  shell model calculation with the results that emerge when one makes the seniority zero and two approximation is only sufficient to ex-

| Transition  | Exact | Seniority O<br>and 2<br>Approximation |
|---|-------|---------------------------------------|
| <sup>2</sup> <sub>1</sub> > <sup>0</sup> <sub>1</sub> | 255   | 262                                   |
| 4 <sub>1</sub> > 2 <sub>1</sub>                       | 65    | 2.5                                   |
| <sup>2</sup> <sub>2</sub> <sup>2</sup> <sub>1</sub>   | 175   | 45                                    |
|   |       |                                       |

### TABLE IV.

Values of B(E2) in arbitrary units for  $\frac{62}{28}$ Ni. The results tabulated in column 2 are the results of the exact shell model calculation and those given in column 3 are the shell model results when the ground state is taken to be seniority zero and the excited states seniority two.

plain the transition between the first excited  $2^+$  level and the ground state. The other transition rates are inadequately described, the 10% seniority four admixtures in the  $4_1^+$  and  $2_2^+$  states drastically change the values of B(E2). Since the two quasi-particle result is merely an approximation to the seniority calculation, it is senseless to use the two quasi-particle eigenfunctions to describe transitions other than the first  $2^+$  to ground state transition. However, for this latter transition the approximate calculation compares quite favourably with the results of the exact calculation. That is, where the exact calculation gives 255, the BCS and two quasi-particle approximations give 213. If one uses the projected wave functions the  $B(\mathbb{R}2)$  becomes 242 in excellent agreement with the shell model result.

In summary, the results that have been presented here show:

(1) The BCS wave function for the ground state of an even-even nucleus provides an approximation to the seniority zero shell model calculation and the two quasiparticle theory is an approximation to the seniority two results.

(2) As far as energies are concerned there is some hope that the BOS and quasiparticle approximations will reproduce the results of the exact calculations for states with even values of J. However, the approximations can only come close to the shell model results if the energy one is trying to calculate for the physical system with  $\overline{N}$  particles is symmetric about  $\overline{N}$ . If the energy is not symmetric as a function of N about  $\overline{N}$  then to get agreement with the exact calculation one must project from the BCS wave function or the two quasi-particle eigenfunction the part describing  $\overline{N}$  particles, normalize this projected wave function and then calculate the energy using this projected wave function. For odd values of J the shell model wave functions have large sentority four components and hence the two quasi-particle calculation is not justified.

(3) The two quasi-particle approximation to the first  $2^+$  level and the BCS result for the ground state lead to an E2 transition rate between these levels in good agreement with the exact calculations. On the other hand, the first excited  $4^+$ level and the second  $2^+$  level have a sufficient seniority four contaminant in their wave functions (at least for  $\frac{62}{26}$ Ni) to give a marked difference between the truncated seniority zero and two shell model calculation and the full configuration result. Thus to study these transitions it is necessary to take into a cocumt four quasi-particle states in the description of the levels. The fomalism for whis has been set up by Pal, Gambhir and Raz (6).

Some of the material discussed here is unpublished work done in collaboration with Dr.S. Cohen and Dr.M.H. Macfarlane of Argonne National Laboratory.

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# ELEMENTRY PARTICLES AND NUCLEAR STRUCTURE

## B. Banerjee Tata Institute of Fundamental Research Colaba, Bombay.

I apologise for the presumptuous title of the talk. The only elementry particles I shall talk about are the pions and their use in extracting nuclear structure information.

I shall begin by recalling the basic properties of the pions. They exist in three charge states (i -spin - t = 1) with the following masses and life-times:

|          | Mass  |   | Lifetime             |
|----------|-------|---|----------------------|
| <b>±</b> | (MeV) |   | (Sec)                |
| TI       | 139.6 | · | $2.6 \times 10^{-8}$ |
| TTO      | 135.0 |   | $2 \times 10^{-16}$  |

The nature of the pion-nuclear force as known from the phase-shift analysis upto pion (laboratory) energy of 300 MeV can be summarised as follows:

At low energies ( $\angle 100$  MeV) where the relative S-state of the ( $\pi N$ ) system is important, the force is attrative in the  $T = \frac{1}{2}$  state and weakly repulsive in the  $T = \frac{3}{2}$  state. Here T is total isotopic spin of the ( $\pi N$ ) system. At a higher energy the relative p-state becomes important. In this state the force is strongly attractive and produces a resonance in the  $T = \frac{3}{2}$ ,  $J = \frac{3}{2}$  state at 190 MeV.

Next we list the properties of the pions which make them of interest as nuclear probes:

1) Pions are distinguishable from nucleons and they have zero spin. So there is no complication due to spin and exclusion principle.

 2) Elementry pion nuclear interaction upto pion kinetic energies of the order of 300 MeV is much simpler and better understood than the nucleon-nucleon interaction.
 3) A slow negative pion is captured in a Bohr orbit around the nucleus, consequently many details about the nuclear interaction of slow energy pions with nuclei, can be inferred from the energy shifts and transition rates of the TT-mesic X-rays.

4) The pion captured by the nucleus has almost zero momentum. So to conserve energy and momentum the pion must be captured by at least two nucleons (since the probability of finding more than two nucleons together is small). This gives rise to the possibility of determining the correlation function of two nucleon at short distances. This was first pointed out by Brueckner, Serber and Watson in 1951 (1). We shall discuss this process in greater detail later on.

The various processes that can be observed in the reactions of a nucleus of

charge Z and neutron number N with pions is as follows:

(a) Elastic Scattering

| (b) Absorptions | TT + (N       | , z) ->       | (N - z, Z)               | + (NN) | →(N - 1,             | Z - 2)      | + (N <b>P</b> ) |
|-----------------|---------------|---------------|--------------------------|--------|----------------------|-------------|-----------------|
| ,               | TT++ (N       | , 2)>         | (N - 1, Z                | - 1) + | (PP) → (N            | - 2, Z)     | + (NP)          |
| (c) Single char | rge exchanges | $\pi^{\mp} +$ | (N, Z)>                  | •π°+   | (N ± 1, Z            | ±1)         |                 |
| (d) Double chag | ge exchange:  | $\pi^{\mp}$ + | $(N, Z) \longrightarrow$ | πŦ+    | (N <del>+</del> 2, Z | <u>+</u> 2) |                 |
| (e) Radiative / | bsorption:    | π +           | $(N, Z) \rightarrow$     | ¥+     | (N + 1, 2            | - 1)        |                 |

In this talk we shall discuss the processes a, b, d and e since experimentally nothin much is known about c.

ELASTIC SCATTERING:

This can be treated in the same way as the nucleon-nucleon scattering 1.e., assuming an optical potential and fixing the parameters expirically. However the advantage in pion-nucleus scattering is that it can be theoretically deduced with much greater certainty that the nucleon-nucleus scattering for reasons already stated. The following important characteristic of the ( $\pi$ N) system should also be noted.

i) The important p-wave (TT N) scattering amplitude implies an average non-local potential.

ii) The existence of real absorption of pions at zero energy and even at negative energies gives rise to a non-vanishing imaginary part in the low energy region.

Ericson and Ericson (2) have recently calculated the optical potential at low energies using a theory of multiple scattering based on impulse approximation and a systematic expansion in nuclear correlation function. The two basic imputs are the single-nucleon

$$\overline{11} + \overline{N} \rightarrow \overline{11} + \overline{N}$$

and the two nucleon

 $\overline{11} + N + N \longrightarrow N + \overline{N}$ 

amplitudes

We have here a brief summary of their calculations following Sens (3). The  $TT + N \rightarrow TT + N$  scattering amplitude at low energy can be written as

.... (1)

$$f_{j}(\vec{\tau}) = (k_{0} + c_{0} k_{1} \cdot k_{j}) \delta(\vec{\tau} \cdot \vec{\tau}_{j})$$

where  $\vec{\gamma}_{j}$  is the position of the nucleon and  $k_{j}$  and  $k_{j}$  are the initial and final

momenta of the pion.  $b_0$  and  $C_0$  are related respectively to the s and p-wave ( $\pi$  N) scattering lengths.

The  $\overline{\mathbf{M}} + \mathbf{N} + \mathbf{N} \rightarrow \overline{\mathbf{M}} + \mathbf{N} + \mathbf{N}$  amplitude (extremely simplified) will have the form  $f_{ij}(\vec{\mathbf{v}}) = (\mathcal{B}_0 + \mathcal{C}_0 \vec{\mathbf{k}}_i \vec{\mathbf{k}}_j) \, \delta(\vec{\mathbf{v}} - \vec{\mathbf{v}}_j) \, \delta(\vec{\mathbf{v}} - \frac{1}{2} (\vec{\mathbf{v}}_i + \vec{\mathbf{v}}_j))$  (2)

This assumes that the two nucleons are in relative S-state. The complex quantities  $B_{c}$  and  $C_{c}$  are determined from the process:

$$N + N \longrightarrow \overline{II} + N + N$$

and

$$TT + d \longrightarrow N + N$$

These two amplitudes yield via the multiple scattering theory a pion-nuclear potential

$$V(\mathbf{T}) = -4\pi \left[ \mathcal{L}_{o} \mathcal{P} + \mathcal{P}_{o} \mathcal{P}^{\dagger} + \mathcal{C}_{o} \vec{\nabla} \mathcal{P} \vec{\nabla} + \mathcal{C}_{o} \nabla \mathcal{P}^{\dagger} \vec{\nabla} \right] \qquad \dots (3)$$

where  $\mathcal{P}(\vec{r})$  is the density of the nucleus. The gradient terms are obviously important at the surface of the nucleus. Two effects have been neglected inwriting down  $V(\vec{r})$  - isospin dependence and the pionic analogue of dipole scattering on dense media.

To test this potential, the shifts and width of the levels of mesic atoms are calculated. This is done by solving the Schrödinger equation for the meson,  $\nabla U + (k^2 - \nabla (Y)) \Psi = 0$ 

with the complete expression for the complex potential V(3). From the calculations following qualitative features emerge:

i) The 15 level shift is dominated by the local, s-wave  $\pi N(l_0)$  and  $\pi 2N(\text{ReB}_0)$  interactions.

ii) The 2p and 3d level shifts are dominated by the non-local p-wave  $TN(c_0)$  and T2N(ReC) interactions.

iii) The [S level width is determined by the local, s-wave TT2N (Im Bo) interaction.

iv) The 2p and 3d level shifts are dominated by the non-local p-wave  $TT_2 N$  (ImC<sub>0</sub>) interaction.

Ericson and Ericson have also considered several corrections concerning Fermi notion, finite correlation length and isospin terms. The comparison of  $b_0$ ,  $c_0$ ,  $ImB_0$  and  $ImC_0$  obtained both from pion-scattering and production data with those obtained from X-ray data are shown below.

The effective  $b_0$  and  $c_0$  include the corrections mentioned above and also the contributions Re B<sub>0</sub> and Re C<sub>0</sub> are added.

### ABSORPTION OF PIONS:

We have already given arguments to show that the pions must be absorbed by

at least two nucleons. This seems to be the dominant mode of absorption as found experimentally (4). The emission of the two nucleons can be treated in two defferent ways and we describe both the approaches:

1. In the conventional approach the interaction between the pion and the nucleus is assumed to be of the following form:

 $H = \frac{f}{M} \stackrel{A}{\underset{i=1}{\overset{}_{=}}} \left[ \Psi_{N}^{\dagger}(i) \left( \overrightarrow{\sigma_{n}} \cdot \overrightarrow{\nabla_{n}}(i) \right) \overrightarrow{\tau_{n}} - \Psi_{N}^{\dagger}(i) \cdot \overrightarrow{q}(i) - \frac{M}{M} \cdot \Psi_{N}^{\dagger}(i) \left( \overrightarrow{\sigma_{n}} \cdot \overrightarrow{\nabla_{N}}(i) \right) \overrightarrow{\tau_{n}} \cdot \Psi_{N}^{\dagger}(i) \overrightarrow{q}(i) \right]$  (4)

Here  $\forall_N$  and  $\forall_N$  are the nucleon creation and destruction operators,  $\vec{\phi}$  is the pion field operator,  $\mathcal{A}$  and  $\mathcal{M}$  are respectively the pion and nucleon masses and f is the pion nucleon coupling constant.

To introduce the correlation between the nucleon a wave function for the nucleon of the following form is used:

$$\Psi = \Phi \pi_{i$$

where  $\Psi$  is usually a determinant of harmonic oscillator wavefunctions. The most recent calculation (for <sup>16</sup>0) on these lines is that of Letorneux and Eisenberg (5). They have assumed f of the form given by Dabrowski (6)

$$f = 0 \quad \forall < \gamma_e \\ = 1 - e^{-\beta [(\forall / \gamma_c)^2 - 1]} \quad \forall > \gamma_c \\ \gamma_c = 0.4 \text{ fm}, \beta = 1.4$$

whe re

The angular distribution of the emitted np and nn pairs along with the experimental results is shown in Fig. 1.

In this work the following effects have also been included.

i) The modification of the pion wave-function due to the finite charge distribution of the nucleus and the pion-nucleus potential.

ii) The final state interaction of the two outgoing nucleons. The authors find that the last effect is important for explaining the angular distribution but it makes the ratio R of the number of (n,n) - pairs to (p,n) pairs very small. For <sup>16</sup>0 the theoretical value ~0.5 whereas the experimental value is  $3.4 \pm 1.1$  (4). One explanation advanced is that the np-correlation length  $\beta_{np}$  is different form the ppcorrelation length  $\beta_{pp}$ .

2. We notice that the model of pion capture described above treats the process as a two-step one. The nucleon 1 (say) absorbs the pion and since the probability of having two nucleons close together is higher than finding more than two, the nucleons 1 and 2 leave the region of interaction without further collisions. The difficulty in this approach is that the two steps are arbitrarily selected out of the many possible ways a meson can be absorbed by the two nucleons. Even if it is allowed that it is the dominant process we would not know how tocalculate the



second step since the meson physics involved is extremely complicated. In other words the conventional approach presents an over-simplified picture of the twobody character of the pion-nuclear interaction.

Recently Eckstein (7) following Brueckner, Serber and Watson has proposed an alternative approach. Here the Hamiltonian describing the interaction of the pion with the capturing nucleons is treated phenomenologically. The pion is assumed to be in a relative s-state with respect to the pair of nucleons. Also only the capture in relative s-state of the two nucleons is considered.

The pheonomienological Hamiltonian is of the form

$$H_{12} = \int d^{3}v_{1} d^{3}v_{2} \Psi_{N}^{\dagger}(\vec{v}_{1}) \Psi_{N}^{\dagger}(\vec{v}_{2}) M_{12} \Psi_{N}(\vec{v}_{1}) \Psi_{N}(\vec{v}_{1})$$
where  $M_{12} = \left[ q_{0} \frac{1}{2} (\vec{c}_{1}^{2} + \vec{c}_{2}^{2}) \cdot \vec{k} \frac{1}{2} (\vec{z}_{1}^{2} - \vec{v}_{1}^{2}) \cdot \vec{\psi} + q_{1} \frac{1}{2} (\vec{c}_{1}^{2} - \vec{c}_{2}^{2}) \cdot \vec{k} \frac{1}{2} (\vec{z}_{1}^{2} + \vec{z}_{2}^{2}) \cdot \vec{\psi} \right] T_{12}^{\tau} T_{12}^{\tau} \mathcal{I}(\vec{z}_{1}^{2} - \vec{z}_{2}^{2})$ 
(3)

Here  $\mathcal{T}_1$ ,  $\mathcal{T}_1$  and  $\mathcal{T}_1$ ,  $\mathcal{T}_2$  are the iso-spin and spin operators respectively of the two nucleons and k is the relative momentum of the outgoing nucleons.  $T_{12}^{\sigma}$ ,  $T_{12}^{\star}$ are the spin, isospin triplet projection operators. The first term in Eq. (5) describes the transition from the  ${}^3S_1$  state of the two nucleons to the  ${}^3p_1$  state which the second term describes the transition from the  ${}^1S_0$  to the  ${}^3P_0$  state. The emplitudes of these transitions,  $g_0$  and  $g_1$  are determined from the reactions.

and

 $p + p \longrightarrow \pi^{+} + d$   $p + p \longrightarrow \pi^{0} + p + p$ 

We note that these amplitudes among others have been used by Ericson and Ericson for determining  $f_{a_1}(\tau)$  in Eq. (2).

Eckstein has used this effective Hamiltonian to calculate the braching ratio of the various modes of capture in <sup>4</sup>He which Divakaran (8) has calculated the absolute capture rate in <sup>3</sup>He. These calculations agree very well with the experimental results, we have calculated the ratio R of the number of neutron pairs emitted to the number of neutron-proton pairs, the angular distribution as a function of the opening angle between the outgoing nucleon and the total capture rate in <sup>12</sup>C using the same Hamiltonian.

The ratio R agrees with the experimental results but the total capture rate comes out smaller than the experimental value. This is to be expected since it is assumed the two capturing nucleons are in a relative s-state only.

In concluding this section we mention a rather remarkable experimental result (4) which shows that R is more or less constant for a very large number of nuclei.

## DOUBLE CHARGE EXCHANGE:

This was first suggested by De Shalit and Drell.

This reaction has the following points of interest:

i) One can change the charge by two so one can study proton (neutron) rich nuclei outside the valley of stability. Also interesting proton or neutron system like the following:

$$\overline{\Pi} + {}^{3}\text{He} \longrightarrow {}^{3}n + \Pi^{+}$$
$$\overline{\Pi} + {}^{3}\text{H} \longrightarrow {}^{3}p + \Pi^{-}$$

can be studied.

11) Isobaric analogue states which differ by  $\Delta T_{p} = \pm 2can$  be produced.

Unfortunately both the theoretical and experimental results show the cross section to be quite small. The theoretical calculations have been carried out by Parsons et al (9), Brown and Barshay (10) and Becker and Maric (11). One experimental result due to Batusov et al (12) is shown in figure (2).

#### RADIATIVE CAPTURE:

Recently there has been one nice experiment (13) using the radiative capture for determining the single nn-scattering length  $\binom{1}{a_{nn}}$ 

 $T + d \rightarrow n + n + \delta$ 

The pion is captured from the s-orbit. The shape of the energy angle spectrum of the two final neutrons show a marked dependence on the assumed nn scattering length.

This experiment however does not determine the sign of  $a_{nn}$ . The value obtained by Haddock et al (13) is -16.4 ± 1.9 fm whereas  $a_{np}$  is -23.7 fm. This indicates a small violation of charge independence.

There have been two calculations of the radiative capture in complex nuclei using impulse approximation treating the nucleons to be infinitely heavy (static limit) In this limit the effective Hamiltonian is obtained from the inverse process

$$\gamma + n \longrightarrow \pi + p$$

The threshold amplitude of this process is

$$F = \frac{\ell}{\sqrt{2}\pi} \frac{f}{\mu} \times \vec{c} \cdot \vec{e}$$

where  $\in$  is the polarisation vector of the photon and  $\overline{G}$  the spin of the nucleon. Therefore the effective Hamiltonian of the capture process is

$$H_{aff} = \lambda \int_{\overline{a}}^{\ell} \pi \int_{\overline{a}}^{f} \int_{\overline{a}}^{H} \frac{f}{\lambda^{i}} \int_{\overline{a}}^{H} \tau_{a}^{-1} \left( \vec{\sigma}_{a} \cdot \vec{\epsilon} \right) \delta \left( \vec{\gamma} - \vec{\gamma}_{a} \right)$$

This is the same as the axial vector Hamiltonian occuring in muon capture.

So the same analysis is applicable here. It is well-known that the states excited in muon capture is closed shell nuclei are the isobaric analogues of the "giant diple" states excited in photon capture (14). One would therefore expect to see the same states in radiative pion capture with the added advantage that in the final state one has a photon instead of a neutrino. Calculations have been carried out on these lines using H<sub>eff</sub> by Delorme and Ericson (15) and Anderson and Eisenberg (16)

In conclusion we mention that the equivalence of radiative pion capture and muon capture has been demonstrated without using the impulse approximation argument given above, by Pietschmann et al (17) and Ericson and Figuereau (18).

Fig. 1 shows total angular distributions of ejected pairs in  ${}^{16}$ O (5). The curve labeled a refers to 2P pion absorption with a np pair, and curve b is for 2P(nn). Curves c and d refer to 1S emission of a np and nn pair respectively. The units are  $10^{15} \text{ sec}^{-1}$  for 2P absorption and  $10^{17} \text{ sec}^{-1}$  for 1S absorption. The dots are for np emission and boxes are for nn data.

Fig. 2 shows total cross-section for double charge exchange of  $\Pi^{e}$  mesons as a function of energy (12).

## TABLE I

## Comparison between pion scattering and production, and pionic X-ray data

|       | ÷ .     | From pion scattering<br>and production data       | From pionic<br>X <b>-rays</b>   |
|-------|---------|---|---|
| b eff | <u></u> | $-0.014 \pm 0.005^{a}$<br>- 0.028 $\pm 0.006^{b}$ | - 0.029 <u>+</u> 0.006 <sup>a</sup> ,d)   |
|       |         | •   | $= 0.0197 \pm 0.0004^{c} \\ = 0.028 \pm 0.005^{e} $   |
| c eff | •       | $0.19 \pm 0.02^{\rm c}$                           | $\begin{array}{rrr} 0.21 & \pm 0.07 & d \\ 0.131 & \pm 0.011 & c \end{array}$                 |
| Im B  |         | 0.0116 <u>+</u> 0.0014 <sup>B)</sup>              | $0.0163 \pm 0.0013^{c})$<br>$0.0160 \pm 0.0040^{e})$  |
| Im C  |         | $0.088 \pm 0.013^{d}$                             | $\begin{array}{r} - & - \\ 0.134 & \pm & 0.034^{d} \\ 0.146 & \pm & 0.020^{c} \\ \end{array}$ |
|       |         |   | 0.130 ± 0.0405/   |

a) See Ref. 19

b) See Refs. 19 and 20; the difference with (a) results from the use of different scattering lengths.

c) See Ref. 20

d) See Ref. 2 /

e) Same data as (c) but differently analysed, see Ref. 21.

|   | n)       |
|---|----------|
| $\mathbf{arget} \qquad (\mathbf{n}-\mathbf{n}) \qquad (\mathbf{p}-\mathbf{n}) \qquad \mathbf{Ratio} \qquad (\mathbf{n}-\mathbf{n})$ | P)       |
| <sup>6</sup> Li .41 ± .17 .11 ± .03 3.7 ± 1.0   |          |
| <sup>6</sup> L1 small $.69 \pm .28$ $.23 \pm .06$ $3.0 \pm .8$  |          |
| $7_{L1}$ .50 ± .21 .13 ± .04 3.7 ± 1.0  |          |
| ${}^{9}$ Be .33 ± .13 .10 ± .02 3.3 ± .9  |          |
| $10_{B}$ .19 ± .08 .08 ± .02 2.3 ± .8   |          |
| $11_{B}$ .23 ± .10 .05 ± .01 4.4 ± 1.3  |          |
| $12_{0}$ .14 ± .06 .06 ± .02 2.5 ± 1.0  | l.       |
| $14_{\rm N}$ .14 ± .06 .04 ± .01 3.7 ± 1.1  | · .      |
| $16_0$ .27 ± .11 .08 ± .02 3.4 ± 1.1  | · .      |
| 160 small .39 ± .16 .10 ± .03 3.8 ± 1.0   |          |
| $27_{Al}$ .07 ± .03 ± .01 2.4 ± .9  | ).       |
| Cu $.08 \pm 0.5$ $.04 \pm .01$ $2.0 \pm 1.4$  | ł        |
| <b>Pb</b> $.06 \pm .06$ $.01 \pm .01$ $4.7 \pm 4.7$   |          |
| Weighted average of p-shell nuclei 3.3 + .9   | )        |
| (Weighted average of Ratio at $180^{\circ}$ 5.1 + 1.6   | <b>i</b> |

Number of Correlated Emissions per stopped Pion and Ratio

TABLE II

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### DISCUSSION:

G. Ramachandran: In deriving the optical potential for elastic pion scattering do you need the  $h_1$  k term?

B. Banerjee: That and the other relevant terms have been included in these calculations. I have not mentioned them to keep the discussion simple.

K. Srinivasa Rao: Do you have any comments to make about the modified Kisslinyer model which has been used by Baker, Rainwater and Williams to account for  $\eta$  elastic scattering by nuclei?

B. Banerjee: I feel Ericson and Enson calculations are an improvement over those you mention.

A.K. Jain: How much is the effect of Impulse approximation?

B. Banerjee: The Impulse approximation should be reasonally good, since each nucleon gets about 70 MeV from the pion.

**P.P.** Kane: (1) Why do you ignore the ten year old experiments on the inelastic interactions at 31 MeV by myself and 58 MeV of  $\pi^+$  on carbon? (2) How will you include the form-factor of the pion into your considerations?

S.C.K. Nair: (Comment)

The final state interaction between the two outgoing neutrons is very important and any conclusions one may draw from a calculation without taking care of this could be quite erroneous.

#### ISOSPIN IMPURITIES OF LOW LYING NUCLEAR STATES

## S.K. Mitra Tata Institute of Fundamental Research Colaba, Bombay-5.

## INTRODUCTION:

I shall be talking about isospin impurities of nuclear states. The informations contained in this talk have been obtained essentially from beta decay experiments and I shall therefore limit myself to low lying states generated by beta decay. The interest in the present topic has grown recently with the accumulation of a large amount of data on Fermi matrix elements  $M_F$  in unfavoured beta transitions connecting states with different isospins i.e.  $\Delta T \neq 0$ . We shall see shortly that these are intimately related to isospin impurities. The concept of isobaric spin has been with us since quite some time and we have seen that it is very useful in classifying nuclear states. Along with it, we have notions like charge symmetry and charge independence of nuclear forces for which there is over-whelming evidence. Then, recently we have seen the discovery of isobaric analogue states in medium and heavy nuclei and this has given us a tremendous confidence in the isospin formalism. Isobaric spin has thus come to be regarded as a good quantum number.

At this stage, we ask a few questions-

1) How good is this quantum number any way?

2) Whether it is true for heavier nuclei?

3) And since there are finer measurements, one wonders how much is the charge dependence, if any, of specifically nuclear forces even though it may be only few per cent? In this context, one would like to examine the isospin purity of nuclear states. One can have impurities due to a perturbation like the Coulomb interaction or a charge dependent nucleon-nucleon interaction which would mix states having different isobaric spins. In that case, one hopes to obtain elements like  $\langle \Psi_{\alpha,\tau_i} | H_c | \Psi_{b,\tau_i} \rangle$ . We shall call them "effective Coulomb matrix elements". These are observables and if  $H_c$  is known, these could be very useful in the investigation of nuclear structure. As a matter of fact, in principle they are like or in the same footing as energies, electric and magnetic multipole moments, transition probabilities etc.

In the present talk, I shall try to summarise.

1) the present state of measurements of the Fermi matrix elements M<sub>p</sub>, mentioning also the techniques involved

2) the isospin impurities and their systematics

3) the "Coulomb matrix elements"  $\langle H_{\lambda} \rangle$  and

4) finally some qualitative aspects of the charge dependence of nuclear forces which is the outcome of these measurements. Let me mention at the very outset that the question of charge dependence again is not something new for us. We have bothered about it almost since the begining because we had troubles practically every where. There were, for example, deviations in the energy levels of mirror nuclei and there were transitions which were forbidden by the isobaric spin selection rules. This will be just another way of looking at things, through the eyes of beta decay.

Let me start with the Fermi matrix element  $M_{\mathbf{F}}$ .

# FERMI MATRIX ELEMENT M<sub>F</sub> :

These occur in the simplest types of beta transitions, known as allowed. Consider a beta decay between two nuclear states  $J + \xrightarrow{\mathcal{A}} J +$  (see Fig. 1). Such a transition is governed by two types of matrix elements- the Fermi matrix element  $\mathbb{M}_{F}$  and the Gamow Teller matrix element  $\mathbb{M}_{GT}$ . In the former case, the electron and the anti-neutrino are emitted with antiparallel spins; in the latter the spins are parallel. The total transition strength is expressed in  $\beta$  decay language by an ft value.



where  $C_V$  and  $C_A$  are the coupling constants for the vector and the axial vector interaction respectively. The selction rules for the Fermi part are  $\Delta J = 0$  and for the Gamow Teller part  $\Delta J = 0 \pm 1$  (no  $0 \rightarrow 0$ ) and there is no parity change in both. In addition, there is the isobaric spin selection rule, which is  $\Delta T = 0$ for the Fermi /3 transition. This becomes evident if we write the Fermi matrix element  $M_{\rm p} = \int 1$  in detail

$$M_{F} = \int 1 = \Psi_{f}^{*} T_{\mp} \Psi_{i} dr$$

where  $T + = \sum_{i=1}^{n} T_{+}$  is the total isobaric spin operator. T + can only connect states of the same isobaric spin T, it increases (for the plus sing) and decreases (for the minus sign) the component of Tz by one unit. Thus all the matrix elements will vanish except between members of an isobaric multiplet i.e. super allowed transitions. In such cases

$$M_{sup} = \int 1 = \left[ T(T + *) - Tz Tz \right]^{\frac{1}{2}}$$

For example in mirror transitions  $T = Tz = \frac{1}{2}$ ,  $Tz = -\frac{1}{2}$ 

and  $\int 1$  mirror = 1 In the well known  $0 + \rightarrow 0 +$  transitions like  $\frac{14}{8}0 \rightarrow \frac{14}{7}N$  or  $\frac{34}{17}c_1 \rightarrow \frac{34}{16}S$ , T=1,  $T_z=1$ ,  $T_{z'}=0$ and  $\int 1 0 + \rightarrow 0 + = \sqrt{2}$ 

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For all other transitions, the isobaric spin selection rule yields  $M_F = 0$ . However, experimentally we do observe a large number of Fermi transitions with  $\Delta T = 1$ . Besides, there are a number of  $0+ \rightarrow 0+$  transitions, where  $M_{GT} = \int \sigma = 0$  and they can be possible only through Fermi decay. The question arises how do they

SOURCES OF M

occur?

Apparently there are two possible sources

- 1) Isobaric Spin Impurities and
- 2) Meson Exchange Effects
- 1) Isobaric Spin Impurities:

As I said earlier, the Coulomb interaction between protons or a charge dependent part in nucleon-nucleon interaction mixes states of different isobaric spin. So the nuclear states are no longer pure isospin states and we have to write them as mixtures.

For exemple,

$$\begin{aligned} \Psi_{i} &= \left( J, M, T, T_{3} \right) + \left( T + 1 \right) \left( J, M, T + 1, T_{3} \right) + \\ \Psi_{f} &= \left( J, M, T - 1, T_{3} - 1 \right) + \left( T \right) \left( J, M, T, T_{3} - 1 \right) + \\ for electron decay and \\ \Psi_{f} &= \left( J, M, T + 1, T_{3} + 1 \right) + \left( T + 2 \right) \left( J, M, T + 2, T_{3} + 1 \right) + \\ for positron decay \end{aligned}$$

 $\mathcal{L}(T)$ ,  $\mathcal{L}(T + 1)$ ,  $\mathcal{L}(T + 2)$  are isobaric spin impurity coefficients. We can connect  $\Psi_i$  and  $\Psi_f$  by a Fermi decay. For electrons

$$M_{\mathbf{F}}^{-} = \langle \Psi_{\mathbf{j}}^{*} | \mathbf{T} - | \Psi_{\mathbf{x}} \rangle = \mathscr{A}(\mathbf{T}) \langle \mathbf{J}, \mathbf{N}, \mathbf{T}, \mathbf{T}_{3} - 1 | \mathbf{T}_{-} | \mathbf{J}, \mathbf{M}, \mathbf{T}, \mathbf{T}_{3} \rangle$$
$$= \mathscr{A}(\mathbf{T}) \sqrt{(\mathbf{T} + 1) - \mathbf{T}_{3}} (\mathbf{T}_{3} - 1)$$
$$= \mathscr{A}(\mathbf{T}) \cdot \sqrt{2\mathbf{T}}$$

This shows the relation between  ${\rm M}_{\rm F}$  and  $\checkmark$ 

Similarly for positrons

$$M_{\rm F}^+ = \alpha ({\rm T} + 1) \sqrt{2({\rm T} + 1)}$$

This picture has become more physical with the discovery of isobaric analogue states and | J, M, T, T<sub>3</sub>-1 $\rangle$  can be indentified as the analogue of the initial state | J, M, T, T<sub>3</sub> $\rangle$ . A virtual  $\beta$  transition between them would be superallowed. The mixture can be written in terms of the "effective" Coulomb matrix element  $\langle H_c \rangle$  between the analogue state and the final state using first order perturbation theory.

$$\mathcal{L} = \frac{\left\langle \mathcal{V}_{an} \middle| H_{c} \middle| \mathcal{V}_{q\gamma} \right\rangle}{E_{an} - E_{gr}} = \frac{\left\langle H_{c} \right\rangle}{\Delta E_{o}}$$

 $\Delta E_{\rm c}$  is the energy separation of the final and the analogue states and is given by

$$\Delta E_{o} = \Delta E_{c} - (m_{n} - m_{p}) c^{2} \pm (E_{kin}/\beta \pm m_{e}c^{2})$$

Where  $\Delta E_c$  is the Coulomb energy difference between the parent and the daughter nuclei. The upper sign is for electrons and the lower for positrons.  $\Delta E_c$  can be calculated using the formula given by Anderson (see in ref. 12).

## 2) Meson Exchange Effects:

This occurs only in the conventional theory of  $\beta$ -decay where the pion current does not take part in the interaction, the virtual pions in the physical nucleon state thereby inducing a Fermi transition with  $\Delta T \neq 0$ . However under the present conserved vector current theory (1) of  $\beta$  decay, the contribution of virtual pion states to the  $\Delta T = 0$  Fermi transition is strictly zero, because the  $\beta$  interaction Hamiltonian must commute with the total isobaric spin operator.

This has been experimentally verified by Bloom et al (2) and Haase (3) who studied two decays belonging to an isospin triplet, on the suggestion of Bouchiat (4). It was a very interesting experiment. Let us consider the T = 1 multiplet which consists of the ground state of <sup>24</sup>Al and <sup>24</sup>Na and of the 9.5 MeV level of <sup>24</sup>Mg. The ground states of <sup>24</sup>Al and <sup>24</sup>Na decay to the 4.12 MeV 4+ state of <sup>24</sup>Mg which is T = 0(Fig. 2). Any contribution due to isospin impurities is same in the two decays and hence any detectable difference in the observed  $M_F$  in the two cases could be attributed to meson exchange effects Experimentally.

 $M_{\rm p}^{-} - M_{\rm F}^{+} = 0.0008 + 0.0060$ 

which is consistent with the CVC theory. Hence the contribution due to the second source is zero and we need consider only that due to the first one.

# EVALUATION OF M

(a) For the  $0+ \rightarrow 0+$  transitions, it is simple. The GT matrix element is identically zero and we can calculate  $M_F$  simply from the ft value. The latter depends only on the end point energy and the life time of the transition.

(b) For the majority of cases, one has  $M_{GT}$  also and ft value is not enough. In such cases, one uses a technique known as  $\beta - \gamma$  circular polarization correlation method which is recently developed. This has provided an extremely sensitive way to detect the interference term between the Fermi and Gamow-Teller interaction and one can determine the mixing ratio  $\int I / \int_{C} \text{ or } C_{\gamma} M_{F}/C_{A}$  M<sub>GT</sub> in  $\Delta T \neq 0$  transitions. It is applicable to cases where there is a gamma ray following the  $\beta$ -ray and as the name suggests one has to measure the circular polarization of the  $\gamma$ -ray and also the angular correlation of the beta and the circularly polarized gamma ray.

## ORIGIN OF THE TECHNIQUE:

A few words about the origin of the technique will not be out of place. These experiments were conceivable only after 1956 when Lee and Yang (5) announced that parity is not conserved in weak interaction. As a consequence, they suggested that one will be able to measure quantities which are pseudoscalars. In beta decay 1) the first pseudoscalar to be measured was the quantity  $\langle \vec{v} \cdot \vec{l} \rangle$  the angular distribution of electrons from polarized nuclei observed by the Wu et al (6). 2) Another quantity is the longitudinal polarization of electrons  $\langle \vec{\sigma}, \vec{p} \rangle$  which was observed by Frauenfelder (7).

3) A third quantity is the circular polarization of  $\gamma$ -ray following  $\beta$  decay which was measured for the first time by Schopper (8) and in the one we shall need. This follows from the electron polarization. Since the electrons emitted in  $\beta$  decay are polarized, the nucleus is left in a polarized state with respect to the direction of the electron. If it immediately emits a  $\gamma$ -ray, the  $\gamma$ -ray is circularly polarized with respect to the direction of the electron, the amount of polarization varying with the angle between the  $\beta$  and the  $\gamma$ -rays.

ANGULAR CORRELATION BETWEEN THE  $\beta$  and the CIRCULARLY POLARIZED  $\gamma$  -RAYS:

The angular correlation between  $\beta$  and circular polarized  $\gamma$ -rays for allowed  $\beta$  decay has the form

 $\mathbb{W}(\Theta_{\beta}, \gamma) = 1 + \mathcal{C}(\mathcal{V}/\mathcal{C}) \wedge \cos \Theta$ 

Positive or negative circular polarization is denoted by  $7 = \pm 1$ . A is related to the degree of circular polarization and is called the asymmetry parameter. It depends on the type of beta interaction, the ratio X and the spins of the nuclear levels. As usual, the formula is complicated. However, for a mixed allowed  $\beta$  transition followed by a pure  $\gamma$ -ray of multipolarity L in a spin sequence

$$J \xrightarrow{\sqrt{3}} J \xrightarrow{\delta} J_{1}$$

$$A \text{ is given by (9)}$$

$$A = \frac{\sqrt{3}}{6} \frac{1}{1+x2} \left\{ \frac{2}{\sqrt{J(J+1)}} + 4x \right\} F_{1} (LLJ_{1}J).$$

where  $X = C_V M_F / C_A M_{GT}$ . The angular momentum coefficients  $F_1$  (L L J<sub>1</sub> J) are tabulated (9). The upper sign applies for  $/3^-$  decay and the lower for  $/3^+$  decay. Thus a measurement of A would lead to the determination of X. We define, the polarization  $P_c$  (9) by

$$P_{c}(\Theta) = \frac{\Psi(\Theta_{p}+1) - \Psi(\Theta_{p}-1)}{\Psi(\Theta_{p}+1) + \Psi(\Theta_{p}+1)}$$

How to measure the circular polarization?

MEASUREMENT OF  $P_{c}(\Theta)$ :

The most standard way of measuring circular polarization is one using Compton scattering by polarized electrons. The intensity of scattered radiation depends on the relative direction of the proton and the electron spin. Reversing the spin of the scattering electron results in a change of scattered intensity if the  $\forall$  ray is polarized. One uses magnetized iron for this purpose as source of polarized elect-

The differential scattering cross section for the scattering of  $\mathbf{y}$  radiation with circular polarization P<sub>2</sub> from an electron with spin  $\mathbf{S}$  is given by (10)

$$\frac{d\sigma}{d\Omega} = \frac{1}{2} \frac{e^4}{m^* C^4} \left(\frac{k}{k_0}\right)^2 \left\{ \varphi_0 + \int P_c \varphi_c \right\}$$
where  $\varphi_0 = 1 + \cos^2 \theta + (k_0 - k) (1 - \cos \theta)$   
 $\varphi_c = -(1 - \cos \theta) \left[ (k_0 + k) \cos \theta \cos \psi + k \sin \theta \cos \theta \sin \psi \right]$   
 $\theta = \text{scattering angle}$   
 $\psi = \text{angle between } \vec{k}_0 \text{ and } \vec{S}$   
 $\varphi = \text{angle between } (\vec{k} \cdot \vec{S}) \text{ plane and } (\vec{k}_0 \cdot \vec{k}) \text{ plane}$   
 $f = \text{fraction of polarized electrons per atom.}$ 

Reversal of spin direction  $\vec{S} \rightarrow \vec{S}$  corresponds to  $\forall \rightarrow \psi + \mathbf{T}$  and causes a change of sign of  $\psi_c$ . The relative difference in counting rate on reversing the electron spin is

$$E = \frac{N_{-} - N_{+}}{(N_{-} + N_{+})/2} = 2f P_{c} (\Phi_{c} / \Phi_{o})$$

One normally uses an arrangement as shown (Fig. 3). This is known as "ring geometry". One can see that the angles  $\Theta$  and  $\Psi$  are not constant. So one has to take the weighted average of  $\Phi_e/\phi_o$  over the geometry to get  $\langle d\sigma_c/d\sigma_o \rangle$ 

$$\mathbf{E} = 2f \mathbf{P}_{c} \left\langle d\boldsymbol{\sigma}_{c} \right/ d\boldsymbol{\sigma}_{c} \right\rangle$$

Order of the effect:

For So  ${}^{60}$ Co, A = -0.33, v/c  $\approx$  0.7, cos  $\Theta$  = 0.91 P<sub>c</sub> = A (v/c) cos  $\Theta \approx$  0.2 E = 0.16 x 0.2 x 0.4  $\approx$  1.3%

since 2f = 0.16 and  $\langle d\sigma c / d\sigma \rangle \approx 0.4$  for  $\gamma$ -rays of 1.25 MeV

So even though the initial polarization is large, the measured effect is quite small. Observation of such small effects and measuring them to some accuracy necessitates the collection of a large number of coincidence counts. A million counts give only ten to fifteen per cent accuracy and the experiments are therefore quite tedious. Even under favourable conditions it takes quite often a month to collect a million counts. And then, since the effect is small, one has problems of stability of electronics, drift etc. Normally one employs automatic recording of data. Coincidence counts and "singles" are taken for a fixed time interval (in our case about 7 min.). At the end of this interval, the data are printed out and the magnetic field is reversed and the counting starts again. The counts associated with opposite magnetic field directions are compared.

In our arrangement, this counting interval is controlled by a crystal oscillator. After the preset interval, a "master" pulse is generated which

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FIG. 3

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(i) stops the counting for a period of 4 sec.

(ii) prints out the data stored in the printers and resets them

(111) actuates a relay which operates the mercury commutator for reversing the magnet current.

(iv) reverses the direction of the compensating coil current

(v) selects the particular scaler for coincidence counting

After this "dead" time, the counting is resumed in the opposite field direction. This dead time is necessary to avoid any pick ups during transients caused by the sudden reversal of the magnetic field.

#### CORRECTION:

One applies the following corrections

(i) chance coincidences (ii) 7-7 background coincidences and (iii) transmission through the central conical lead stopper

All this make this experiment quite difficult and time consuming; the results are also not reproducible quite often. Earlier people were very enthusiastic just to report a measurement even though it could be off by a factor of two. As such there were large discrepancies between the results.

46<u>Sc</u>:

A notable case was  $^{46}$ Sc in which there were all sorts of measurements which did not agree with each other (Table I). In fact  $^{46}$ Sc was said to be "scandalous" at that time. A close inspection of the geometries used by various authors revealed that all of them had neglected the correction due to transmission and hence obtained effects according to their geometry. This was pointed by us (11) in our measurement which happens to be eighteenth.

## RESULTS:

During the last few years there were many good measurements which were reproducible. Besides there were a number of theoretical calculations available and it is time to look for some general trends and systematics. In the present review, the data have mainly been taken from the work in the following laboratories.

1) Measurements by Bloom and Mann et al at University of California, Livermore

2) Measurements by Daniel at Heidelberg

3) Our measurements at T.I.F.R.

Most of the data presented here is from an article published by us sometime back (12). The results are summarised in Table 2. There are several cases for which an unambiguous result has not yet been obtained. e.g.  ${}^{41}$ Ar,  ${}^{48}$ V,  ${}^{52}$ Mn and  ${}^{59}$ Fe. The last case  ${}^{59}$ Fe has been investigated by us recently in detail and is reported below! There are two  $\beta$ -V cascades in this decay of the type  $3/2^{-1}(3) 3/2^{-1}(3) 7/2^{-1}$ . They are 273 keV/ $\beta \rightarrow 1.29$  MeV V- ray and 475 keV/ $\beta$ -1.10 MeV  $\delta$ -ray. Earlier there was some confusion about the spin of 1.10 and 1.29 MeV states in  $^{59}$ Co. They are now known to be both 3/2 due to the work of Blair and Armstrong (13). The previously measured values of A are shown in Table 3. A look at the table shows that it warrants another measurement. Our measured values of A are

A = -0.132 + 0.037 for 475 keV /3 group

and A = -0.18 + 0.04 for 273 keV /3 group

There is another trouble in  ${}^{59}$ Fe. The 1.29 MeV state in  ${}^{59}$ Co is now known to possess a lifetime of about 0.6 ns (14). There is a possibility that/3-7correlation involving this state is perturbed depending on the chemical form of the source. We have measured the correlation involving this state in both liquid and solid forms and have not found any attenuation.

Using the log ft value, the Fermi matrix elements have been calculated from the values of X shown in Table 2. It can be noted that they are very small.

### $0+ \rightarrow 0+ Decays:$

In Table 4, we have compiled the  $0+\longrightarrow 0+$  decays observed so far. Here the ft value directly yields the Fermi matrix element  $M_F$ . Five cases are shown. There is one more  ${}^{66}$ Ge, but the ft value is not very certain in this. There was one slight ambiguity about the spin of  ${}^{64}$ Ga, but that has also been settled by Bloom et al (15) recently. From an inspection of the tables, the following conclusions can be drawn. The Fermi matrix element is much smaller compared to the GT matrix element in almost all cases, viz  $\left| M_F / M_{GT} \right| < 0.1$ . If the absolute values of  $M_F$  are considered, one sees that in all cases  $\left| M_F \right| \leq 10^{-2}$  implying that the isospin selection rule which requires  $M_F = 0$  is astonishingly fulfilled for unfavoured beta transitions with  $\Delta T = \pm 1$  (comparing with  $M_F = 1$  for the neutron and  $M_F = \sqrt{2}$  in the  $0+\longrightarrow 0+$  transitions like in  ${}^{14}$ O)

But right now we are concerned in the other way worrying more about the small  $M_F$ 's because they give us the quantities we need at the moment - the isospin impurities. The isospin impurities  $\propto$  and the effective Coulomb matrix elements  $\langle H_C \rangle$  have been calculated from the values of  $M_F$  and presented in Table 5. The  $\propto$ 's and  $\langle H_C \rangle$ 's are plotted against mass number and one is able to observe some systematics and features of their behaviour over the periodic table (Fig. 4 and 5).

In the mass region  $20 \angle A \angle 60$ , there are some spread and fluctuations in  $\angle \cdot$  However, except in the uncetain case of <sup>41</sup>Ar and <sup>44</sup>Sc, all the other values of  $\angle A$  are less than 0.3 per cent. In the mass region just beyond A = 60, one encounters relatively larger values of  $\angle A$ . For <sup>66</sup>Ga and <sup>72</sup>Ga, it is about 0.5 per cent.

59Fei





FIG. 6

 $\overline{\langle H_0 \rangle}$ 

Similar features are observed in the case of  $\langle H_c \rangle$ . Only difference is that in this case  $\measuredangle$  is multiplied by  $\triangle E_o$ . In the mass region 20  $\langle A \langle 60$ , the value of  $\langle H_c \rangle$  is less than 20 keV. In the intermediate region, <sup>72</sup>Ga is found to have a rather large Coulomb matrix element  $\approx$  50 keV. This is also true for <sup>64</sup>Ga and <sup>66</sup>Ge. For heavier nuclei in the region 110  $\langle A \langle 234, \langle H_c \rangle$  is very small  $\leq$  5 keV.

## DISCUSSION:

At this stage let us compare with some theory to see where we are. Recently Sliv and Kharitonov (16) have made a calculation of of 2 using a realistic nuclear model and taking accurate approximations for the Coulomb effect. This has been compared with the experimentally observed values in Fig. 6. One observes that in nuclei beyond Z = 40, the intensity admixture of isobaric spin is theoretically predicted to be about 2 per cent in contrast to the experimentally observed values which are in fact few orders of magnitude smaller. One also finds a trend of smaller values of  $\propto^2$  as one goes to heavier nuclei indicating that isopsin impurity of nuclear states improves when one goes to heavier nuclei. This is quite a striking result. So far, we used to be concerned with validity of isospin quantum number in light nuclei, In light nuclei, T is a good quantum number for low lying levels simply because the nearest levels of different T are usually at quite high excitation energies and because the Coulomb forces are weak in light nuclei. At the beginning it was surprising that the concept of isospin should be applicable to heavier nuclei, but an explanation can be given in terms of the shell model (17). There, even though we have large Coulomb forces, it appears to be more than compensated by the neutron excess. It is well known that because of neutron excess the shell model states of neutrons are filled to a higher level than for protons. Hence if a proton is converted into a neutron it finds no empty place in its old shell and would have to go to a much higher unfilled level. This is very unlikely. In the intermediate region the neutron excess is small and consequently isobaric spin may bot be a good quantum number in this mass region.

Blin-Stoyle and his colleagues (18,19) have discussed extensively the isobario spin impurities resulting from Coulomb effects and also from a short range charge dependent potential for some specific nuclei. From a glance at Fig. 6 one is likely to comclude that the effects of Coulomb forces as calculated by Sliv et al (16) are apparently annulled by the presence of charge dependent nuclear forces. However there is an important difference between nuclear and Coulomb interactions; the latter are long range, whereas of course the former are short range and cancellation between the two sources of isobaric spin mixing appears unlikely. It is possible
that the calculation of  $\alpha^2$  taking the Coulomb effect is not correct.

# Blin-Stoyle's Approach:

The charge dependent perturbation H' can be separated into two parts

$$H^{\dagger} = H_{o} + H_{n}$$

where H<sub>c</sub> is the Coulomb potential which can be written in isospin terminology.  $A_{a} \sim \left( \frac{1}{2} - \gamma_{a}^{(i)} \right) \left( \frac{1}{2} - \gamma_{a}^{(j)} \right)$ 

$$H_{e} = \sum_{i > j=1}^{n} \frac{e^{-\frac{1}{2} - \frac{1}{3} - \frac{1}{3}} \frac{1}{2}}{y_{ij}}$$

For the nuclear part  $H_n$ , Blin-Stoyle introduced a phenomenological potential of the form A (1) (0) (1) (1)

$$H_{n} = \sum_{i>j=1}^{\infty} \left\{ p\left(2_{3}^{n}+2_{3}^{(j)}\right) + q\left(2_{3}^{n}+2_{3}^{(j)}\right) + q\left(2_{3}^{n}+2_{3}^{(j)}\right) + \left(2_{3}^{n}+2_{3}^{(j)}\right) + 2_{3}^{n}+2_{3$$

The coefficients p, q, r and s measure the departure of the nuclear forces from charge independence. If p = r = 0, the forces are charge symmetric i.e. the p-p and n-p forces are equal but differ from the n-p force. For the potential depth the value Vo = -51.9 MeV is usually chosen (18) and the radial dependence is determined by  $\overline{\beta}^{\frac{1}{2}} = 1.73f$ .

With such a potential one can calculate many observable quantities which in turn can be related to the coefficients p,q,r and s. Novakovic (20) has derived an expression relating p and r to the mass difference between <sup>24</sup>Al and <sup>24</sup>Na

△ M = ( -221.3 / + 17.9r + 7.129) MeV M(expt) = 8.499 MeV. Thus we get - 221.3p + 17.9r = 1.370

Then one can calculate Fermi matrix elements  $M_F$  in  $\Delta T = 1$  transitions, difference in ft values in the  $\beta$  decay of <sup>14</sup>C and <sup>14</sup>O, the difference in energies for the lowest T = 1 triad in the A = 14 nuclei, the difference in n-p and p-p scattering length etc.

Blin-Stoyle and Navakovic (18) had calculated the Fermi matrix element in  $\Delta T = \pm 1$  decays in <sup>24</sup>Na, <sup>41</sup>Ar, <sup>44</sup>Sc and <sup>52</sup>Mn using the above potential and j - j coupled shell model. Comparing it with the experimental data they concluded that a few per cent charge dependent nuclear force may be present. However the comparatively larger values of p and r obtained this way are not consistent with smaller values of p and r which would explain the binding energies of <sup>3</sup>H and <sup>3</sup>He. Recently Blin-Stoyle and Yap (19) have done calculations in the case of <sup>24</sup>Na assuming Nilason wave functions. They show that the small experimental M<sub>p</sub> observed occurs because of an inhibition due to the K selection rule in the decay of <sup>24</sup>Na. Their result

0.052 > 2r - p > -0.078

is also consistent with the result 0.003 > 3r - p > 0.001 obtained from a comparison of the binding energies of <sup>3</sup>H and <sup>3</sup>He.

Damgard (21) has recently calculated the  $M_F$  values of the T forbidden pure Fermi transitions in  ${}^{156}Eu$ ,  ${}^{170}Lu$  and  ${}^{234}Np$  by the simple application of a coulomb force only using Nilsson wave functions appropriate to these deformed nuclei and also taking pairing into account. The agreement with experimental results are excellent, particularly in  ${}^{156}Eu$  and  ${}^{170}Lu$ .

These reveal that the calculated values of  $M_F$  are strongly model dependent. More such calculations will perhaps clarify the present data.

#### CONCLUSIONS:

Let me summarise the present situation concerning the values of p, r, q and s from various experiments.

1) From the energy difference of  ${}^{3}$ H and  ${}^{3}$ He, we get  $3r - p \approx (0.1 \text{ to } 0.3 \text{ per cent})$ 2) From a comparison of p-p and n-p scattering length,  $3s - q \approx 1$  per cent

3) From the values of  $M_F$  in  $\Delta T = \pm 1$  transitions, q - 2s  $\approx$  3 per cent

Although the theoretical as well as experimental uncertainities are still considerable, the data are consistent with

 $0.05 \leq q \leq 0.15$   $0.015 \leq s \leq 0.055$ 

This implies a comparatively large violation of charge dependence. Such a charge dependent nucleon interaction can be attributed to the mass difference between charged and neutral pions and p mesons.

Before I conclude, I shall make some general remarks.

1. Before the detection of parity violation in decay, there was practically no experimental technique available for gauging isospin purity. Only in a few special cases in light nuclei, Wilkinson (22) could determine the isospin impurities.

2. Now we are flooded with data. Besides showing that isospin purity improves with heavier nuclei it has also furnished us the "Coulomb" matrix elements which would be useful in nuclear structure investigations.

3. T is proving much more useful than one might have expected. Quoting Robson, I may say "it seems nature wishes to preserve this quantum number". TABLE I.

| Author              | Year            | Asymmetry Parameter A    | $X = \frac{C_V M_F}{C_A M_{GT}}$ |
|---------------------|-----------------|--------------------------|----------------------------------|
| Boehm and Wapstre   | 1957            | 0.33 ± 0.04              | - 0,42 ± 0.09                    |
| Lundby et al        | 1958            | 0.29 <u>+</u> 0.11       | - 0.32 + 0.14                    |
| Jungst and Schopper | 1958            | 0.24 + 0.04              | - 0.22 + 0.08                    |
| Steffen             | 1959            | 0.24 ± 0.02              | - 0.22 ± 0.04                    |
| Bloom et al         | 1960 <b>/62</b> | 0.075+ 0.017             | + 0.020+ 0.025                   |
| Daniel and Kuntze   | 1961            | 0.10 <u>+</u> 0.02       | - 0.02 ± 0.02                    |
| Boehm and Rogers    | 1962            | 0.215 <u>+</u> 0.019     | - 0.19 <u>+</u> 0.03             |
| Berthier            | 1962            | 0.11 ± 0.02              | - 0+04 ± 0+03                    |
| Haase et al         | 1962            | 0.079± 0.012             | + 0.005+ 0.015                   |
| Singru and Steffen  | 1963            | 0.19 ± 0.03              | - 0.15 ± 0.05                    |
| Daniel et al        | 1963            | 0.113+ 0.008             | - 0.040 <u>+</u> 0.011           |
| Miskel et al        | 1963            | • 0 •097 <u>+</u> 0 •012 | - 0.017 <u>+</u> 0.105           |
| Chabre              | 1963            | 0.11 ± 0.01              | - 0.04 ± 0.02                    |
| Wei et al           | 1964            | 0.077± 0.01              | + 0.011 <u>+</u> 0.013           |
| Mann et al          | 1964            | 0.094± 0.007             | - 0.013 <u>+</u> 0.008           |
| Mitra and Padhi     | 1965            | 0.13 ± 0.02              | - 0.064+ 0.030                   |

Comparison of various measurements on the beta gamma circular polarization correlation in <sup>46</sup>Se.

| TABLE II. |
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|-----------|

Tabulation of  $\beta$ -V circular polarization correlation measurements in mixed allowed beta transitions

| Nuclide           | Spin<br>Parity        | Asymmetry<br>Parameter<br>A | X                      | log ft | м <sub>г</sub> . 10 <sup>3</sup>     |  |
|-------------------|-----------------------|-----------------------------|------------------------|--------|--------------------------------------|--|
|                   |                       |                             |                        |        | · · ·                                |  |
| <sup>20</sup> F   | 2+                    | 0.174 ± 0.014               | - 0.009 ± 0.017        | 4.99   | 0.7 ± 1.2                            |  |
| 24 <sub>Na</sub>  | 4 <sup>+</sup>        | 0.091 ± 0.010               | - 0.010 <u>+</u> 0.015 | 6.13   | 0.7 + 1.0                            |  |
| 24                | 4+                    | - 0.086 ± 0.039             | 0.004 <u>+</u> 0.052   | 6.1    | 0.3 <u>+</u> 3.7                     |  |
| 41 <sub>Ar</sub>  | 7/2                   | 0.083 ± 0.035               | 0.016 ± 0.046          | 5.0    | 4.0 ±11.4                            |  |
| <sup>44</sup> Sc  | 2+                    | - 0.127 + 0.014             | - 0.048 + 0.017        | 5.3    | 8.4 + 3.0                            |  |
| 46 <sub>Sc</sub>  | 4+                    | 0.13 ± 0.02                 | - 0.064 + 0.028        | 6.2    | 4.0 + 1.8                            |  |
| 48 <sub>Sc</sub>  | 6                     | -<br>0.063 + 0.013          | - 0.011 + 0.018        | 5.5    | -<br>1.7 + 2.5                       |  |
| 48 <sub>v</sub>   | 4                     | - 0.037 + 0.026             | - 0.062 + 0.035        | 6.1    | 4.3 + 2.5                            |  |
| 52 <sub>Mn</sub>  | ,<br>+<br>6           | - 0.060 + 0.008             | 0.007 + 0.013          | 5,5    | 1.0 + 1.8                            |  |
| 56 <sub>CO</sub>  | ,+<br>,               | 0.014 + 0.022               |                        | 87     | 0.5 + 0.1                            |  |
| 58                | -<br>                 |                             |                        | 6.6    |                                      |  |
| 59 <sub>8</sub>   | 2<br>7/0 <sup>-</sup> |                             |                        | 6.74   |                                      |  |
| 72_               | 5/2                   | - 0.191 ± 0.017             | - 0.118 + 0.055        | 0+14   | J+Y ± 1+2                            |  |
| 68.<br>I101m      | 3                     | - 0.13 + 0.04               | 0.265 + 0.040          | 6.2    | 15.9 <u>+</u> 2.4                    |  |
| Ag .              | 6                     | 0.07 ± 0.02                 | $-0.020 \pm 0.028$     | 8.3    | 0 <b>.</b> 11 <u>+</u> 0 <b>.</b> 14 |  |
| SP                | 3                     | 0.30 ± 0.03                 | - 0.120 <u>+</u> 0.028 | 7.7    | 1.3 ± 0.3                            |  |
| <sup>134</sup> Cs | 4+                    | - 0.075 ± 0.010             | 0.217 + 0.015          | 8.9    | 0.59 <u>+</u> 0.04                   |  |
| 152<br>Eu         | 3                     | 0.15 ± 0.02                 | 0.015 ± 0.017          | 10.6   | 0.01 <u>+</u> 0.01                   |  |
| 228 <b>4</b> 0    | · 3                   | - 0.25 ± 0.07               | 0.396 ± 0.080          | 8.5    | -<br>1.6 ± 0.3                       |  |

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# TABLE III.

Summary of various beta gamma circular polarization correlation measurements in <sup>59</sup>Fe

| 475 keV<br>eta group         | 273 keV<br>beta group | Author and Year           |  |  |
|------------------------------|-----------------------|---------------------------|--|--|
|                              |                       |                           |  |  |
| · 0 • 46 ± 0 • 08            | - 0.04 <u>+</u> 0.11  | Forster and Sanders 196   |  |  |
| - 0 •066 <u>+</u> 0 •037     | - 0.40 ± 0.20         | Haase and Palmer 196      |  |  |
| - 0 <b>.13 <u>+</u> 0.04</b> | - 0.17 - 0.10         | Collin et al 196          |  |  |
| - 0.205 <u>+</u> 0.019       | - 0.042+ 0.043        | Mann et al 196            |  |  |
| - 0.25 + 0.07                | - 0.02 + 0.15         | Kneissl and Schneider 196 |  |  |
| - 0.195+ 0.017               | - 0.154+ 0.023        | Tirsell and Mann 196      |  |  |

TABLE IV.

 $0^+ \longrightarrow 0^+$  type of  $\beta$  decays ( $\Delta T = \pm 1$ )

| Nuclido           |   | 3                                | - |
|-------------------|---|----------------------------------|---|
| N UCT THE         | (sec)   | ™ <sub>3</sub> , 10 <sup>-</sup> |   |
| 64 <sub>Ga</sub>  | (4.0 + 0.1) .10 <sup>6</sup>                    | 39.0 + 0.5                       |   |
| 66<br>Ga          | (8.00 <u>+</u> 0.13).10 <sup>7</sup>            | 8.7 ± 0.1                        |   |
| 156 <sub>Eu</sub> | $(5.8 \pm 0.6) .10^9$                           | 1.02+ 0.05                       |   |
| 170 <sub>Lu</sub> | $(5.7 \pm 1.5) .10^9$                           | 1.03+ 0.15                       |   |
| 234 <sub>Np</sub> | (3.4 <sup>+2.5</sup> ) .10 <sup>8</sup><br>-1.6 | 4.2 <sup>+1.6</sup><br>-1.0      |   |

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| TA | BLE | V. | • |
|----|-----|----|---|
|    |     |    |   |

| Nuclide                              | ± .        | Isospin<br><sup>T</sup> i | ™ <sub>F</sub> .10 <sup>3</sup> | .10 <sup>3</sup>                     | E <sub>o</sub><br>(MeV) | 'Hc<br>(keV)       |
|--------------------------------------|------------|---------------------------|---------------------------------|--------------------------------------|-------------------------|--------------------|
| 20 <sub>F</sub>                      | -          | 1                         | 0.7 ± 1.2                       | 0.5 ± 0.8                            | 8.56                    | 4.3 ± 6.8          |
| 24 <sub>Na</sub><br>11 <sup>Na</sup> | -          | 1                         | 0.7 ± 1.0                       | 0.5 + 0.7                            | 5.24                    | 2.6 ± 3.7          |
| 24<br>13 <sup>A1</sup>               | +          | 1                         | 0.3 ± 3.7                       | 0.2 + 2.5                            | 5.41                    | 1.1 ± 13.5         |
| 41<br>18 <sup>Ar</sup>               | -          | 5/2                       | 4.0 ± 11.4                      | 1.8 <u>+</u> 5.1                     | 7.04                    | 12.7 <u>+</u> 36.0 |
| 44<br>21 <sup>Se</sup>               | +          | 1                         | 8.4 <u>+</u> 3.0                | 4.2 <u>+</u> 1.5                     | 3.98                    | 16.7 <u>+</u> 6.0  |
| 46<br>21 <sup>50</sup>               |            | 2                         | 4.0 <u>+</u> 1.8                | 2.0 ± 0.9                            | 7.11                    | 14.2 <u>+</u> 6.4  |
| 48<br>21 <sup>50</sup>               | -          | 3                         | 1.7 <u>+</u> 2.5                | 0.7 <u>+</u> 1.0                     | 7.28                    | 5.1 <u>+</u> 7.3   |
| 48 <sub>7</sub><br>23                | • +        | 1                         | 4.3 + 2.5                       | 2.2 <u>+</u> 1.2                     | 5 <b>.31</b>            | 11.7 <u>+</u> 6.4  |
| 52<br>25 <sup>Mn</sup>               | +          | 1                         | 1.0 <u>+</u> 1.8                | 0.5 <u>+</u> 0.9                     | 5.98                    | 3.0 <u>+</u> 5.4   |
| <sup>56</sup> 27 <sup>Co</sup>       | +          | <sup>5</sup> 1            | 0.5 <u>+</u> 0.1                | 0.25 <u>+</u> 0.05                   | 5.57                    | 1.4 <u>+</u> 0.3   |
| 58<br>27 <sup>Co</sup>               | +          | 2                         | 0.9 <u>+</u> 0.5                | 0.4 ± 0.2                            | 6 <b>.47</b>            | 2.6 ± 1.3          |
| 59<br>26 <b>Fe</b>                   | -          | 7/2                       | 3.9 ± 1.2                       | 1.5 <u>+</u> 0.5                     | 8.39                    | 12.6 <u>+</u> 4.2  |
| 64<br>31 <sup>Ga</sup>               | +          | 1                         | 39.0 <u>+</u> 0.5               | 19.50 <u>+</u> 0.25                  | 2.03                    | 39.6 <u>+</u> 0.5  |
| <sup>66</sup> Ga<br>31 <sup>Ga</sup> | <b>+</b> . | 2                         | 8.7 ± 0.1                       | 3.55 <u>+</u> 0.04                   | 3.82                    | 13.6 <u>+</u> 0.2  |
| 72<br>31 <sup>Ga</sup>               | -          | 5                         | 15.9 <u>+</u> 2.4               | 5.0 <u>+</u> 0.7                     | 9.98                    | 50.0 <u>+</u> 7.0  |
| 110m<br>47 Ag                        | -          | 8                         | 0.11 ± 0.14                     | 0.03.+0.04                           | 12.94                   | 0.4 ± 0.5          |
| 124<br>51 <sup>Sb</sup>              | -          | <b>11</b> ·               | 1.3 ± 0.3                       | 0.28 ± 0.06                          | 13.63                   | 3.8 <u>+</u> 0.8   |
| 134<br>55 <sup>Cs</sup>              | -          | 12 <sup>-</sup>           | 0.59 <u>+</u> 0.04              | 0.12 ± 0.01                          | 14.41                   | 1.7 <u>+</u> 0.2   |
| 152<br>63 <sup>Eu</sup>              | -          | 13                        | 0.01 <u>+</u> 0.01              | 0 •002 <u>+0 •002</u>                | 15.98                   | 0.03+0.03          |
| 156<br>63 <sup>Eu</sup>              | -          | 15                        | 1.02+ 0.05                      | 0 <b>.</b> 19 <u>+</u> 0 <b>.</b> 01 | 17.30                   | 3.3 <u>+</u> 0.2   |
| 170<br>71 <sup>Lu</sup>              | +          | 14                        | 1.03 ± 0.15                     | 0.19 ± 0.03                          | 13.05                   | 2.5 <u>+</u> 0.4   |
| 228<br>89 <sup>AC</sup>              | -          | 25                        | 1.6 <u>+</u> 0.3                | 0 <b>.23 ±</b> 0.05                  | 21.01                   | 4.8 <u>+</u> 1.0   |
| 234 <sub>Np</sub>                    | <b>+</b> * | 24                        | 4.2+1.6                         | 0.6 <u>+</u> 0.2                     | 17.94                   | 10.8 <u>+</u> 3.6  |

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RECENT ADVANCES IN NUCLEAR FISSION STUDIES

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# INTRODUCTION:

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The Nuclear Fission process which involves the massive motion and subsequent division of an ensemble of nucleons is naturally expected to be more complex than certain other nuclear phenomena where only a few outermost nucleons are actively involved. In the past, the Nuclear Fission Studies have, therefore, been mainly aimed to obtain information concerning the mechanism of the fission process. These experimental and theoretical studies are now just beginning to provide a better theoretical insight into the various aspects of this collective phenomena (1). In the recent years partly due to better understanding of the process and partly due to the availability of the shigh resolution detectors and multiparameter data acquisition system, a new line of study has emerged. It is due to the recognization of the fact that nuclear fission is most suited to investigate certain properties of the nuclei and nuclear structure, which are difficult to study by other means. It is now realized that the nuclear fission studies can play an important role in investigating (i) the spectroscopy of the neutron rich nuclei and (ii) the properties of the highly elongated nuclear shapes. This paper is largely devoted to some recent work which are quite encouraging with respect to the possibility of investigating the spectroscopy of neutron rich nuclei through the study of deexcitation of primary fission fragments. A brief mention is also made about the uniqueness of the fission process in offering a way to study nuclei in a state of unusually large deformation. Finally the effect of closed nuclear shells on the fission barrier heights is disucssed with regard to its consequences on the assumed instability of the superheavy nuclei.

A general outline of the different stages during the fission process is given pictorially in Fig. 1. An increase in the nuclear surface energy by an amount more than the decrease in the coulomb energy for small nuclear deformations gives rise to a fission barrier with a corresponding saddle point in the deformation space. The nucleus passing over the fission barrier is in a state of unusually large deformation and also in a state of conditional equilibrium. There are evidences to show that the nucleus stays in this stage for sufficiently long time to define the nuclear states of such a system. Consequently the angular distribution of the fragments in fission induced by medium energy projectiles can provide information about the states and other properties of this highly deformed nuclear stage.

During descent from the saddle, the deformation increases and finally the nucleus breaks. These deformed nuclei undergo damped oscillations around their stable shapes pumping all the deformation energy into the nucleonic excitation.

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The two resulting fragments each having about 15 MeV excitation energy are then accelerated to relatively large kinetic-energies owing to coulomb repulsion between them. Promptly thereafter, a greater part of the excitation energy is dissipated by neutron emission. The residual excitation energy is then emitted in the form of gamma rays. Approximately 8 - 10 MeV of energy is carried off by about 8 - 10 gamma rays. A small fraction of about 6 per cent of these gamma transitions undergo internal conversion primarily in the K and L shells giving rise to conversion electrons and characteristic X-rays.

GAMMA DE-EXCITATION AND STUDY OF NEUTRON RICH NUCLEI:

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# (a) Emission of gamma rays, conversion electrons and X-rays:

The Fragment-Gamma angular correlation studies (2) have shown that gamma radiations are not emitted isotropically with respect to the fission axis. There are about 10% more gamma rays emitted parallel to the fission axis than perpendicular to it. These results on the angular anisotropy together with the data on life times, average energies, and multiplicities of these gamma rays suggest that fragments are formed with a rather large angular momentum of about 10 % and the predominant mode of deexciation is quadrupole in nature. Investigations of the life time of the gamma emitting states have shown that the radiation could be divided into two classes with greatly different half lives. About 85% of the total radiations are emitted with a half life of about  $10^{-11}$  sec. The remaining 15% is emitted. with a half life in the region of  $10^{-9}$  sec. From this it is evident that the slow component of radiation must correspond to the final steges of the gamma deexciation cascade and the corresponding gemma emitting states are the low lying states of the final fragment nuclei. In fact, as will be seen later, the low energy parts of the spectrum of the gamma rays emitted from specified fragment nuclei do show peaks corresponding to descrete gamma transitions.

It is known that these final fragment nuclei are formed in the neutron rich region far away from the line of  $\beta$  stability and cover a larg region of nuclear periodic table as shown in Fig. 2. This region is not easy to reach by conventional neutron irradiation means and consequently there exists a big gap in our knowledge about the properties of several of these nuclei. Through a study of gamma deexcitation of fragments, we therefore, have a natural means of studying in a single experiment the transitions between states of these neutron rich nuclei. Moreover, since fragments are formed with a large angular momentum, several of the low lying collective states are expected to be populated during deexcitation. The only other way to populate these collective states of high angular momentum is through heavy ion induced reactions thereby needing a particle accelerator. It is therefore, evident that a systematic investigation of the state of these neutron rich nuclei can be made through the study of fission gamma radiation provided we are able to separate the transitions from individual fragment nuclei of known mass and charge. A physical determination of the nuclear charges of fragments of specified masses can be made by measure ing the energies of their characteristic X-Rays emitted during the fragment deexcitation process. Therefore, with the availability of the high resolution detectors and multiparameter data system, the above investigations are just beginning with a considerable future promise. Recent investigations (4-6) of another important feature of fragment deexcitation process, namely the emission of K and L conversion electrons and the corresponding X-Rays have contributed significantly towards this promise.

It is expected that some of the low energy gamma transitions will have a significant probability of undergoing internal conversion primarily in the K and L shells with the consequent emission of conversion electrons and the characteristic X-Rays. Though X-Rays emission in fission has been visualised earlier, it has been investigated in detail only recently primarily due to the availability of high resolution lithium drifted silicon detectors. These experiments (4-6) have shown that almost all the K X-Rays emitted during fission result from the internal conversion process taking place during the later stages of gamma deexcitation. The other possibility could have been that certain K shell electrons are knocked out during the fission act as well. But due to the fact that the K shell electrons are moving significantly faster than the fragments, no vacancy in the K shell seems to be created in the fission act. If, therefore, all the K-X Rays are emitted due to the internal conversion process alone, certain informations concerning these low lying states of these nuclei can be obtained from the observed K X-Ray yield from different fragment nuclei. In addition from a precise measurement of the energy of these X-Rays, or from a comparison of the gamma ray and the corresponding conversion electron peaks the nuclear charge of the emitting fragment can be determined.

# (b) Identification of M, Z of the emitting fragment:

Coincident measurements of the kinetic energies  $E_1$  and  $E_2$  of the pair fragments can yield the fragment masses  $M_1$  and  $M_2$  through the momentum conservation relation  $M_1E_1 = M_2E_2$  and  $M_1 + M_2 = M$ , where M is the mass of the compound nucleus. But since the measured energies  $E_1$  and  $E_2$  correspond to those the fragments have after the emission of neutrons, a knowledge of the number of neutrons emitted from different fragments is required to evaluate the fragment masses both before and after the neutron emission. It can be shown (7) that a simultaneous measurement of three parameters namely  $E_1$ ,  $E_2$  and  $V_1$  (the velocity of one of the fragments), can give the exact masses of the final fragment nuclei without needing the information on the number of neutrons emitted. A simultaneous measurement of the K X-Ray energies can provide the nuclear charges of the fragments in that event. In principle therefore a simultaneous measurement of the five parameters  $E_1$ ,  $E_2$ ,  $V_1$ ,  $E_X$  and  $E_Y$ event by event is required to sort out the gamma ray spectra for different fragment nuclei. Such five parameter experiments have not been attempted so far for reasons of extremely low counting rates for five fold coincidences even for a strong  $^{252}$ Of fission source. In fact the most experiments carried out so far are mainly three parameter experiments measuring  $E_1$ ,  $E_2$ ,  $E_1$  or  $E_1$ ,  $E_2$ ,  $E_X$  or  $E_1$ ,  $E_2$ ,  $E_1$  or  $E_1$ ,  $E_2$ ,  $E_2$ , or  $E_1$ ,  $E_2$ ,  $E_1$  or  $E_1$ ,  $E_2$ ,  $E_2$ ,  $E_1$ ,  $E_2$ ,  $E_1$ ,  $E_2$ ,  $E_1$ ,  $E_2$ ,  $E_2$ ,  $E_1$ ,  $E_2$ ,  $E_1$ ,  $E_2$ ,  $E_2$ ,  $E_1$ ,  $E_2$ ,  $E_1$ ,  $E_2$ ,  $E_1$ ,  $E_2$ ,  $E_2$ ,  $E_1$ ,  $E_2$ ,  $E_1$ ,  $E_2$ ,  $E_2$ ,  $E_1$ ,  $E_2$ ,  $E_2$ ,  $E_1$ ,  $E_2$ ,  $E_1$ ,  $E_2$ ,  $E_1$ ,  $E_2$ ,  $E_1$ ,  $E_2$ ,  $E_2$ ,  $E_1$ ,  $E_2$ ,  $E_1$ ,  $E_2$ ,  $E_1$ ,  $E_2$ ,  $E_2$ ,  $E_1$ ,  $E_2$ ,  $E_1$ ,  $E_2$ ,  $E_1$ ,  $E_2$ ,  $E_2$ ,  $E_1$ ,  $E_2$ ,  $E_1$ ,  $E_2$ ,  $E_1$ ,  $E_2$ ,  $E_2$ ,  $E_1$ ,  $E_2$ ,  $E_1$ ,  $E_2$ ,  $E_1$ ,  $E_2$ ,  $E_1$ ,  $E_$ 

(i) Three Parameter Experiments:

Fig. 3 shows a block diagram of a typical three parameter experiment (5) to measure the yield and spectra of gamma rays, conversion electrons and K X-Rays emitted from  $^{252}$ Cf fragments of specified masses. A 8 mm thick lithium drifted germanium detector was used for the gamma ray measurements and a = 3 mm thick lithiuum drifted silicon detector for K X-Rays and electron measurements. Pulse heights corresponding to the kinetic energies of the pair fragments and the energy of the associated radiationwere recorded! in a correlated way event by event on the magnetic tape. These data were analysed to obtain gamma ray, electron or K X-Ray yields and spectra in coincidence with different fragment masses.

(ii) K X-Ray Results:

From the analysis of the above data, itwas found (5) that the number of K X-Rays emitted between 0-50 n sec is  $(0.56 \pm .04)$  per fission, the contribution from the light and the heavy group being  $(0.24 \pm .02)$  and  $(0.32 \pm .02)$  respectively. The K X-Ray yield obtained from those measurements is in agreement with the value of 0.57 measured in the time interval 0-150 n sec by Glendenin and Griffin (4), but in their measurements the relative contributions to the X-Ray yield from the light and heavy fragments was found to be  $(0.16 \pm .02)$  and  $(0.4 \pm 0.02)$  respectively. In the Berkeley measurements (5), the average half life for X-Ray emission was estimated from the measured intensity of detected X-Rays for X-Rays observed at 0° and 180° with respect to the direction of motion of the emitting fragment. For obtaining these average lives it was necessary to assume that the X-Ray emission is of exponential nature with a single decay constant. The observed variation of  $T_{\frac{1}{2}}$  versus fragment mass or charge number is shown in Fig. 4. On the basis of these estimated half lives it follows that fractions of about 0.20, 0.57 and 0.23 are emitted between 0-0.1 m sec, 0.1 to 1.0 n sec and 1.0 to 50 n sec respectively.

A comparison of the number of gamma rays and K X-Rays emitted from <sup>252</sup>Cf fragments shows that bout six per cent of the total transition in the fragment nuclei undergo internal conversion in the K shell. Moreover, from the measured time of emission of these K X-Rays it follows that these six per cent radiations mostly

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FIG. 4

belong to the gamma component of fractional intensity 0.15 which are emitted with **A** half life in the region  $10^{-9}-10^{-10}$  sec. Since it is mainly the low energy transitions (E  $\gamma < 200$  keV) which have significantly high conversion coefficients, a comparison of the known yield of these low energy gamma rays with the observed conversion electron yield shows that conversion coefficients are of the order of unity. This can be expected for the transitions of the E<sub>2</sub> and M<sub>1</sub> type for the nuclei in the region of fission fragments. Fig. 5 shows a plot of T<sub>1</sub> versus the transition energies for different types of transitions taken from ref. (6), where the region covered by the converted transitions in the fragment nuclei is shown inside the square. It is apparent from this figure that most of the converted transitions in fragments do indeed belong to E<sub>2</sub> and M<sub>1</sub> type.

The measured yield of the K-X-Rays emitted between 0 to 50 n sec from different <sup>252</sup>Cf fragments is shown in Fig. 6, which show interesting correlation of the X-Ray yield with the expected internal conversion probabilities in various fragment nuclei. This variation of the K X-Ray yield as a function of mass is expected to reveal the relative abundance of low energy transitions in various fragment nuclei, on the basis of the unknown behaviour of conversion coefficients as function of transition energy. The minimum yield from nuclei near the doubly d osed shells of Z = 50 and N = 82 is consistent with the neighbour transition energies and lower number of transitions expected for these spherical nuclei. On the other hand, relatively large K X-Ray yield in the regions of fragment masses 108 and 152 implies an abundance of low energy transition in these regions. As pointed out by Atneoson et al (6) for a large internal conversion probability it is not only necessary to have the existence of closely spaced levels but it is also necessary to ensure that the deexcitation also takes place through a sequence of these levels. These properties are characteristic of rotational transitions thereby suggesting that the fragment nuclei with these large X-Ray yields may have stable deformations. In fact, an abrupt rise in the observed yield for masses greater than 144 is connected with the known deformed region beginning at neutron number of 88. Following this reasoning, the observed abundance of the low energy transitions in the light fragment region also suggests the existence of a new region of stable deformation for these neutron rich nuclei near mass 110 having most probable charge Z = 45. It may be remarked that these nuclei have neutron numbers and proton numbers nearly half way between the closed neutron and proton shells, namely between N = 50, 82 and Z = 40 (subshell), 50. Further, it may be noted that in this region the energies of the first 2<sup>+</sup> states drop markedly as the neutron number increases, further indicating the onset of stable deformations in this neutron rich region. We, therefore, realise that these K X-Ray yield measurements from individual fragments can provide general features of the transitions in the various fragment nuclei. It also becomes apparent that similar investigation should be carried out for the K X-Rays emitted from fragments produced in the thermal fission of relatively lighter nuclei like 2350, for in this case the ligt fragments span a different region of neutron rich nuclei near mass 98. The measurement on the yield of K X-Rays from 236 U fragments have been recently carried

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FIG. 5



NFY 3

-69-

FIG. 6

out at Trombay showing similar correlations. These results are presented later in this Symposium.

It is also evident that a precise measurement of the energy of these K X-Rays provides a physical means to determine the charge of the emitting fragment. The most probable charges of <sup>252</sup>Cf fragments for various masses, as determined from the three parameter K X-Ray measurements (5) are shown in Fig. 7. In this figure, the values of  $\left\{ Z_p - \frac{Z}{4} \right\}$  are plotted against the mass ratio, where Z and A are the charge and mass of the fissioning nucleus and  $Z_p$  is the most probable charge for fragments of initial mass Ai. The results of the radiochemical measurements of the fragment charges for the spontaneous fission of 252 Cf and also for the thermal neutron fission of 235U are also shown in the figure for comparison with the K X-Ray measurements. It is important, that for the K X-Ray measurements to be applicable, the internal conversion probability should not vary erratically as a function of fragment mass and charge. Even though, the K X.Ray yield is known to vary with the mass and charge, the X-Ray yield variation is rather smooth to suggest that the measured Z<sub>n</sub> values should not deviate appreciably from the true values. The excellent agreement between the most probable charges measured by the radiochemical and the X-Ray measurements seems to show the validity of the X-Ray method for a physical determination of the nuclear charges of the fragments. Moreover, a further check to the validity of the method is obtained by ensuring that the sum of the charges of the two fragment nuclei should add up to the total charge of the initial nucleus.

In the last two years, the continued improvement of semiconductor detectors has led to a resolution of less than 1 keV making it possible to directly separate the K X-Rays of two adjacent elements in the region of fission fragments. The spectra of K X-Rays emitted from  $^{252}$ Cf fragment nuclei measured by Watson et al (7) with this high resolution detector system is shown in Fig. 8, where the locations of K<sub>d</sub> and K<sub>b</sub> X-Ray groups for various elements are shown by brackets. From these measurements it is possible directly to obtain yields of K X-Rays emitted from different fragment charges providing informations complimentary to those obtained for the X-Ray yields from different fragment masses.

In a recent work at Trombay (8) it has been shown that the K X-Rays emitted from fragment nuclei can serve as an effective probe to investigate the emission mechanism of long range alpha particles emitted during fission. The emission of these particles changes the constitution of the fragment nuclei in a way depending on whether these particles are emitted from the light fragment group or the heavy or from both. These changes in the constitution of nuclei in the two groups is expected to reflect on the average energy and the yield of the K X-Rays from different groups providing in turn information concerning the origin of these long range alpha particles.

With this motivation, at Trombay, the yield and the energy distribution of the K X-Rays emitted by  $^{252}$ Cf fission fragments have been simultaneously determined

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FIG. 7

MUB-5453



FIG. 8

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for the cases of ternary and binary fissions with a cooled lithium drifted silicon detector. These K X-Ray energy distributions for the two cases are shown in Fig. 9. The K X-Ray yields in ternary fission are found to be greater than in binary fission by  $(25 \pm 6)$  and  $(14 \pm 6)\%$  for fragments in the light and the heavy groups, respectively. On the basis of extrapolation of the known schematics of the low lying states of even nuclei for fragments in the high yield region, the transition energies are expected to decrease with increasing neutron number for same value of 2. Therefore, if these particles were emitted at the expense of nucleons from both fragments, the ternary fragments in both the groups will have agreater neutron to proton ratio, giving rise to an increase in the K X-Ray yields in both groups, as observed experimentally. From further analysis of these results, it was inferred that these particles do not originate at the expense of nucleons from either of the fragment groups alone, but are liberated from the fissioning nucleus as a whole, implying emission just before or at the instant of scission.

### (ii) Gamma Ray and Electron Spectra:

Although, the general properties of the transitions occuring in different fragment nuclei can be inferred from the observed K X-Ray yields, the information concerning the energies and multipolarities of these transitions can only be obtained by a measurement of the gamma ray and conversion electron spectra for fragment nuclei of specified mass and charge. These three parameter data on  $E_1$ ,  $E_2$  and  $E_1$ ,  $E_2$ , and  $E_1$ ,  $E_2$ . E for the  $^{252}$ Cf fragments nuclei have been recently carried out (5) to obtain gamma ray and electron spectra for different fragment masses. Gamma spectrum observed in coincidence with a typical fragment mass range 109-111 (137-139) as shown in Fig. 10 revealing several descrete gamma transitions. Although, because of the finite mass resolution there is an intermixing of the adjacent fragment masses in any selected mass range, it is possible to exactly determine for any particular gamma ray line the masses of the emitting fragment pair from the observed variation in the intensity of the gamma ray line as a function of mass. Since as such this gives the masses of the fragment pair, in coincidence with which the gamma may line was observed, the next question is to decide which of the two fragment nuclei emitted this gamma ray. The emitting fragment of the fragment pair can be identified from the magnitude and sign of the Doppler shift in the gamma ray line when (a) the light fragment is moving towards the gamma detector and (b) the complimentary heavy fragment is moving towards the detector. The gamma ray spectra sorted for the cases (a) when the light fragments and (b) when the complimentation heavy fragments are moving towards the gamma detector are shown in Fig. 10 (a) and (b). By a comparison of Fig. 10 (a) and (b) each peak can be identified with heavy or liht fragments and the peaks can be correspondingly corrected for the Doppler shifts. Further by determining the nuclear charges from the measurement of the energies of the K X-Rays both mass and charge of the emitting fragment nucleus can be identified. If in addition, measurements of conversion.electron spectra for selected masses can be carried out, it can serve not only to confirm the charge of the emitting fragment, but also to measure the internal conversion pro-

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FIG. 10

### babilities.

However, the measurements of the spectra of electrons emitted from fragment nuclei poses the difficulty of detecting electrons with good solid angle without the interfencing effects of fission fragments and gamma rays. Recently this difficulty was eliminated (5) by using an inhomogeneous magnetic field to steer the electrons around a block of lead, which shielded the electron detector from fragments and gamma rays. From the correlated three parameter E1, E2, E measurements, the spectra of conversion electrons for various fragment masses were obtained. The geometry of detection was such that electron emitted at the approximate time of 1 n sec after fission were detected. Fig. 11 shows a typical electron spectra observed in coincidence with fragment mass intervals of 105-107 and 143 - 145, together with the gamma ray spectra associated with the same fragment nuclei, where gamma rays were observed at 90° with the fragment flight path. It can be seen that several examples of K and L conversion lines are indicated. In the same figure, the gamma ray energies as expected on the basis of the observed K and L conversion lines are shown by arrows and identified by the letters of the corresponding electron peaks. This typical comparison of the gamma ray and conversion electron spectra is meant to show that the positions of the electron peaks are consistent with the position of the corresponding gamma rays on the basis of the electron binding energies in the K and L shells. It is evident that such a consistency ensures that the nuclear charges have been correctly assigned to the emitting fregment nuclei. From the several transitions identified for different fragment nuclei in these studies by Watson et al (5) a few selected examples are listed in Table I. The values of the half lives shown in Table I were estimated by determining the intensity of a particular electron line in two different equal time intervals. For the L lines, the number in parenthesis are the calculated energies for the cases where these could not be identified in the electron spectrum. It is quite likely that these cases correspond to E, or M, transitions, especially for light fragment nuclei, where expected large K to L ratios will lead to insignificant conversions in the L shell. Since  $E_{0}$  transitions consistently display smallest K to L ratios, these are easiest to identify on the basis of measured K to L ratios.

It is evident that these detailed measurements of the conversion electron and gamma spectra can really provide a cross check on the general conclusions derived from the K X-Ray yield measurements. In particular the expected abundance of the low energy transitions in the regions of mass 108 and 152 is substantiated by the above measurements. Two of the observed transitions in  $^{110}_{44}$ Ru namely the gamma ray lines of 97.7 and 238.0 keV are particularly good candidates for the transitions  $2^+$  to  $0^+$  and  $4^+$  to  $2^+$  in the rotational band. The magnitude of the nuclear deformations involved for  $^{110}$ Ru has been estimated by Watson (5) by calculating the intrinsic quadrupole moment  $Q_0$  from the measured transition energies and life times and correlating it with the quadrupole deformation parameter by Nathan and Nielsson. The value of  $Q_0$  estimated for the 97.7 keV transition is 4 barns. The quadrupole deformation parameter is given by the equation

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FIG. 12

$$E = -1 \pm \sqrt{1 + 2\delta}$$

where

 $Q_0 = \frac{4}{3} z < h^2 < 5$ 

This gives a value of  $\acute{E}$  of about 0.3 which is comparable in magnitude to the distortion parameter for the known deformed nuclei in the rare earth region. These results therefore, seem to confirm the existence of a region of stable deformation. In the rare earth region, two transitions namely 157.2 per gamma line assigned to  $^{148}$ Ce and 87.2 keV transition assigned to  $^{156}$ Nd appear to be associated with the even-even 2<sup>+</sup> to 0<sup>+</sup> transitions. Several other transitions in these fragment nuclei both of even and odd character are discussed by Watson. However, it becomes evident from the above few examples that an analysis of the several observed transitions in fragment nuclei promises to make significant contribution on the nuclear strucutre of these neutron rich nuclei.

#### STUDY OF HIGHLY ELONGATED NUCLEAR SHAPES:

The door for such studies opened with the following concept first put forward by A. Bohr (9) to explain the observed fragment angular distributions in photofission. Although the initial nucleus is highly excited with closely spaced levels, the nucleus passing over the fission barrier is relatively cold since most of its excitation energy is expended as deformation energy. Consequently the fissioning nucleus while elongated to the saddle point shape, being in conditional equilibrium there, should exhibit spectrum of states similar to that observed in the case of stably deformed nuclei. This point of view has been well supported by the fission fragment angular distribution results. In the last few years a large amount of work has been carried out (1) to extract several information about the spectrum of states exhibited by such a highly deformed nucleus from a study of fragment angular distributions.

The basis assumption involved in the development of the theory is that the nucleus at saddle point can be described by the wave function of symmetric top i.e.,  $D_{MK}^{I}$ , where I, M and K (projection of I on nuclear symmetry exis) characterize the different states on-the basis of collective model. The angular distribution of fission fragments is then given by

The observed  $90^{\circ}$  peaking in the photofission of even-even nuclei near threshold to then expected on the basis of Eq (2) since for dipole absorption I = I, and for even-even nuclei the lowest value of K is zero.

After Bohr's suggestion, the theory has been further extended to medium excitation energies by applying statistical theory of nuclear levels at saddle point. In this case the excitation energy of the nucleus at the barrier is sufficiently high to allow contribution from several K states. In general

$$W() \sum_{K I} \sum_{M} G(I,M) F(K) \left| D_{MK}^{I}(\Theta) \right|^{2} \dots (3)$$

Where G(I,M) is the prob-ability that a nucleus fissions through states (I,M) and (F(K) is the distribution of K-states. In the case of medium energy projectiles  $\vec{T} \sim \vec{\ell}$  and  $\vec{M} \approx 0$ . G(I) can be obtained from optical model calculations of transmission coefficients. On the basis of statistical theory, the distribution F(K) is given by  $F(K) \propto \frac{K^2/2K_0^2}{e_1}$  where  $K_0^2 = \text{Jeff. T} \neq \vec{L}$  and  $\text{Jeff} = \frac{J_{11}}{J_1} = \frac{J_{11}}{J_1}$ and T is the thermodynamical temperature. For a system of independent particles in a potential well exhibiting uniform single particle spacing, the value of J is expected to correspond to the rigid moment of inertia, and

 $T \ll (E_{\chi} - E_{B})^{\frac{1}{2}}$  where  $E_{\chi}$  and  $E_{B}$  are the initial nuclear excitation energy and fission barrier height respectively.

From an analysis of the measured fragment angular distribution on the basis of Eq.(3) it is then possible to obtain the value of the relevent nuclear parameter  $K_{a}^{2}$  connected with the single particle excitations of the saddle point nucleus.  $K_{a}^{2}$ measures the mean square value of the projection of angular momentum on the nuclear symmetry axis. It is known that in the presence of pairing interaction among single particle states, the spectrum of excitation which can contribute to the total projection no longer extends continuously to ground state. In the case of even nuclei such excitations occur only above 2  $\Delta$ . As a result, a superfluid nucleus will have a value of K<sup>2</sup> significantly lesser than its non interacting counter part. This effect of pairing correlations is found to be present in the values of K deduced from fragment angular distributions at low and intermediate excitation energies. At these energies the relationship between  $K_0^2$  and  $(E_X - E_B)$  is found to be linear rather than quadratic as expected on statistical theory. Measured fragment angular distributions at the intermediate energies for the neutron induced fission of 239 Pu have been analysed by Griffin (10) on the the superfluid model to extract the value of critical energy E e above which pairing effects disappear. The value of 2  $\Delta$  obtained on this basis for the saddle point nucleus of <sup>240</sup>Pu was found to be 2.3 MeV, which is about twice the ground state energy group of this nucleus. Recently certain fragment angular distribution studies (1) in the reaction of the type (d, pf) and  $(\alpha', \alpha' f)$  in <sup>239</sup>Pu have supported the above deduction of  $2\Delta$ .

It has been suggested that the pairing effects observed in nuclei are partly connected with the finite size of nuclei, in particular with the influence of nuclear sufface. For infinite nuclear matter, the calculations by Emory and Sessler (11) show nearly zero energy gap. In certain slab model calculations by Heneley and Wilets (12) also the energy gap is found sensitive to the thickness diminishing towards zero as slab becomes thicker. It is therfore likely that a larger energy gap for the saddle shape <sup>240</sup>Pu nucleus results from a larger surface to volume ratio of this deformed nucleus. Since the surface to volume ratio of the saddle shape nucleus is known to increase as  $Z^2/A$  decreases, from the above reasoning a much large energy gap of about 4 MeV may exist for the saddle shape of a ligher nucleus like <sup>260</sup>Pb. Present studies of the angular distributions in the <sup>206</sup>Pb( $\ll$ , f) may give new information on this problem.

At medium excitation energies, where pairing effects are expected to disappear, the deduced values of  $K_0^2$  can provide information on the rigid moment of inertia Jeff and consequently on the shape of the nucleus at the saddle point. These deduced values of  $J_0/_{Jeff}$  plotted as a function of  $Z^2/_A$  are shown in Fig. 2. The variation of  $J_0/_{Jeff}$  as a function of  $Z^2/_A$ , as expected on the liquid drop calculations is also shown in the figure for comparison. As pointed out by Strutinski this discrepancy may be at least in part due to the assumption of constant surface tension in the liquid drop calculations. The agreement becomes better by allowing the surface tension to increase with the increasing curvature of the nuclear surface. These results may, therefore, serve as a guide to evaluate curvature correction effects on nuclear surface tensions.

At high bombarding energies, the nuclear saddle shapes are expected to be modified due to the additional balancing effect of rotational energy and, therefore, in such case the value of Jeff will be dependent on the bombarding energy. Recent determinations (13) of  $K_0^2$  as a function of excitation energy of  $^{238}U(\checkmark, f)$  reaction are shown in Fig. 13 (a). The discrepency between experiment and theory at high bombarding energies is assumed to be due to the effect of rotational energy, and the calculated change in  $J_{\rm Sp}/J_{\rm Jeff}$  as a function of  $\langle L^2 \rangle$  is shown in Fig. 13 (b).

The most exciting aspect of the study of saddle point nucleus lies in its uniqueness in providing a way to study nuclear matter in a very stretched configuration. It is expected that this aspect will motivate carrying out new and better experiments in the direction.

# SYSTEMATICS OF FISSION BARRIER HEIGHTS:

The energy required to reach the fission barrier is given by  $B_f = \frac{B}{S} - M_o$ , where  $M_g$  and  $M_o$  are the masses of the stretched saddle point nucleus and the ground state nucleus respectively. For a pure  $\swarrow_2$  type of deformation, the value of  $B_{\rho}^{L,D}$  on the simple liquid drop model is given by,

 $B_{f}^{L.D} = M_{s} - M_{o}$  $\approx (\frac{2}{3} {}^{E_{s}^{0}} - \frac{1}{3} {}^{E_{e}^{0}}) {}_{e}^{2}$ 

.... (4)

where  $E_{s}^{0}$  and  $E_{c}^{0}$  are the surface and Coulomb energy of the initial nucleus. It fol-



FIG. 13

∆ = (EXPERIMENTAL MASS LIQUID DROP MASS)



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lows from Eq. (4) that  $B_f$  is expected to decrease with the increase in the value of  $Z^2/_A$  and it turns out that nuclei having  $Z^2/_A$  approaching a critical value around 46 should have a vanishingly smallfläsion barrier height. On the basis of this model such nuclei will be unstable towards fission and therefore cannot exist.

In the above simplified treatment, the effect of nuclear shells on interaction energy have been neglected. It is apparent from Fig. 14 that the ground state masses are significantly suppressed at the closed nuclear shells. On this basis,

$$B_{f}^{Shell} = M_{s}^{L.D} - M_{s}^{Shell} - M_{o}^{L.D.} + M_{o}^{Shell}$$

where  $M_s^{\text{Shell}}$  and  $M_o^{\text{Shell}}$  are the shell corrections to the liquid drop masses, which could be both negative or positive.

Since the energy gaps at the closed shells are the result of degeneracies associated with a spherical potential it is reasonable to assume that the shell correction to the liquid drop masses will disappear for sufficiently distorted configuration. It is therefore, expected that the shell correction  $M_g^{Shell}$  to the saddle point masses should be approaching zero and, therefore,

$$B_{f}^{\text{Shell}} = M_{s}^{\text{L}.\text{D}} - M_{o}^{\text{L}.\text{D}} + M_{o}^{\text{Shell}}$$
$$= B_{o}^{\text{L}.\text{D}} + M_{o}^{\text{Shel}}$$

It then follows that for a doubly magic nucleus where  $M_0^{Shell}$  is positive, the fission barrier height is increased because of shell effects. The calculated values (14) of barrier height along the line of  $\beta$  stability are shown in Fig. 15, where the smooth curve is from liquid drop model and the dashed curve results after accounting for shell effects. The expected increase of  $B_f$  due to shell effects near closed shell of Z = 62 and N = 126 is in fact verified by experimental measurements of  $B_f$ in this region. However, discrepancy between the calculated and measured thresholds exists for heavy nuclei in the upanium region, where the calculated barrier heights are about 1 to 2 MeV lower than the experimental values. This disagreement mass suggest that the shell effects are not completely wiped out at the saddle shapes of these nuclei.

A very interesting consequence of the effect of closed nuclear shells on the fission barrier heights has been the prediction (14) of an 'island of stability' near mass 300. In this region one expects the next closed shells after Z = 82 and N = 126, and consequently a positive value of  $M_0^{Shell}$ . For these nuclei even though  $B_f^{L.D}$  is nearly zero, these may still have a fission barrier height equal to  $B_f^{Shell}$ . This Interesting prediction has led several workers to calculate the next magic numbers, and the possible candidates for the doubly magic nucleus suggested are  $126 \times 310 \ 184, \ 114 \times 298 \ 164 \ .$  With the next generations of superheavy ion accelerations, an intensive experimental effort is expected to explore the possibilities of producing these superheavy nuclei.



|             | ·   | Certain             | transitions                         | identified fr | om neutron r                                   | ich <sup>202</sup> Cf f | ragment nuce          | . <u>.</u> . |       |  |
|-------------|-----|---------------------|-------------------------------------|---------------|--|-------------------------|-----------------------|--------------|-------|--|
| Mass<br>No. | Z   | Isotope             | K line<br>K Line<br>Energy<br>(keV) | tı            | L line I <sub>K</sub><br>Energy IL<br>(keV) IL | Multi-<br>polarity      | Gamma energy<br>(keV) |              |       |  |
|             | X   |                     |                                     | с (прес)<br>Х |  |                         |                       | Observed     | Cal.  |  |
|             |     |                     |                                     |               |  | - <b></b>               | *                     |              |       |  |
| 106         | 44  | 106 <sub>Ru</sub>   | 71.0                                | . 1.1         | 37.3   | 4.8                     | ·E <sub>2</sub>       | 94.2         | 94.0  |  |
|             |     |                     | 148.8                               | 1.4           | (167.1)  |                         | ٤                     |              | 170.8 |  |
| 110         | 44  | 110 <sub>Ru</sub>   | 50.2                                | 2.2           | (69.4)   | <b>•</b> 4              | <b>-</b> .            | 73.2         | 73.2  |  |
|             | · · |                     | 74.5                                | 0.9           | 94.5   | 5.7                     | E                     | 97.7         | 97.5  |  |
| -           | -   | -                   | 125.8                               | · _           | (145.0)  | -                       | -                     | 149.2        | 145.8 |  |
| -           |     | -                   | 215.1                               | -             | 235.4  | 4.0                     | E <sub>2</sub>        | 238.0        | 238.1 |  |
| 144         | 56  | 144 <sub>Ba</sub>   | 77.6                                | 2.6           | 110.4  | 5.3                     | M <sub>1</sub>        | 115.2        | 115.9 |  |
| · <b>_</b>  | 56  | 144 <sub>Ba</sub>   | 104.3                               | -             | (136.1)  | -                       | -                     | 142.6        | 142.6 |  |
| -           | 55  | . 144 <sub>Cs</sub> | 160.8                               | 1.0           | 192.5  | 4.1                     | Eg                    | 198.2        | 197.7 |  |
| -           | -   | -                   | 242.4                               | -             | (274.2)  | -                       | -                     | -            | 280.7 |  |
| 148         | 58  | 148 <sub>Ce</sub>   | 116.2                               | 1.3           | 151.6  | 3.7                     | E                     | 157.2        | 157.5 |  |
| 156         | 60  | <sup>156</sup> Na   | 42.6                                | 1,9           | 83.3   | 1.8                     | E <sub>2</sub>        | 87.2         | 87.1  |  |

TABLE I.

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It may be remarked that there are several other aspects of the fission phenomenon of current interest, which have not been reviewed here. The main among these are the new theoretical efforts to symmetrically explain the divisions of mass, charge, kinetic energy and excitation energy in the fission processes. The other phenomenon is the occasional emission of a long range charged particle, which has engaged current interest as it promises to yield information about the conditions existing during scission of an elongated nuclear matter.

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#### DISCUSSION:

C.L. Thaper: Some rather expensive experiments using nuclear explosion have been performed. Could you tell if they have been intended to throw any light on some aspects of nuclear fission? Do they have any scope in this respect, assuming of course, that one can afford and justify the luxury of such experiments?

S.S. Kapoor: Nuclear explosions have been used for certain fission experiments such as measurements of mass distribution for different resonances. I think these have given useful informations.

I think these explosions were to be carried out anyway for other reasons, so justification for carrying out fission experiments may not be required. S. Mukherji: How accurate are the fragment massess - or how well are the emitted neutron numbers known as a function of the prompt fragment masses?

S.S. Kapoor: The agreement of the most probable charges versus masses as obtained from K-X Ray measurements to those obtained by Radio chemical method points out that the physical measurements of both mass and charge must be correct to less than 1 mass or charge number.

The number of neutrons as a function of mass as obtained by different workers seems to be in good agreement implying that these measured values of  $\mathcal{V}(M)$  could be taken as correct.

G.K. Mehta: Is there any way to find the orgin of this large angular momentum of the fission fragments?

S.S. Kapoor: I do not know of any way to determine the origin of this large angular momentum. It has been suggested that this arises due to the non homogeneous coulomb field of the couplementary fragment acting at scission point.

# NONRESONANT COHERENT SCATTERING OF GAMMA RAYS

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## INTRODUCTION:

Coherent scattering of gamma rays occur mainly through the non-resonant processes of Rayleigh scattering, nuclear Thomson scattering and Delbruck scattering. Nuclear resonance scattering, though a coherent process, occur only under specially adopted experimental situations and has not been considered here.

The elastic scattering of gamma rays of not too high energies is dominated by Rayleigh Scattering or the cooperative scattering of photons by the bound electrons of an atom. Nuclear Thomson scattering may be described classically as a process in which the nucleus as a whole is set into vibration by the incident radiation followed eventually by the dissipation of energy in the form of radiation of the same frequency as the incident photon. The intensity of the nuclear Thomson process can be easily calculated by extending Thomson's classical equation for the electron to the nuclear case. Unless  $q = \frac{2h\gamma}{c}$  Sin  $\theta/2$ , the momentum transferred by the photon during the elastic encounters is very high or the atomic number of the scatterer is too low, nuclear Thomson scattering forms a negligible part of the total coherent scattering intensity. Delbruck scattering is an interesting second order effect predicted by quantum electrodynamics (1), which corresponds to the virtual production of electronpositron pair and their subsequent annihilation. In the present report, we shall confine our attention to q less than 2.5 mc (m = electronic mass) and h/ less than 1.5 MeV and hence the non-resonant coherent scattering will be considered almost entirely in terms of the Rayleigh process alone. Also the polarisation phenomena observed during coherent scattering will not be discussed here.

# THEORETICAL CONSIDERATIONS (1):

In the Feynmann-Dyson Scheme, Rayleigh scattering is, to the lowest nonvanishing order of perturbation theory, a two-vertex process shown in Fig. 1. In the first diagram, the incident photon is absorbed before the emitted photon while in the second diagram the order is reversed. As indicated by double lines, the electron in the initial, intermediate and final states is under the influence of the Coulomb fields of the nucleus and other atomic electrons and hence boundstate electronic wave functions have to be used for the initial and final states while for the intermediate state both bound and continum state wave functions have

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to be used for the initial and final states while for the intermediate state both bound and continum state wave functions are to be considered. An exact treatment of Rayleigh scattering is, therefore, very complicated.

In terms of the conventional second-order pertur-bation theory, the transition amplitude corresponding to Rayleigh scattering is given, in the usual notation, by

$$M = \frac{\sum \langle f | H' | n \rangle \langle n | H' | i \rangle}{E_i - E_n \pm h \gamma} \qquad \dots (1)$$

the + and - signs in the denomina tor correspond to the first and the second Feynmann diagrams respectively (Fig. 1). The perturbation Hamoltonian is given by

$$H' = \ell \cdot \underline{\alpha} \cdot \underline{A} (\underline{\alpha}) \qquad \dots (2)$$

which in the non-relativistic limit is .

$$H' = \frac{i\ell}{mc} \quad \nabla \cdot \underline{A} \qquad \dots (2a)$$

A formalism to solve exactly the second order perturbation theory has been developed by Brown et al (3) in Birmingham and exact Rayleigh scattering amplitudes have been calculated (4) for K-electrons of Hg for five specific gamma ray energies (h  $\mathcal{V} = 0.32$ , 0.64, 1.28, 2.56 and 5.12 mc<sup>2</sup>). Even for the limited cases considered, the scattering cross section can be accurately predicted only when q exceeds the intrinsic momentum  $\ll$ mcZ of K-electrons, so that bulk of the coherent scattering is accounted for by the K-sehll, making it necessary to know the L-shell contribution only approximately. Brown and Mayers have also developed a semiempirical formula, the modified form factor relation, which is useful for cases where accurate theoretical calculations are non-existent.

Franz (5) and later Bethe (6) using Feynmann's method have shown that in the non-relativistic limit and in cases where binding in the intermediate states can be neglected, the differential cross-section for coherent scattering is given by the form-factor approximation

$$\frac{d\sigma}{d\Omega_{2}} = \frac{1}{2} \left( \frac{e^{2}}{mc^{2}} \right)^{2} \left( 1 + \cos^{2} \Theta \right) \left| F(q,Z) \right|^{2}, \qquad \dots (3)$$

where the form factor is defined as the matrix element

$$F(q,Z) = \langle 0 | \sum_{j=1}^{Z} e^{\frac{i}{\hbar}} \frac{q \cdot x_j}{2} | 0 \rangle \qquad \dots (3a)$$

where  $|0\rangle$  is the ground ket of the atom and  $\underline{x}_j$  is the position vector of the jth, electron in the atom relative to the nucleus. If  $p(\underline{x})$  is the total electron density at  $\underline{x}$ , F(q,Z) becomes

For a spherically symmetric charge distribution,

$$F(q, Z) = 4\pi \int_{0}^{\infty} \rho(v) \frac{\sin kv}{kv} dv \qquad \dots (4a)$$
where  $k = \frac{v}{k}$ 

For hydrogen in the ground state, an analytic expression for the form factor is available: --2

$$F(q, z = 1) = \left[1 + \left(\frac{1}{2} \frac{\hbar^2}{m \epsilon^2} q\right)^2\right]^{\alpha} \qquad \dots (5)$$

For other atoms it is necessary to invoke the aid of different atomic models for the calculation of the form factor. The Thomas-Fermi model treats the a tom as a statistical assembly of a Fermi-Dirac gas at absolute zero so that the effects of atomic shell structure is smoothed out; near the edge of the atom TF model predicts an excessively smeared out electron distribution so that coherent scattering is under-estimated for low values of q, on the other hand near the nucleus the model predicts a too high density of electrons so that scattering for large values of q is overestimated. Exchange effects are taken into account in the Thomas-Fermi-Dirac model and therefore it gives better values of the form factor than the TF model. T FD form factors have been tabulated by Ibers (7). The self-consistent atomic models of Hartree (8), Hartree-Fock-Slater (8) and Dirac-Slater (9) predict shell dependent maxima and minima of electron densities. Because of exchange potential, electrons are more tightly bound in HFS model than in H model, so that electron distribution in the former is relatively more compact. Similarly relativistic and exchange effects make DS model electron distribution more compact than HFS model. Nelms and Oppenheim (11) in an excellent article have reviewed atomic form factors and have given results of calculation of form factors using Hartree model. Hanson et al have given tables of HFS form factors while Cromer and Weber have tabulated DS form factors.

Limitations of form factor calculations have been discussed among others by Levinger (12).

#### EXPERIMENTAL TECHNIQUES:

It is convenient to classify together experimental techniques adopted by various workers according to the angle of scattering of the photons. Small angles of scattering have been used in the investigations by Storruste (12), Schopper (13), Storruste and Thom (14), Kane and Holzwarth (15), Nath and Ghose (16) and more recently by Hauser and Mussgnug (17). With the exception of the last two measurements, the scattering geometry of the experiments have been defined by the conventional shadow cone technique. This type of geometry usually results in a comparitivity large sample-dependent back-ground especially when the angle of scattering is  $\leq 5^{\circ}$ . To avoid this difficulty Nath and Ghose worked out a modification of the usual shadow cone technique, by interposing at suitable intervals between the sources and

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the detector a large number of annular filters (Fig. 2). Hauser and Mussgnug used annihilation radiation and took advantage of the fact that the two annihilation Quanta are emitted collinearly from the source. One annihilation photon is scattered by the scatterer and is detected by the "scattering detector" while the backward scattered photon is detected in coincidence by the "coincidence Detector", (Fig. 3). This method allowed the investigators to continue their measurements down to 0.5<sup>0</sup> angle of scattering.

For moderate angles of scattering conventional double cone geometry is adequate.

Large angle measurements have been undertaken among others by Storruste (12), Goldzahl and Eberhard (23), Hara et al (24), Cindro and Ilakovak (25), Standing and Jovanovitch (26), Anand and Sood (27), Narasimha Murty et al (28), and others. In this region, experimental measurements are complicated by the occurance of photons from hard noncoherent scattering. The conventional procedure of subtracting the noncoherent fraction from the observed spectrum by a low Z scatterer is no longer valid for correcting the hard component of the noncoherent radiation. Standing and Jovanovitch (26) used an ingenious device (28) to improve the effective resolution of scintillation counter (Fig. 4). Standing et al used a NaI(T1) crystal which was specially mounted with two windows on its end faces. The radiation was incident on the curved surfaces of the cylindrical crystal while two photomultipliers comented on the windows viewed the crystal. The spectrum was then obtained by scanning the pulses from one of the photomultipliers, coincidence gated at some desired energy level by the pulses from the other photomultiplier. Using this arrangement it was possible to peel off the hard Compton spectrum from the coherent peak. However, in this arrangement the light division between the two photomultipliers is fixed and cannot be varied to suit different experimental situations; the photons strike the crystal along the curved surface and not along the axis of the crystal; a minor disadvantage is that the crystal requires special mounting with two windows. A recent modification of the arrangement by Roy, Chatterjee and Ghose (29) is shown Fig. 5. In this arrangement conventional single ended crystals are used. Light division is controlled by a perforated aluminium reflector as shown in the figure. Photons are incident along the axis of the scintillator. The assembly will be used for the measurement of coherent scattering at very small and very large angles, determination of photoelectric cross section and other investigations.

RESULTS AND EMPIRICAL FORMULA:

 $\frac{d \sigma}{d \rho} = \frac{1}{2} (1 + \cos^2 \theta) Z^{n(q)} f(q)$ 

Nath and Ghose (30) have analysed the experimental results for momentum transfers upto 2.5 mc and photon energies less than 1.5 MeV and have developed an empirical formula for the differential Rayleigh scattering cross section. Form factor approximations of Rayleigh scattering can be expressed in the form

.... (7a)

O'25° O'25° O'min TARGET

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FIG . 4 \$ 5



FIG-3
So that the reduced cross section

$$G'(q) = \frac{d}{d} \frac{G}{\Omega_2} - \frac{1}{2}(1+\cos^2\theta) \qquad \dots \quad (1)$$

is a function of q only for a given scatterer and its functional dependence on the energy E of the photon is implicit through q and not explicit at all. We tested this hypothesis in the case of Pb and Sn. It was seen that while it is true for photon energies less than 0.4 MeV, there is indeed explicit energy dependence for radiations of higher energies. Retaining the polarisation factor  $\frac{1}{2}(1+\cos^2\theta)$  in agreement with the measurements carried out upto 0.662 MeV, we have therefore, expressed the empirical formula in the form

$$\frac{d\sigma}{d\Omega} = \frac{1}{2}(1+\cos^2\theta) \ z^{n(q)} f(q) \ \varphi(E,q) \qquad \dots (8)$$

where  $\phi(E,q)$  takes into account, the explicit energy dependence of the cross section. The form of  $\Phi(E,q)$  which explain the experimental results satisfactorily is given by

$$\phi(E,q) = (1.34 E - 4.4)^{-0.35q}$$
 for  $E \ge 0.4 \text{ MeV} = 1$  for  $E \le 0.4 \text{ MeV}$ .. (9)

Further analysis has shown that it is convenient to represent the normalised cross section

where Zo is the atomic weight of a standard scatterer. Lead was chosen as standard, since large number of investigations have been reported on this scatterer. Defining relative Z and reduced f of the absorber through the relations

 $Zr = Z/Z_{0}$ .... (12a)

in the

.... (12b)

it was found by trial that for q  $\geqslant$  0.1mc.  $f_r(q)$  can be expressed by a simple relation of the type

$$f_r(q) = aq^{-m}$$
 .... (13a)

while for  $0 \leq q \leq 0$ . Inc, a suitable form of  $f_{p}(q)$  is

$$f_{p}(q) = (b + cq)^{-p}$$
 .... (13b)

The final expression for  $f_r(q)$  was derived as

 $f_r(q) = f(q) Zo^{n(q)}$ 

 $f_r(q) = (3.15q)^{-2.50}, q \ge 0.1$  mc. .... (14a)

$$= (0.14 + 2.65q)^{-3.20} \text{ for } 0 \leq q \leq 0.1 \text{ mc.} \qquad \dots (14b)$$

In fitting the experimental values of n(q) reported by different workers (15,16,27)

7b)

by a smooth function some difficulties were encountered. It was found that n(q)generally increases with q, the rate of increase, which is fast near q = 0, slows down near about q = 0.1mc. At q = 0, we assumed that n(0) takes the form factor value 2, which is also valid on general grounds. A close examination of the experimental data shows that there exists wide difference in the trends of the value of n(q) in the range q = 0.5 mc to q = 0.8 mc. We believe that this is due to the inadequate separation of hard compton component from the measured scattered intensity. The necessary correction is relatively more important for low Z elements and this adequately explains apparent lowering of n(q) values in this region. In fitting the Z-dependence curve greater weight was, therefore, attached to low q data as well as to data for q 0\*1mc n(q) can be represented by a simple polynomial

$$n(q) = 2.90 + 0.08q + 1.27q^2 - 0.36q^3 \qquad \dots (15)$$

For  $q \leq 0.1$ mc, an additional term - 0.90 exp  $(-500q^2)$  was necessary to account for the rapid drop of n(q) as q tends to zero. This additional term practically vanished for q > 0.1mc and hence eq. (15) was modified to

$$n(q) = 2.90 + 0.08q + 1.27q^2 - 0.36q^3 - 0.90 \exp(-500q^2)$$
 .... (16)

The final expression for Rayleigh scattering cross section was finally obtained as

$$\frac{d c}{d S_{-}} = \frac{1}{2} (1 + \cos^2 \theta) \phi (E,q) (\frac{Z}{82})^{n(q)} f_r(q), \qquad \dots (17)$$

where  $\phi$  (E,q) is given by eq. (9), n(q) by eq. (16) and  $f_r(q)$  by eqns. (14a and b).

Figs. 6, 7, 8, 9 show experimental cross sections along with their predicted counterparts. The empirical formula agrees satisfactorily with the experimental measurements of Pb throughout the momentum range considered here. There is some disagreement at small angles (17,18). The discripency observed by Nath is smaller than that observed by Hauser and Mussgnug and further experiments are desirable at this point. It is to be noted that in the case of 1.33 MeV for q > 0.5mc. only the experimental results of Standing and Jovanovitch (26) are accurate. Earlier measurements were inaccurate for reasons discussed above.

Apart from the range of q = 0.5mc to  $q \sim 1mc$  unit there is general agreement of the experimental and empirically calculated data for Sn. The discrepancies observed can be satisfactorily explained in terms of hard Compton contribution.

The agreement between the experimental and theoretical values is quite satisfactory for Cu.

The results for carbon for very low values of q - show however that, here the disagreement with the empirical formula is violent. This is to be expected, since the smooth variation predicted by  $Z^n$  formula is certainly not be expected to be valid for such low Z elements and the empirical formula is not expected to be



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capable of accounting for any individual fluctuation of cross section due to atomic structure effects. That the formula predicts cross sections within + 20% of their experimental values, should be considered as quite satisfactory.

Investigations carried out by Hauser and Mussgnug (17) have yielded certain very interesting results. These authors' have shown that contrary to the expectation, for the elements Pb, Bi and Th form factor predictions show considerable divergence from the experimental values. This has been attributed by the authors to an outer atomic charge distribution which is different from other elements investigated by them. Further they observed that whereas the cross sections for Pb abd Bi, the experimental results are below the predicted values at small angles, the situation is reversed for Th. More experimental measurements are desirable before an unambigous explanation of the observed anomaly is given.

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## THE PROBLEM OF LAMEDA TRANSITIONS IN SOLIDS

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# INTRODUCTION:

In 1922, Simon discovered that the specific heat of ammonium chloride showed an abnormally high and sharp peak at about  $243^{\circ}$ K, though the behaviour was normal a few degrees away on either side. In the next few years similar anomalies were detected in a number of other materials and perhaps the best known example is the phase transition in liquid helium-4 at  $2.17^{\circ}$ K. The shape of the specific heat curve had a slight resemblence to the Greek letter  $\Lambda$  and so these type of transitions have come to be called lamda transitions. In view of the similarities among the phenomena near lamda transitions and the phenomena near the familiar liquid-gas critical point, these phenomena have come to be called critical point phenomena in recent literature.

It was noticed in liquid helium that there was no latent heat or volume change at the transition, such as what wouls be the case with an ordinary phase transition obeying the Clausius-Clapeyron equation

$$\frac{DP}{DT} = \frac{S_1 - S_2}{V_1 - V_2}$$

where DP/DT is the slope of the transition line and  $S_1 - S_2$  the entropy change across the transition. It seemed that only the specific heat  $C_p$  and the coefficient of thermal expansion X changed in the two phases and so Ehrenfest introduced the idea of a second order phase transition for which

$$\frac{DP}{DT} = \frac{C_{p1} - C_{p2}}{TV(X_1 - X_2)} = \frac{X_1 - X_2}{k_1 - k_2}$$

(k = isothermal compressibility). In many text-books one finds the remark that the Ehrenfest relations explain the experimental observations very well.

Unfortunately this is no longer quite correct. The breakthrough, which initiated the present great interest in the field of critical phenomena, came with the experiment of Buckingham, Fairbank and Kellers in 1957. The succeeded in measuring the specific heat of liquid helium-4 to within a microdegree of the transition and showed that the specific heat had a logarithmic infinity of the form  $\log |T-T_c|$ . High resolution measurements since then we have revealed similar infinities in the coefficients of thermal expansion and compressibility of liquid helium and in the thermodynamic properties of any other materials. Equations involving the subtraction of one large quantity from another are notoriously unreliable and it appears best to inter relate  $C_p$ , and k through a scheme of Pippard, namely

$$C_{p} = TV(DP/DT)\chi + C_{o}$$
$$\chi = (DP/DT)k + \chi_{o}$$

where  $C_0$  and  $\mathcal{N}_0$  are constants compared to the rapidly varying  $C_p$ ,  $\mathcal{N}$  and k.

# LIQUID-GAS CRITICAL POINTS:

It is interesting that the reason why the Ehrenfest relations were so widely accepted was that a large number of theoretical models of phase transitions had in fact predicted second phase charges. The Weiss model of ferromagnetism or the Bragg-Williams model of order-disorder transitions are well known examples in solid state theory. The fore-runner of all these is the Van der Waals theory of liquid-gas transition especially at the critical point. From the equation of state one can calculate, using thermodynamic arguments, the behaviour of the fluid near the critical point. The main predictions which can be compared with the experiments are as follows : (i) The specific heat at constant volume Cyc is finite and discontinuous at the critical point. If the temperature variation is proportional to  $(T)^$ where  $\Delta T = |T - T_c|$ , then  $\alpha = 0$ . (ii) The coexistence curve is quadratic. If the density difference varies as  $(\Delta T)^{\beta}$  near  $T_{c}$ , then  $\beta = \frac{1}{2}$ . (iii) The isothermal compressibility goes to infinity as the inverse of  $|T - T_c|$ , i.e., along  $\rho = \rho_c^{\gamma h_0} k$  varies as  $(\Delta T)^{-\gamma}$  with  $\gamma = 1$ . (iv) Along a critical isotherm the excess pressure is proportional to the cube of the excess density, i.e., at  $T = T_c$ ,  $|f - f_c|$  varies as  $|f - f_c|^{1/6}$  with S = 3. On closer examination it turns out that these predictions are not dependent upon the exact form of the equation of the state. They arise from the expansion of the free energy as power series in  $|T - T_c|$  or  $|V - V_c|$  and the application of conditions like  $|\frac{\partial V_{\partial P}}{\partial P}| = |\frac{\partial V_{\partial P}}{\partial P^2} = 0$ at  $T = T_c$ . These conclusions are thus the same for all Van der Waals type of equations giving the continuity of the liquid and gas states.

The experimental check upon these predictions has taken shape in recent years. It was noticed in 1946 by Guggenheim that the co-existence curve was more nearly cubic than quadratic, that is  $\beta$  was was nearly 1/3 rather than 1/2. Recent work clusters  $\beta$  round 0.33 to within  $\pm$  10%. A more dramatic failure of the Van der Waals type of theory was provided by the measurement of  $C_v$  near the critical point, first done by Voronel and coworkers for argon in 1962. The specific heat goes to infinity as  $\log |T - T_c|$ , though the high temperature side a power law variation of  $C_v$  with  $c/\sim 1/10$  fits the data equally well. Measurements of  $\gamma$  and  $\delta$  are less extensive and their values appear to be  $\gamma \sim 4/3$ ,  $\delta \sim 4$ . The measurements near critical points ere of very considerable difficulty the details of which will not be discussed here. It is however, clear that the Van der Waals type of theories, though adequate for qualitative purposes, fail badly when examined in detail near the critical point.

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# MAGNETIC TRANSITIONS IN SOLIDS:

Going back to solids, let us first consider the magnetic transitions. The early Weiss model of ferromagnetism gave definite results for the behaviour near the Curie point. (i) The specific heat is finite but discontinuous across  $T_c$ . If  $C_M$  varies as  $(\Delta T)^{-\alpha}$  then  $\alpha = 0$ . (ii) Spontaneous magnetization goes to zero as  $(\Delta T)^{\beta}$ where  $\beta = 1/2$ . (iii) The zero field isothermal susceptibility  $\partial M/\partial H$  goes to infinity as  $(\Delta T)^{-\gamma}$  where  $\gamma = 1$ . (iv) Along a critical isotherm M varies as  $H^{1/\delta}$ with  $\delta = 3$ .

At first sight it appears rather curious that the exponents  $\langle , \beta, \gamma, \delta \rangle$  should have the same theoretical values 0, 1/2, 1, 3. One can understand this in two ways. Firstly we know that the thermodynamics of magnetization is obtained from nonmagnetic systems on replacing V by - M and p by H. Therefore  $C_v$  goes to  $C_M$ ,  $(\partial V/\partial P)_T$ goes to  $(\partial M/\partial H)_T$  and so on. But there is a more fundamental reason. Even if one works with other models of ferromagnetism, such as with Landau's theory, one gets the same exponents and the reason is traceable to the expansion of the free energy in powers of  $|T - T_0|$  and so on near  $T_0$ . The situation is the same as in the case of Van der Waals type theories of liquid-gas critical point.

In the last few years a number of experiments have been made to check these predictions. The results on many ferro- and antiferromagnets have consistently disagreed with these exponents. The specific heats all go to infinity logarithmically, though on the high temperature side  $\propto$  may be as much as 1/10. Spontaneous magnetization in ferromagnets give  $\beta \sim 0.33$ , while susceptibility give  $\gamma \sim 1.33$ . & Franges around 4.2. The observed spread about 1/3, 4/3 and 4.2 is of the order of about 10%.

## ISING MODEL:

It is surprising that the experimental values of the critical exponents are the same to within 10% in both cases. It is trivial to say that liquid-gas transitions and magnetic transitions refer to different phenomena. But the surprising observation of the same exponents in both theory and experiment raises the possibility that near the transition what matters more is the statistical thermodynamics of the ordering rather than the specific nature of molecular forces. The first suggestion in this direction was made by Yang and Lee in 1952, when they showed the isomorphism of the lattice-ges model of liquid-gas transition with the Ising model of magnetism. In the theory of magnetism the basic mechanism is the exchange interaction between adjacent spins. This falls off so fast with distance that one usually restricts it to the first meighbours in the Ising or Heisenberg models. In solid state theory they give clear-cut models. Now one of the differences between a gas and To a first approximation a liquid is the presence of short range order in liquids. and in the absence of better models one may consider the molecules in liquids to be moving in cells formed by the immediate neighbours, the more distant neighbours

giving a smoothed potential. The motion is then largely controlled by the nearest neighbours. Then the spin-up or the spin-down state of the adjacent spin is equivalent to the occupation or nonoccupation of an adjacent cell, the total number of spins corresponds to the total volume, the spontaneous magnetization of the magnetic case corresponds to the density of the liquid and so on. Thus it is possible to associate the same mathematical formalism of the Ising model with both magnetic and liquid-gas transitions.

Let us next turn to the theoretical predictions of the Ising model. The first remark to be made is that the three dimensional Ising model has not been exactly solved so far and remains a challenging problem. The two dimensional case was solved in 1944 by Onsager, a work which stands as a monumnet to be admired from a distance by others. In the absence of exact solutions several workers have used series solutions valid below and above  $T_c$  and tried extrapolation techniques to estimate the values of the critical exponents. The estimates are uncertain to about 10%, but the mejority of workers agree on the following conclusions. (i) The specific heat goes to infinity as  $\log |T_c - T|$  below the transition, while above  $T_c$  it may either a logarithmic infinity or a power law singularity with  $\alpha \sim 0.1$ . (ii)  $\beta \sim 0.31$  (iii)  $\gamma = 1.25 - 1.33$  (iv)  $\delta \sim 5$ . These values are also roughly the same in the Heisenberg model.

On the whole these values agree better with the experimental estimates that the values based on Van der Waals or Landau models. Indeed the agreement suggests the directions in which developments are to be sought, namely refining the estimates of the exponents. It may happen that second order discrepancies may crop up, especially those arising from the specific structural aspects of the materials. But it is obvious that the new estimates are nearer truth than the earlier values of the exponents. It also raises rather thorny questions on the basic theory of the statistical mechanics fo phase transitions, namely how well-behaved will be the free energy functions which cannot be expanded as a series solutions about the transition point. These questions are largely unanswered at the moment.

### EFFECT OF LONG RANGE INTERACTIONS:

It is next natural to ask the question whether the same exponents will be valid for other phase transitions in solids. In the magnetic case and perhaps in the liquidgas case the basic interactions are of short range. In ferroelectricity, for instance, the dipolar interactions are definitely of long range. There is some evidence that when the interactions are long range the critical phenomena are different. The theory of superconductivity invokes essentially long range Cooper pairing of electrons via electron-phonon interactions. The superconducting transition of type I superconductors at zero field is the only known case of clear-cut Ehrenfest second order phase transition. In the case of ferreelectricity, the dielectric constant above  $T_c$  follows T = 1 quite well. On the theoretical side, a one-dimensional gas was analyzed by Kac, Kemmer and Uhlenbeck to show that the Van der Waals behaviour is obtained when the range of interactions goes to infinity. This is roughly in line with the experimental situation except for one serious discrepancy, namely the specific heats in ferroelectrics go again to logarithmic or other infinities and do not obey the classical prescription of remaining finite but discontinuous across the transition. Thus the situation in ferroelectrics, where long range dipolar interactions are dominant, remains to be clarified.

## NON-EQUILIERIUM PHENOMENA:

So far the discussion has been restricted to equilibrium phenomena. The matters become even more complicated when transport phenomena are considered. The experimental situation is far from clear as regards the exponents of the temperature and other variations. Theoretical predictions are even more unsatisfactory at present and a large body of work remains to be done.

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#### DISCUSSION:

P. Singh : a) I would like you to comment on the physical cause of such transitions.

b) In ferromagnetic metals the Heisenberg model does not seem to hold. How will you modify your theory in that case?

E.S. Raja Gopal :

a) One can say in a broad way that the transition arises when, say the exchange interaction tries to align the spins against the disturbing influence of thermal agitation and succeeds in introducing the alignment in magnetism. At the moment one cannot say at what rate the transition will occur, especially whether it will be cooperative or not. In almost all cases the ordered state is attained at low temperatures.

b) This is included in the list of values given. The differences caused by the Heisenberg model in the values of  $\alpha$ ,  $\beta$ ,  $\gamma$ ,  $\delta$  are of the order of 5 - 10%. For instance,  $\gamma$  has a value of 1.33 in the Heisenberg model and 1.25 in the Ising model (as compared with 1.00 in the Weiss model). R. Vijayaraghavan :

I think in the T  $\ll$  T<sub>c</sub> range, spin wave theory holds good. Near T<sub>c</sub>,  $\delta$  = 3 has been verified for magnetization.

E.S. Raja Gopal :

In the  $T \ll T_c$  range, spin wave theory is all right and  $M \ll H^{\delta}$  come out near  $\delta = 3$ . But as one goes closer to  $T_c$ , the variation is approximately  $\delta = 4.2 - 4.4$  and the critical exponent under discussion is strictly for  $T = T_c$  case.

# HIGH FREQUENCY ULTRASONIC WAVES IN SOLIDS

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## ABSTRACT

A brief survey of the ultrasonic pulse-echo technique for the study of solids is presented. One measures, using this technique, the velocity and the attenuation (or changes in these by varying external conditions) of sound waves in the medium. The velocity measurements give the second order (also, third order) elastic constants, and the attenuation represents the losses due to different types of interactions. The survey deals with a few types of phenomena: dislocation damping, domain wall losses in ferromagnetic metals, and interaction of conduction electrons. The last topic is dealt with some detail. In this the transport properties at low temperatures, fermi surface measurements and superconductivity are discussed.

The theoretical approaches to the problem of the interactions of the ultrasonic waves are different in the two limiting cases  $ql_e < 1$  and  $ql_e < 1$ , where q is the magnitude of the wave vector of the ultrasonic wave and  $l_e$  the mean free path of electrons. For  $ql_e < 1$  the experimental results agree well with the theoretical predictions. Significant deviations have, however, been observed for  $ql_e > 1$  and, so far, there is no general agreement about the causes of these deviations.

## SUPERCONDUCTING MATERIALS

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# INTRODUCTION : MATERIALS vs PHENOMENON

Superconductivity as a phenomenon has been a source of enjoyment (and employment) for physicists for many years. As a material study it become popular only recently. The traditional approach of the physicist is to find a material which exhibits the phenomenon he wants to study, and then to forget about the material and concentrate on the phenomenon. It was found very early that tin, lead, indium, mercury all become superconducting. However, indium was expensive and mercury could not be handled in solid form at room temperature. Thus experimenters tended to favour lead and tin. Of these the transition temperature of tin is in a more convenient range experimentally. Consequently, most physicists who have studied superconductivity have studied tin. Now this approach certainly had its successes - the thermodynamical, electromagnetic and even the microscopic quantum mechanical aspects of superconductivity were all worked out successfully with the aid of experiments on tin. The physicist thought he was studying 'superconductivity'; a metallurgist would have said he was studying tin!

Some things were missed by concentrating on the phenomenon and neglecting the materials aspect. For example Type II superconductivity was not appreciated until the 1960's, even though it is by far the most important and prevalent case. In concentrating on Type I superconductors like tin physicists were looking at a special case. Another, less specific, appreciation that was missed by concentrating on only a few materials was a feeling for the universal aspect of the phenomenon. Superconductivity was thought of as a very special situation in nature, requiring very special conditions for its appearance. It's not that way at all. At low temperatures, a transition to superconductivity occurs in the electron gas of most metals though certainly not all - whether elements, compounds or solid solutions. It's the usual thing. Some thousands of superconducting phases are known. It's a much more common phenomenon than ferromagnetism, for example.

A picture of the periodic table illustrates this for the elements. The 'magnetic' (ferromagnetic, antiferromagnetic, strongly paramagnetic) elements are numerically overwhelmed by the superconductors. As for alloys and compounds, practically all combinations of superconducting elements with other superconducting elements are superconducting, as are also a great many combinations of superconductors with nonsuperconductors, and even quite a few phases formed between elements which are not themselves superconducting at all. With very, very few exceptions the only ferromagnetic phases are those which contain Cr, Mn, Fe, Co, Ni or one of the rare earth or actinide elements.

On leave from University of California, Berkeley, California, U.S.A.

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At any rate, there is no danger now of the materials aspect of superconductivity being overlooked. Since the development of real and anticipated engineering applications interest and activity in the field has increased many fold.

We can ask academic questions: Will all elements eventually become superconducting, if, the temperature is low enough? If not, can we clearly and concisely state the critical electronic, crystallographic or other considerations which are essential for superconductivity? Can we predict the  $T_c$  knowing the composition and structure?

We can also ask practical questions, which are still scientific ones in that they cannot be arswered without a better basic scientific understanding of superconducting materials than we have now: How can low frequency as losses be reduced or eleminated? What do we do to a given composition to make it carry the highest possible critical current? And, most exciting of all, can we make superconductors with transition temperatures a lot higher than the highest now known ( $20.04^{\circ}$ K)? There is no established upper bound for T<sub>c</sub> from theory, to date. On the other hand, a large amount of experimental effort, synthesis of many new phases, etc. in recent years has not resulted in any superconductors with transition temperatures markedly above the highest known 10-15 years ago. So perhaps, there is a fundamental upper bound on T<sub>c</sub> of about 20<sup>°</sup>K; if so we should be trying to understand it.

# SUPERCONDUCTING ELEMENTS, ALLOYS AND COMPOUNDS

The occurrence of superconductivity in the elements and in compounds and alloys has been reviewed by various authors (1-4), consequently we will not go over this ground again. We comment only on one important class of superconductors discovered in recent years, the so-called 'superconducting semiconductors'. These are made by taking a semiconducting material and increasing the carrier density to  $10^{18}$ -- $10^{20}/\text{cm}^3$ --carrier concentrations which are very high indeed for semiconductors, but substantially lower than the  $10^{22}/\text{cm}^3$  characteristic of metals. The carrier deneity is made by doping, by compounding the material off stoichiometry, or sometimes by reduction of constituents in the base material. The transition temperatures are invariably low and thus the materials are of no engineering interest, but the ability to control the carrier concentration and to relate the properties of the superconducting material to those of the base material makes an ideal system for fundamental study. Some examples are GeTe<sup>(5)</sup>, SnTe<sup>(6)</sup>, SrTiO<sub>3</sub><sup>(7-9)</sup>. The last named is also sometimes referred to as 'superconducting ceramic'. It may be ceramic mechanically, but electrically it is a metal.

It is important to realize that all the superconductors of this class, like all other superconductors, are metals in the normal state just above the transition temperature. The label 'superconducting semiconductors' describes their origin, not their physical state at oryogenic temperatures. The carrier concentrations are high enough to make the material full degenerate, and the electrical resistance-temperature characteristic just above T, is never that of a semiconductor. Usually it is

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flat. For example  $(^{7})$ , SrTiO<sub>3</sub> samples prepared to have a carrier density in the range 6.9 x 10<sup>18</sup> to 5.5 x 10<sup>20</sup>/cm<sup>3</sup> have a resistivity which is temperature independent, at 300 micro-ohm-cm, below 10°K. The T<sub>c</sub> in this case is about 0.050°K at both ends of the carrier concentration range, rising to a maximum of 0.300°K at 9 x 10<sup>19</sup> carriers/cm<sup>3</sup>, in the middle of the range.

## TECHNOLOGICAL ASPECTS

The physical properties of crucial technological importance for superconducting materials are transition temperature, critical field, and critical current density. All should be as high as possible. Actually however, just giving three numbers, for the above three properties, does not completely characterize a superconducting material. To characterize the material with respect to the variable temperature, field and current, we must specify a surface in the positive octant of a three dimensional T-H-J space. Points under this surface (i.e., between the surface and the origin) represent superconducting states of the material. By giving the usual three numbers (T for H=O, J=O; H for T=O, J=O; and J for H=O, T=O) we specify only the points where this surface cuts the axes. For some applications these points are irrelevant since they do not correspond to actual operating conditions. For example, if we wish to construct a magnet the value of J at H=O is not very important. What we are interested in is the value of J at whatever field we are designing the magnet to produce. To give concreteness to the discussion consider Fig. 1 and 2. These are sections through the T-H-J surface for one of the best materials produced to date in the laboratory -- Nb<sub>3</sub>Sn made by coevaporation of the elements (10). Fig. 1 shows critical field as a function of temperature for zero transport current. The critical temperature at zero field is 18.2°K; the critical field at T=O is over 200kgauss. Fig. 2 gives  $J_{e}$  vs H at T = 4.2°K; (this temperature, the helium boiling point, is the normal operating temperature).

Looking at Fig. 1 and Fig. 2, we notice immediately two things. First, the curve of Fig. 1 is quitr regular and smooth, and the curve of Fig. 2 is not. This reflects reality. Critical current is a much more structure sensitive property than critical field. The critical current for a given composition is a strong function of microstructure, point defect concentration, dislocation density, cold work and thermal history, etc. The current carrying state of a superconductor cannot be the lowest energy state in the thermodynamical sense. It must be a metastable state. The level of current which can be metastably maintained depends on the number and effectiveness of the pinning centres which stabilise it. These pinning centres can be surfaces, precipitate particles, dislocation tangles, composition variations, etc.

The other thing we notice is the magnitude of the critical current densities in Fig. 2. A critical current density of millions of amps (even one crore amps!) per square cm of conductor cross section is enormous. It's almost unbelievable. Copper melts at current density of a little over 100 amps/cm<sup>2</sup>. For technological purposes (magnetic field generation, power transmission, motors and transformers) high critical







FIG. 2. Critical current characteristic for best known laboratory sample of Nb<sub>3</sub>Sn. Hypothetical operating point refers to a proposed superconducting transmission line. current is the most important property of a superconductor. It is more important, actually, then the zero resistance, though of course the two go together. To appreciate the magnitude of the allowable critical current densities, consider the example given by Garwin and Matisoo<sup>(11)</sup> who proposed a superconducting transmission line with capacity of  $10^{11}$  watts--half the present peak generating capacity of the U.S. All this power would go through a conductor with a diameter about the same as that of your arm!

The only technological application which is reasonably well developed to date is magnets. Fig. 3, taken from the review articles of A.C.  $Prior^{(12)}$  shows the critical current--crittical field curves of a number of commercial magnet materials. The characteristics here are not quite as good as that of Fig. 2, but these are commercial, not laboratory, materials. The construction of superconducting magnets capable of generating very high fields has received a lot of attention (magnets of 150 kgauss, with a working volume big enough to put your hand into have been built) and consequently, the development of materials with moderate critical currents at very high fields has been of great interest. However, it now appears that the bulk of applications in the future, especially the high volume applications, will call for materials with very high critical currents at low or moderate fields. The cost of the material is also an important factor. Thus attention should not be focussed only on the extreme high field end of the curves of Fig. 3.

## TODAY'S BEST SUPERCONDUCTORS

The data of Fig. 1, Fig. 2 and Fig. 3 describe, for technological design purposes, the best superconducting materials available today. However, when assessing the prospects of a particular superconducting compound--the possibilities that it could be developed into a useful superconducting material--it is sufficient, for a start, to note just its transition temperature  $T_c$  (at H=0, J=0). This is because the transition is a measure of the strength of the superconductivity-- the stability of the superconducting state. It is also very fortunate experimentally, because  $T_c$  is easy to measure and not very strongly structure sensitive.

The highest transition temperature superconductors known today are beta-wolfram structure compounds, mostly binary compounds, formula  $A_3B_3$ , of one transition metal(A) with one non-transition metal (B). This structure is shown in Fig. 4. It is cubic structure, not very complicated, but with interesting special features. The non-transition metal atoms at the corners define the cube. The transition metal atoms are arranged in lines parallel to the cube edges and passing through the face centres. There are three sets of lines, mutually orthogonal but not intersecting. Thus there must be something of a one dimensional aspect to the potential in which the electrons move. This is particularly so because the transition metal ions are characteristically pushed very close together in the chain. Along the chain the distance between centres of transition metal atoms is substantially less than the



Fig. 3. Characteristics of Commercial Magnet Materials



FIG. 4

atomic diameter as determined from the distance of closest approach in the crystal of the pure element. Thus there is quite a bit of A-A overlap along the line of the chain, which presumably leads to band information even for electrons which would normally be part of the ion core. There is also some A-B overlap, though less. The situation is drawn to scale in Fig. 5 for the beta-wolfram compound Nb<sub>3</sub>Sn, the exemplary case and until recently the highest superconductor known.

The high transition temperature compounds in the beta-wolfram structure are given in Table I. Four of these,  $V_3Si$ ,  $V_3Ga$ ,  $Nb_3Sn$  and  $Nb_3Al$  were found within a span of two or three years, 1953-1956, by Matthias and co-workers at the University of Chicago and Bell Telephone Laboratories. Then followed a decade of fruitless search in many laboratories for a superconductor with higher  $T_c$  than  $Nb_3Sn$ (18.2°K). Thousand of new phases were synthesized and tested, including all known or possible beta-wolfram compounds, and many new superconductors were found, but one with higher  $T_c$  than  $Nb_3Sn$ . Then the mixed phase  $(Nb_3Al)_{0.8}(Nb_3Ge)_{0.2}$  was found by Matthias and co-workers<sup>(13)</sup> to be superconducting with a critical temperature of 20.04°K.

The high T of the beta-wolfram compounds of Table I is thought to arise from a very high density of states N (density of electron states at the Fermi energy) rather than from an anomalously large electron-phonon coupling parameter V. The high density of states (verified by heat capacity measurements) is thought to come from a very high and narrow band superimposed upon an ordinary s-p band of much lower magnitude and much greater breadth. The width of the narrow band, according to some authors<sup>(14)</sup> is much less than the spread of phonon energies in the crystal, which is of the order of  $k\theta_n$ . The fermi level is centred in this very narrow and very high band, thus giving the high N. Further support for this picture comes from the work of Cohen and others (15) who found that they could account for the various anomalous normal state properties of Nb<sub>3</sub>Sn by assuming a model in which N(E) increased very rapidly in a very small energy range. Some of these normal state properties are really quite unusual; for example the crystal softens on cooling. One elastic constant, which measures the resistance to one particular type of shear, decreases steadily as the temperature drops, to a value so low that the restoring force against this particular type of shear almost vanishes and the crystal almost 'melts' at 20°K!

The other known high  $T_c$  superconductors are the face-centered cubic interstitial transition metal carbides and nitrides. Niobium nitride has been known for many years to have  $T_c = 15.5^{\circ}$ K. Matthias found that by adding carbon and forming a mixed niobium carbide-nitride the transition temperature could increased to a maximum value a little over  $17^{\circ}$ K at the optimum composition. Experimentally these carbides and nitrides are usually regarded as unfriendly, since they are difficult to synthesize with controlled stoichiometry and would be difficult to fabricate into useful devices if developed. To date no one has attempted to make a magnet, or any other device using the interstitial



ATOMIC ARRANGEMENT IN Nb3 Sm (DRAWN TO SCALE)

FIG. 5

# FIG. 6

# HYPOTHETICAL ORGANIC SUPERCONDUCTOR



fcc phases. The high  $T_c$  in these materials may come from a high coupling constant rather than from a high density of states (16).

| Compound           | Structure     | Т <sub>с</sub> (°К) |
|--------------------|---------------|---------------------|
| Nb <sub>3</sub> Sn | <b>/3</b> - ₩ | 18.2                |
| Nb <sub>3</sub> A1 | β- ₩          | 17.5                |
| V <sub>3</sub> Ge  | β- W          | 16.8                |
| v <sub>3</sub> si  | β- W          | 17.0                |
| (Nb3A1).8(Nb3Ge).2 | β- ₩          | 20.04               |
| NPN                | fec           | 15.5                |
| NbN-NbC            | fcc           | 17-1                |

TABLE I

## SUTERCONDUCTORS FOR THE FUTURE

If a material could be found that was superconducting at room temperature, or even at nitrogen temperature, it would change the world. All electric power transmission and generation, an much distribution, would be revolutionized, and the relative economics of electric energy in comparison with petroleum and other forms of energy would be shifted in favour of the former. It is intruguing to realize that no firm reason exists for ruling out the possibility of high temperature superconductivity. There is no known theoretical upper bound on the transition temperature except within very restrictive models. So let us considersome possibilities.

Many years ago  $Ogg^{(17,18)}$  reported superconductivity at  $77^{\circ}$ K in a sodiumemmonia phase. Ogg's observation was confirmed by one investigator<sup>(19)</sup> and not confirmed by a number of others<sup>(20-24)</sup>. The sodium-ammonia phase was doubtless metallic, but probably it was not superconducting. It is worth remembering, however, that Ogg's phase was almost certainly a metastable one in a system known to form a variety of metastable phases. Thus the suspicion persists in some quarters that the difficulty in reproducing Ogg's results may reflect only a difficulty in reproducing some particular non-equilibrium phase. Ogg himself reported that he was able to get the superconduction result only a few times in over a hundred tries. The cinventional and accepted view today however, is that Ogg's result was wrong and reflected only incompetence or fraud. Much more recently W.A. Little<sup>(25)</sup> proposed a superconductor which could theoretically have a transition temperature well above room temperature. This also may never come to pass, but if it doesn't the reason will not be incompetence or fraud. Little's superconductor is based on a hypothetical organic molecule-- a long chain molecule like DNA but with alternating double bonds like benzene. This molecule exists only on paper, though efforts to synthesize it are, I understand, actively in progress. Because of all the double bonds there is some question about stability of the molecule, so the general axiom: 'chemistry you can always do', may not be applicable.

The double bonds in Little's molecule provide the primary charge carriers, corresponding to the electrons in a metal. The coherence between electrons is provided by oscillating double bonds in short side chains (essentially photo-sensitive dyeradicals). The molecule is shown in Fig. 6. The role of the phonons in an ordinary superconductor is thus taken by electrons -- the oscillating bonds in the side chains. This is the physical reason for the theoretical transition temperature comes out so high. Recall the ECS formula for  $T_c$  in its simplest form:

$$T_c = \Theta_D e^{-(1/N_O V)}$$

from which the mass dependence of T (isotopic effect) is seen at once to be a

 $T_c \sim M^{-(\frac{1}{2})}$ 

If we substitute an electronic mass for a nuclear mass we thus get an increase in  $T_c$  by a factor of several hundred. The critical field for destruction of superconductivity should be also very high, since it scales with  $T_c$ . In fact the coherence energy of the superconducting state becomes comparable with chemical binding energies and could make an appreciable contribution to stabilizing the molecule.

Little has worked out the coupling constant and  $T_c$  for his hypothetical molecule by extending the accepted ECS microscopic theory to his usual case. The molecule is different from a metal in several ways of course, one of the obvious ones being its one-dimensionality. There is some theoretical question about phase transitions of the superconducting type in one-dimensional systems. Little's work has thus been called into question on theoretical grounds. He has defended it, however, and the theoretical side of the issue appears to be not yet resolved. Meanwhile efforts to synthesize the molecule continue.

Motivated by Little's work, McConnell and coworkers (26-28) have attempted to raise the T<sub>o</sub> of metals, notably, Al and V, by depositing organic molecules upon them. Experimentally the metal and the organic molecules are evaporated on a cold substance, in order to insure a clean surface and suppress undesirable chemical reactions. The idea is that resonant **bond** oscillations in the molecules

(as in Little's side chain molecules) will provide additional coherence energy and thus raise  $T_c$ . Use of the organic molecules has definetely raised the  $T_c$  of the metals. In the case of V this increase is only a few percent, in the case of Al it is several fold. It is not established that his increase comes from an increase in the coherence energy of the superconducting state. It could come from a decrease in the electronic free energy of the normal state, as discussed below.

A very recent attempt to reach higher transition temperature is the 'sandwich superconductor' proposal of Cohen and Douglass (29) and Strongin <u>et al</u> (30). These authors point out that superconductivity arises from an attractive electronclectron interaction (mediated by phonons) diminished by the Coulomb repulsion, and that the latter can be reduced, and perhaps even converted into an attraction, by interposing a non-conductive barrier between the electrons of the coupled pair being considered. The electrically non-conductive barrier layer can still propagate phonons. Thus the original attractive term is still present, though perhaps slightly reduced.

experimentally one deposits metal, insulator, metal, insulator, etc. The layers must be thin--only a few tens of angstroms. A perfect parallel layer sandwich geometry is, however, not essential; one could get higher  $T_c$  with coated granules in contact, for example. Thus one could get a higher  $T_c$  without meaning to, by evaporating a metal under dirty conditions. Quite a number of old experimental observations of  $T_c$ 's higher than expected for the metal being evaporated can be explained on this basis. New experiments carried out by Strongin <u>et</u> <u>al</u> have used the sandwich geometry. Results were extremely encouraging. Successive metal layers deposited in a good vacuum on a cold substance have shown about the same  $T_c$ . If alternate layers are deposited in dirty vacuum, thus presumably forming insulating barriers,  $T_c$  increases dramatically. For example a three fold increase, to over  $5^{\circ}$ K, is observed for Al. Experiments have not yet been done, but doutless will be, to try to raise the transition temperatures of materials that have high  $T_c$  to begin with.

All these evaporation experiments have been done on cold  $(4.2^{\circ}K)$  substrates. This is helpful in suppressing surface migration and undesirable chemical reactions, but it also makes probable a metal configuration which is at least somewhat removed from equilibrium, Consider the electronic part of the free energy in the normal and superconducting states as functions of temperature. The crossing of these two curves (Fig. 7) determines  $T_c$ . Anything which raises normal state free energy increases  $T_c$ . By definition the normal state free energy curves for all metastable configurations are higher than the one for the equilibrium configuration. Thus any treatment which puts the normal state metal into a metastable configuration will raise  $T_c$ . It can be argued that this is the explanation of the McConnell and the Strongin results. Quantitative theoretical estimates of  $T_c$  and <u>subsequent</u> experimental verification will be necessary to climinate this possibility.



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## CLOSING REMARK

It is instructive to recall that the idea of using superconductors to generate magnetic fields is very old-- it originated with Kammerlingh-Ohnes<sup>(31)</sup>. However, early attempts to construct a solenoid magnet using Pb-Bi alloy failed. Only a few hundred gauss could be generated before the superconductor went normal. It is now clear<sup>(32)</sup> that if the early Dutch workers had cold worked their wire, and perhaps shifted the stoichiometry a little, results would have been spectacularly better. The development of superconducting materials and magnets would have begun in earnest in the 1920's, instead of lying dormant until the 1960's. Perhaps right now we are equally close to advance of equal or even greater magnitude. The moral : don't give up!

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#### DISCUSSION:

P. Singh : What other interactions apart from electron-electron interaction through the process of emission and absorption of phonons can possibly lead to superconductivity?

M.F. Merriam: Various other possible interactions have been proposed (e.g., Hamilton, Jenson and Kuper, Phys. Rev. 1964 - S electron coupling for La). There are however, no specific cases - no specific substances - for which it is necessary to invoke some interaction other than electron-phonon to account for the observed facts. The fact that transition temperature is dependent on isotopic mass is sufficient to establish that phonons are important. In most cases the dependence is  $T_{c} \sim M^{-\frac{1}{2}}$ , a dependence which comes automatically from the theory in its simplest form. In those cases where the isotopic mass dependence of  $T_{c}$  is different from  $M^{-\frac{1}{2}}$ it may be that the unusual electron-phonon interaction is still active and that the unusual isotope effect arises from a complicated band structure.

E.S. Raja Gopal : V<sub>3</sub>Ga is reported to have a much higher critical field of 500 kOe. What is its technological status?

M.F. Merriam

The 500 kOe is obtained from a extrapolation and is not firmly established experimentally. There are theoretical reasons (Clogston Paramagnetic limit) for doubting the existence of superconductivity above 300 kOe.

The vanadium compoundshave not generated as much technological interest as the niobium compounds because the required processing temperatures turn out to be much higher ( $\sim 1750^{\circ}$ C) as opposed to  $\sim 1050^{\circ}$ C for the Nb compounds. However, vanadium metal is less costly than niobium, and so the vanadium compounds may become technologically important in future. 'B.S.V. Gopalan : Hus there been any attempt to control the superconductivity by the application of an electric field? Two ways-(a) placing the sample in the field, (b) application of electric field by fixing electrodes on the sample. For instance, in semiconductors electron density can be controlled with field.

M.F. Merriam : The question has meaning mostly in relation to semiconductors, since for metals electric fields do not penetrate, and the response of a metal to an electric field can be analysed in terms of the resultant transport current and its associated magnetic field. (However, there has been one experiment - an attempt to observe a difference in work function in a field emission microscope - in which a negative result was explained with the hypothesis that super conductivity was generated by a high electric field).

In relation to superconductors, the suggestion is intriguing and I know of no experiments which the superconductivity has been studied as a function carrier density controlled by electric field. Carrier density must be at least  $10^{18}/cc$ . if superconductivity is to be observed.

N.C. Mukhopadhyay

How do you explain theoretically e/a magnetic rule observed emperically?

M.F. Merriam :

Transition temperature follows density of states (depends on it exponentially, if coupling constant is approximately constant). If a superconducting phase contains both transition metal and non-transition metal atoms (like Nb<sub>3</sub>Sn, e.g.,) the d band density of states from the transition metal atoms will certainly dominate all s-p band contributions. d-band densities of states in both 4d and 5d transition metal series are know (both theoretically and experimentally) from heat capacity measurements) to undulate with the observed  $T_c$  variations.

## PHONONS IN METALS

S.K. Joshi, Physics Department, University of Roorkee, Roorkee.

# INTRODUCTION:

In this talk I aim at a review of the present status of the theory of lattice vibrations in metals. This field has gone through rapid growth in the past few years. The enormous literature available by now on 'Phonons in Metals' renders an encyclopedic discussion covering all the aspects of the topic beyond the scope of even a most ambitious lecture series, let alone a half an hour talk. We shall be almost exclusively concerned with the basic theory of lattice vibrations in simple metals. The prototypes of simple metals may be taken as sodium, aluminium and magnesium.

The problem of lattice vibrations in metals is basically a many body problem of a number of electrons interacting with ions. In these circumstances, it is understandable, even natural that theorists have sought approximations which render the system tractable to study. The essential approximations in the general theory of lattice dynamics developed within the frame work of Born-Von Karman approach are that the atoms vibrate harmonically about their equilibrium positions and that the electrons in the lattice follow the nuclear motion adiabatically. For a simple metal we assume that the core electrons belonging to the ion move rigidly with the nuclei and the valence electrons respond to charge fluctuations generated by the motion of ions. The motion of the electrons is adiabatic, and that is the eigenfunctions of the electrons adjust themselves instantaneously to the nuclear positions in the perturbed crystal. The adiabatic approximation allows usto decouple the motion of ions now becomes.

where  $E(\underline{R})$  is the energy of electrons for that particular configuration of ion system.  $U_{\underline{I}}(\underline{R}^{(1)} - \underline{R}^{(1')})$  is the direct energy of intereaction between ions 1 and 1' located at  $\underline{R}^{(1)}$  and  $\underline{R}^{(1')}$  respectively.

To introduce the notation I will briefly mention the elements of the classical theory of lattice dynamics. In terms of basic vectors  $a_1$ ,  $a_2$ ,  $a_3$ , the equilibrium position of an ion is

where  $l_1$ ,  $l_2$ ,  $l_3$  are any set of integers. Let the displacement of an atom due to thermal vibration from its equilibrium position be  $q_1^{(1)}$  so that

$$\underline{\mathbf{R}^{(1)}} = \underline{\mathbf{1}} + \underline{\mathbf{u}}^{(1)}$$

we may expand the potential energy V(R) in powers of displacement for small oscillations. In the harmonic approximation, where we drop terms of higher than second power in displacement in the series for V, we have

$$\mathbf{v}(\mathbf{R}) = \mathbf{v}_{0} + \frac{1}{2} \sum_{l,l'} \sum_{\alpha,\beta} \frac{\partial^{2} \mathbf{v}}{\partial \mathbf{u}_{\alpha}^{(1)} \partial \mathbf{u}_{\beta}^{(1')}} \bigg|_{0} \mathbf{u}_{\alpha}^{(1)} \mathbf{u}_{\beta}^{(1')} \cdots \cdots \cdots (3)$$

we abbreviate

as  $v^{(1,1')}$  and the translational symmetry  $\chi\beta$ 

we appreviate  $\frac{\partial \mathcal{U}_{\mathcal{U}}^{(1)}}{\partial \mathcal{U}_{\mathcal{U}}^{(1)}} \partial \mathcal{U}_{\mathcal{U}}^{(1')} |_{0}$  of the lattice means that

v≪β<sup>(1,1')</sup> depend only on the relative cell index  $v_{\alpha\beta}^{(1,1')} = \alpha\beta^{(1-1')}$ .....(4)

The equations of motion for ions of mass M are

$$M \quad \widetilde{\mathcal{U}}_{\mathcal{A}}^{(1)} = \frac{\partial v(\mathbf{R})}{\partial \mathcal{U}_{\mathcal{A}}^{(1)}} = -\sum_{\mathbf{1}', \beta} v_{\mathcal{A}\beta}^{(1-1')} \quad u_{\beta}^{(1')} \quad \dots \dots (5)$$

The force constant  $V^{(1-1')}$  is the negative of the cartesian component of the force on the atom at 1 when the atom at 1' is displaced unit distance along  $\beta$  direction. For a periodic lattice we choose a solution

$$\mathfrak{U}^{(1)} = \frac{1}{\sqrt{MN}} \quad \mathfrak{E}_{q \ eq} \quad e^{\frac{1q}{2} \cdot \underline{1}} \qquad \dots \dots (6)$$

where Eq is the unit polarization vector, q is the propagation vector, N the number of ions in the crystal and aq is the amplitude of the lattice waves. The time dependence is contained in aq

$$\mathbf{u}_{q} = \mathbf{a}_{q0} \qquad \mathbf{e}_{q} \qquad \mathbf{e}_{q}$$

This leads to equations

$$M \omega_{q}^{2} \epsilon_{qq} = \sum_{1'\beta} v^{(1-1')} e^{-1q.(1-1')} \epsilon_{q\beta} \qquad \dots \dots (8)$$

or equivalently

The elements  $D_{\alpha\beta}$  of the dynamical matrix are

p = 1, 2, 3

The three solutions

$$\omega_{\mathbf{p}}(\mathbf{q})$$

(1)

1 ...

are obtained by finding roots of the determinantal equation

We therefore notice that the key to the determination of phonon frequencies  $\omega_{p}(q)$ lies in the determination of  $v^{(2)}$ , and the second order term in  $u^{(1)}$ .

We shall not dwell upon the lattice dynamical models (like Einstein, Debye, anisotropic continuum, anisotropic dispersive continuum models) which assume extremely simple form for the dispersion (11). Such models are still useful in calculating a number of physical properties involving lattice vibrations in a complicated way. We shall omit from our consideration various type of force constant models that have been adopted for different metals. It has been found that to explain experimental dispersion curves obtained mainly by neutron spectrometry, often very long range forces have to be invoked. We shall also not deal with a number of phenomenological models that have been put forth to incorporate the effects of conduction electrons (like de Launay, Fmatia, Krebs, Gilat models). These phenomenological models afe: physically unsatisfactory and are unable to explain the detailed features of dispersion curves in a consistent manner. We shall be here concerned with the first principle calculations of phonon frequencies in metals.

## BASIC THEORY:

It will be illustrative to start with Hartree theory to outline the basic approach, because most of the physics of the problem will be buried in complicated formalism and formulae if we use a more general scheme. We shall indicate modifications needed in the theory when we use Hartree-Fock or some other approximation scheme. The characteristic of the most of the fundamental theories of lattice dynamics is to express the potential as the sum of three contributionsedue to (a) Coulomb interaction between ions (b) core répulsion interaction between ions and (c) ion-electron- ion interaction. The contribution between ions, to the dynamical matrix  $\underline{D}^{(c)}$  can be evaluated by using Ewald's method. The core repulsion is usually parametrised to the Born-Mayer potential. The ion-electron-ion contribution stems from the term  $E(\underline{R})$  im (1). In harmonic approximation, we can now see that, the second order terms in ionic displacements,  $\underline{u}^{(1)}$  in the Taylor expansion of  $E(\underline{R})$  about the equilibrium configuration of ions will determine the ion-electron-ion interaction contribution to phonon frequencies.

The displacement of ions in the crystal due to lattice vibrations provides perturbation terms in the electronic Haziltonian. In the Eartree approximation the

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total electronic wave function  $\Psi(\underline{\mathbf{r}},\underline{\mathbf{R}})$  is factorized into a product of one electron wave functions  $\Psi_k(\mathbf{r},\mathbf{R})$ .  $\Psi_k(\mathbf{r},\mathbf{R})$  will satisfy a self consistent Schrodinger equation,

where  $E_k$  is the one electron energy for electron wave vector k and the one electron Hamiltonian H<sub>1</sub> is of the form

$$H_1 = -\frac{\hbar^2}{2m} - \sqrt{\frac{2}{2} + v_p}$$
 .....(14)

where  $V_{\mathbf{p}} = V_{\mathbf{b}} + V_{\mathbf{H}} = U_{\mathbf{b}}(\underline{\mathbf{r}} - \underline{\mathbf{R}}^{(1)}) + V_{\mathbf{H}}(\underline{\mathbf{r}}, \underline{\mathbf{R}})$  .....(15)

where  $U_b(\underline{r}-\underline{R}^{(1)})$  is the interaction potential due to ions and Hartree potential  $V_H$ is due to interaction with all the other electrons, which is taken equal to the potential due to charge distribution for all other electrons. The total energy E is given in terms of one electron energies by the following expression

nk is the probability that state k is occupied. We can write the perturbation expansions of the Hamiltonian, wase function and energy:

$$H_{1} = H_{1}^{(0)} + H_{1}^{(1)} + H_{1}^{(2)} + \dots$$

$$\Psi_{k} = \Psi_{k}^{(0)} + \Psi_{k}^{(1)} + \Psi_{k}^{(2)} + \dots$$

$$E = E^{(0)} + E^{(1)} + E^{(2)} + \dots$$

Here for example the first order term  $H_1^{(1)}$  is sum of two terms  $V_b^{(1)}$  due to motion of ions and  $V_H^{(1)}$  originating from the response of electrons

We can similarly write  $H_1^{(2)}$ . Use of second order perturbation theory with (16) and explicit expressions for  $V_H^{(0)}$ ,  $V_H^{(1)}$ ,  $V_H^{(2)}$ ,  $\psi_k^{(1)}$  and  $\psi_k^{(2)}$  finally yields the lattice vibrational ion-electron-ion potential energy  $E^{(2)}$ 

$$E^{(2)} = \frac{1}{2} \sum_{k,k'} \frac{n_{k} (1-n_{kl})}{E_{k} - E_{k'}} \left[ \left\langle \Psi_{k}^{(0)} \mid v_{p}^{(1)} \mid \Psi_{kl}^{(0)} \right\rangle \left\langle \Psi_{k'}^{(0)} \mid \Psi_{k}^{(1)} \right\rangle \left\langle \Psi_{k'}^{(0)} \mid \Psi_{k'}^{(0)} \right\rangle \right] + \left\langle \Psi_{k}^{(0)} \mid V_{b}^{(1)} \mid \Psi_{k'}^{(0)} \right\rangle \left\langle \Psi_{k'}^{(0)} \mid v_{p}^{(1)} \mid \Psi_{k}^{(0)} \right\rangle + \sum_{k} n_{k} \left\langle \Psi_{k}^{(0)} \mid v_{b}^{(2)} \mid \Psi_{k}^{(0)} \right\rangle \left\langle \Psi_{k'}^{(0)} \right\rangle \left\langle \Psi_{k'}^{(0)} \mid V_{p}^{(1)} \mid \Psi_{k'}^{(0)} \right\rangle + \sum_{k} n_{k} \left\langle \Psi_{k}^{(0)} \mid V_{b}^{(2)} \mid \Psi_{k'}^{(0)} \right\rangle \left\langle \Psi_{k'}^{(0)} \right\rangle \left\langle \Psi_{k'}^{(0)} \mid V_{b}^{(1)} \mid \Psi_{k'}^{(0)} \right\rangle + \sum_{k} n_{k} \left\langle \Psi_{k}^{(0)} \mid V_{b}^{(2)} \mid \Psi_{k'}^{(0)} \right\rangle \left\langle \Psi_{k'}^{(0)} \right\rangle \left\langle \Psi_{k'}^{(0)} \mid \Psi_{k'}^{(0)} \mid \Psi_{k'}^{(0)} \right\rangle + \sum_{k} n_{k'} \left\langle \Psi_{k'}^{(0)} \mid V_{b}^{(2)} \mid \Psi_{k'}^{(0)} \right\rangle \left\langle \Psi_{k'}^{(0)} \right\rangle \left\langle \Psi_{k'}^{(0)} \mid \Psi_{k'}^{(0)} \mid \Psi_{k'}^{(0)} \right\rangle + \sum_{k} n_{k'} \left\langle \Psi_{k'}^{(0)} \mid \Psi_{k'}^{(0)} \mid \Psi_{k'}^{(0)} \right\rangle \left\langle \Psi_{k'}^{(0)} \mid \Psi_{k'}^{(0)} \right\rangle + \sum_{k} n_{k'} \left\langle \Psi_{k'}^{(0)} \mid \Psi_{k'}^{(0)} \mid \Psi_{k'}^{(0)} \right\rangle \left\langle \Psi_{k'}^{(0)} \mid \Psi_{k'}^{(0)} \right\rangle \left\langle \Psi_{k'}^{(0)} \mid \Psi_{k'}^{(0)} \right\rangle + \sum_{k} n_{k'} \left\langle \Psi_{k'}^{(0)} \mid \Psi_{k'}^{(0)} \mid \Psi_{k'}^{(0)} \right\rangle \left\langle \Psi_{k'}^{(0)} \mid \Psi_{k'}^{(0)} \right\rangle + \sum_{k} n_{k'} \left\langle \Psi_{k'}^{(0)} \mid \Psi_{k'}^{(0)} \mid \Psi_{k'}^{(0)} \right\rangle \left\langle \Psi_{k'}^{(0)} \mid \Psi_{k'}^{(0)} \mid \Psi_{k'}^{(0)} \right\rangle + \sum_{k'} n_{k'} \left\langle \Psi_{k'}^{(0)} \mid \Psi_{k'}^{(0)} \mid \Psi_{k'}^{(0)} \mid \Psi_{k'}^{(0)} \right\rangle \left\langle \Psi_{k'}^{(0)} \mid \Psi_{k'}^{(0)} \mid \Psi_{k'}^{(0)} \right\rangle + \sum_{k'} n_{k'} \left\langle \Psi_{k'}^{(0)} \mid \Psi$$

where the polarization index has been dropped for the sake of simplicity. The matrix element  $\langle \Psi_{k} | (o) | V_{b}^{(1)} | \Psi_{k}^{(o)} \rangle$  can be shown to vanish unless k' = k+q+H. When  $\underline{k}' = \underline{k} + \underline{q} + \underline{H}$ 

is the electron-ion matrix element.  $\underline{M}(\underline{k},\underline{k})$  is a measure of coupling between electron and phonon systems.

Now let  $\delta v_{\rm b}$  donote perturbation due to displacement of the ion in the bare ion potential seen by the conduction electrons. This will cause a change in the electron distribution, which in turn will be responsible for a change  $\delta v_{\rm H}$  in the Hartree potential, and this will have screening effects. The total perturbation  $\delta v_{\rm p} = \delta v_{\rm b} + \delta v_{\rm H}$  is what actually seen by electrons. We thus see that  $\delta v_{\rm p}$ which determines  $\delta v_{\rm H}$  is itself determined by  $\delta v_{\rm H}$  and a self consistent treatment is necessary. Sham and Ziman<sup>(1)</sup> have shown that in the Hartree approximation the Fourier transform of  $v_{\rm p}^{(1)}({\bf r})$  is related to the Fourier transform of potential  $v_{\rm h}^{(1)}({\bf r})$ , through the relation

$$v_{p}^{(1)}(\underline{q} + \underline{H}) = \sum_{H'} \frac{v_{b}^{(1)}(\underline{q} + \underline{H}')}{\in (\underline{q} + \underline{H}, \underline{q} + \underline{H}')} \qquad \dots \dots (22)$$

We shall look upon  $\epsilon_{(q+H, q+H')}$  as a matrix whose rows and columns are labelled by reciprocal lattice vectors. The dielectric matrix is a measure of reduction in strength of  $v_b^{(1)}(q+H')$  and is given by

$$\begin{split} & \in (\underline{q}+\underline{H}, \underline{q}+\underline{H}') = \delta_{H,H'} - \frac{4 \pi e^2}{N(q+H)^2} \sum_{k,H''} \frac{n_k - n_k + q + H''}{E_k - E_{k+q+H''}} \dots (23)^{(23)} \\ & \left\langle \Psi_k^{(0)} \right|_{e} - i(\underline{q}+\underline{H}) \cdot \underline{r} \left| \Psi_{k+q+H'}^{(0)} \right\rangle \left\langle \Psi_{k+q+H''}^{(0)} \right|_{e} i(\underline{q}+\underline{H}') \cdot \underline{r} \right| \Psi_k^{(0)} \right\rangle \end{aligned}$$

The real difficulty lies in inverting the matrix  $\in$  as needed by (22). It is here that the simplicity of the free electron model is manifest, where  $\in$  collapses into the well known scalar dielect ric function

$$E_{HPA}(p) = 1 + \frac{4 \pi e^2}{p^2} S_0(p) \dots (24)$$

where

$$B_{0}(p) = \frac{32N_{I}}{2E_{f}} \left[ \frac{1}{2} + \left( \frac{4k_{f}^{2} - p^{2}}{8k_{f} p} \right) \log \left| \frac{2k_{f} + p}{2k_{f} - p} \right| \right]$$

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Z is the valence of the metal,  $N_I$  number of ions per unit volume,  $E_f$  the Fermi energy and  $k_f$  the Fermi radius. The dielectric screening due to electrons softens the ionic binding (hence the frequencies). This screening occursby a redistribution of electrons. In k space, this will mean a virtual scattering from state <u>k</u> to <u>k</u> + <u>p</u>. If <u>|p</u>|is less than  $2k_f$ , we see that the electrons on the Fermi surface are scattered to intermediate states of the same energy and if <u>|p</u>| is greater than  $2k_f$  scttering occurs only to states of different energy. For p  $\geq 2k_f$  for virtual scattering the minimum excitation energy is proportional  $(p-k_f)^2-k_f^2 = p(p-2k_f)$ . Thus there is a rapid decrease in the ability of conduction electrons to screen  $V_b(p)$  as p increases through the value  $2k_f$ . Therefore phonon frequencies should show an abrupt anomalous increase at  $p = 2k_f$ . This is Kohn effect<sup>(2)</sup>. For virtual scattering

$$= |\underline{q}| = 2k_{\underline{f}}$$

and for virtual umklapp scattering

$$p = q + H = 2k_p$$

The Kohn anomaly is evident as logarithmic singularity at  $p = 2k_f$  in the dielectric function (24).

We have now observed that a throry of phonons in metals involves two central problems: (1) The investigation of the electron response function and (2) the determination of the electron ion matrix element M(k',k).

# DIELECTRIC CONSTANT:

Almost all investigations of phonons in metals use free electon dielectric response function because of enormous complexities that go with form (23). Various approximate forms are in vogue in literature. In  $\xi_{RPA}$  given by (24) the role of exchange and correlation is neglected. There is a wide variation of openion on the proper way to include exchange and correlation effects. A major difficulty in Hartree-Fock theory is that in there the exchange potential operator is a functional of the wave function being sought. Slater's approximation replaces the exchange potential in the Hartree-Fock theory by a local one which is an averaged exchange potential. Toya<sup>(3)</sup> proceeded to calculate the electronic screening effects using second order perturbation theory, Slater's approximated exchange term and free electron approximation. He obtained

$$\mathcal{E}_{T}(p) = 1 + \frac{4\pi e^{2}}{p^{2}} \left(1 + \frac{5}{16} \frac{p^{2}}{k_{f}^{2}}\right) \frac{D}{D_{0}} S_{0}(p) \text{ for } p^{2} \left\langle \frac{16}{5} k_{f}^{2} \cdots (25a) \right\rangle$$

$$= 1 \qquad \text{for } p^{2} \left\langle \frac{16}{5} k_{f}^{2} \cdots (25b) \right\rangle$$

The effect of exchange is incorporated in the second term. Toya assumed f(p) = 1for  $p^2 > \frac{16}{5} k_f^2$  because (25a) suggests  $\mathcal{E}(p) < 1$  in that region which is a rather unphysical result. Toya incorporated correlation effects phenomenologically by multiplying S by D/D in (25a), where D is the density of states at the Fermi surface with exchange and correlation effects and  $D_0$  its value in Hartree approximation.

Kohn and Sham<sup>(4)</sup> have recently discussed an approximate form of exchange potential which corresponds to averaging the Hartree-Fock exchange potential corresponding to electron wave vector  $k_{p}$ . In Slater approximation the averaging is over all k. Kohn and Sham obtained an exchange potential  $\frac{2}{3}$  as great as of Slater. With Kohn and Sham exchange potential we obtain:

In the case of an uniform electron gas the inclusion of correlation leads to screened exchange interaction. A description of exchange potential where screened interaction apperas was given by Robinson et al $^{(5)}$ . To calculate the exchange potential a la Slater, Robinson et al in effect replaced the Coulomb interaction  $\frac{e^2}{r}$  by  $\frac{e^2}{r}$  e<sup>-k</sup>s<sup>r</sup> where  $k_s$  is the screening factor. The dielectric constant in this case is

 $\alpha = k_{g}/k_{g}$  and  $R(\alpha) = 1 - \frac{4}{3} \propto \tan^{-1}(\frac{2}{\alpha}) + \frac{1}{2} \propto^{2} \ln \left[1 + 4 \propto^{-2}\right]$  $-\frac{1}{6} \propto^{2} \left[ 1 - \frac{1}{4} \propto^{2} \ln (1 + 4 \propto^{-2}) \right] \qquad \dots (28)$ 

With the development of many body theory, the role of exchange and correlation in the responses of a free electron gas has become better understood. Hubbard<sup>(6)</sup> has improved upon  $\in_{\mathrm{RP}_{\Delta}}$  by including higher order diagrams and suggested that

$$\epsilon_{\rm H} = 1 + \frac{4\pi e^2}{p^2} = s_{\rm H}(p)$$
 .....(29)

where

$$S_{\rm H}(p) = \frac{S_{\rm o}(p)}{1 - 2 \pi e^2 S_{\rm o}(p) / (p^2 + k_{\rm f}^2 + k_{\rm g}^2)}$$

Geldart and Vosko<sup>(7)</sup> have suggested the following modifications of (30)

$$\hat{E}_{GV}(p) = 1 + \frac{4\pi e^2}{p^2} S_{GV}(p)$$
  

$$S_{GV}(p) = \frac{S_o(p)}{1 - 2\pi e^2 S_o(p)/(p^2 + \xi k_f^2)}$$
.....(30)

Vosko et al determined 🖡 from the compressibility of an interacting gas.

# THE ELECTRON-ION MATRIX ELEMENT:

It is not possible to survey here the numerous calculations of electron-ion matrix element  $\underline{M}(\underline{k}',\underline{k})$ . We shall content ourselves by outlining the general approach and by baming a few prominent methods. We adopt rigid ion approximation i.e. we assume that the potential field around each ion is rigidly attached to it and moves with it. We can thus dissect the effective potential  $V_p$  (of Eq. 15) into a sum of a tomic potentials:

$$V_{p} = \sum_{1} U_{p} (\underline{r} - \underline{R}^{(1)})$$
 .....(31)

We can therefore relate  $U_{\rm b} = U_{\rm p} - U_{\rm H}$ .....(32)  $\mathbf{U}_{\!_{\mathrm{H}}}$  is the potential due to electronic charge due to electrons. We can therefore write

$$\underline{M} (\underline{k}', \underline{k}) = \underline{M}_{p} (\underline{k}', \underline{k}) - \underline{M}_{H} (\underline{k}', \underline{k}) \qquad \dots (33)$$

$$\underline{M}_{p} (\underline{k}', \underline{k}) = \int d^{3}\mathbf{r} \Psi_{k}^{*} (\underline{\mathbf{r}}) \nabla U_{p} \Psi_{k} (\mathbf{r}) \dots (34)$$

where

÷

$$\mathbf{i} \in \underline{M}_{\mathrm{H}} (\underline{k}', \underline{k}) = \underbrace{\underline{\ell}} (\underline{k}' \underline{k}) \quad \frac{4\pi 2e^2}{V_{\mathrm{o}} p^2} \quad \mathbf{G} (|\underline{k}' \underline{k}| \mathbf{r}_{\mathrm{g}}) \quad \dots \dots (35)$$

Where  $G(x) = 3 (\sin x - x \cos x)/x^3$ ,  $V_0$  is the volume of the unit cell. In order to simplify the claculation of  $\underline{M}_p(\underline{k}',\underline{k})$  we assume the  $U_p(\underline{r}-\underline{R}^{(1)})$  vanishes outside the  $1^{\text{th}}$  cell. It can be shown that
In the above we have written  $\Psi_k$  in the Bloch function form  $\Psi_k(\underline{r}) = e^{i\mathbf{k}\cdot\mathbf{r}} \mathbf{u}_k(\mathbf{r})$ 

BARDEENS FORM:

Bardeen<sup>(8)</sup> adopted Wigner-Seitz approximation to evaluate (36) and he took  $\mathcal{W}_{k} = \mathcal{W}_{0}(\mathbf{r})$ . The matrix element obtained by him

$$\mathbf{i} \quad \underbrace{\mathbf{e}} \cdot \underline{\mathbf{M}}(\mathbf{p}) = \underbrace{\mathbf{e}} \cdot \underline{\mathbf{p}} \left[ \frac{4 \pi \overline{\mathbf{z}} e^2}{\mathbf{V}_0 p^2} + (\mathbf{U}_p(\mathbf{r}_s) - \mathbf{E}_0) \right] \quad \mathbf{G}(\mathbf{p}\mathbf{r}_s) \quad \dots \dots (37)$$

has been persistently used in many calculations.

#### OPW AND APW FORMS:

An expression for  $M_p(k',k)$  can be obtained if one expresses  $\Psi_k$  in terms of orthogonalized plane waves  $(OPW's)^{(1)}$ . Golibersuch<sup>(9)</sup> has also obtained a form for  $\underline{M}_p(\underline{k'k})$  on the basis of augmented plane wave(APW) representation for valence wave functions. The latter result may be particularly useful in connection with calculations for transition metals and other complicated solids.

I shall not talk about the OPW based pseudo potential formalism<sup>(10)</sup> because a paper in the following session will exclusively deal with this approach.

Recently Taylor, Moore and Vosko<sup>(12)</sup> have made a reliable calculation of electron-ion matrix element by employing accurate variational wave functions for conduction electrons.

Once  $\underline{M}(\underline{k};\underline{k})$  and  $\underline{\xi}(p)$  are obtained one the basis of models outlined above, it is possible to obtain  $\underline{E}^{(2)}$ . This will enable us to calculate the electronic contribution to phonon frequencies. Claculations of phonon frequencies have been made for a number of simple metals. Table I shows the salient features of a few representative calculations.

It will be appropriate to end the talk by listing some challenging problems of the day. The problem of lattice dynamics of transition metals is interesting and characteristically difficult. For heavy metals spin-orbit effects may have to be included. There is no fundamental theory of alloys. The whole field of anharmonicities in metals lies unexplored.

#### ACKNOWLEDGEMENTS

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#### TABLE I

|                              | ·                           |  |
|------------------------------|-----------------------------|--|
| Metal                        | Reference                   | Features   |
| Alkali metals<br>(mainly Na) | Toya <sup>(2)</sup>         | M(Bardeen) with $\epsilon_{\mathrm{T}}$  |
|                              | Vosko et al <sup>(13)</sup> | M(one OPW) with $\epsilon_{\text{RPA}} \in \epsilon_{\text{H}}$<br>M(Bardeen) with $\epsilon_{\text{RPA}}$ |
|                              | Sham(14)                    | Pseudopotential (OPW based, local and non-local) with ${m arepsilon}_{ m H}$                               |
| Polyvalent metals<br>Al;Pb   | Vosko et al <sup>(13)</sup> | M(one OPW) with $\epsilon_{\rm GV}$<br>M(Bardeen)with $\epsilon_{\rm RPA}$                                 |
|                              | Harrison <sup>(9)</sup>     | Pseudopotential (local) with $\epsilon_{\rm KPA}$  |

### DISCUSSION:

C.S. Warke : You have not included, in the calculation of  $E^{(2)}$ , the effect of the Fermi distortion? i.e., expansion of  $n_{1}(R)$ ?

S.K. Joshi : No, I have not included this Fermi distortion effect. Such effects will be secondary in view of the free electron dielectric function used in most of the calculations. The first attempt should be to include a more realistic dielectric matrix. The improvement of the type mentioned by you may only then be corrections (?) to the dielectric matrix.

# K.S. Chandrasekaran : Is there any evidence, experimental or otherwise about the effective R.M.S. vibrations of the 'Core' electrons and the 'valence' electrons being different?

This would be of interest in view of expected x-ray diffraction effects in the case of noncentrosymmetric structures of the elements (proposed in my forthcoming publication in the Ewald-Festschrift issue of Acta Crystallographica).

S.K. Joshi :

The core electrons should follow the nuclear vibration and there is no question of valence electrons having effective RMS vibration. The latter only respond to core motion due to lattice vibrations.

I do not see any way of correlating the electron response of of conduction to your experimental observations (unpublished?).

C.K. Majumdar :

Hubbard has recently reported a new dislectric function, due to Singwi. Do you know whether it is in analytic form or in numerical form?

S.K. Joshi : No. I did not have access to Singwi's work

#### RADIATION DAMAGE - SOME NEW TRENDS

#### A.V. Patankar, Tata Institute of Fundamental Reseach, Bombay -5, India.

#### INTRODUCTION :

The subject of radiation damage could hardly be called a new subject. With the advent of nuclear reactor engineering as a major technological activity of the present age, it is not surprising that it has been established as a main area of research in the last fifteen years. Almst coincidental with the beginning of reactor studies has been the recognition by solid state physicists of the important role played by the lattice defects in determining so many interesting properties of a solid. It would be appropriate to say that the interest of a physicist in this subject stems from the variety of defects and their combinations which can be induced by energetic radiation. The radiation in this case is used to manipulate solids in ways which are a class of their own. The basic approach in these studies has been to gather and analyse information on the radiation induced defects obtained from the studies of changes in one or more properties of a solid. The information about defects in the dynamic state of irradiation is generally lacking; the notable exceptions being the simulation studies of collision sequences of stoms in crystals made by Vineyard<sup>(1)</sup> and the experimental work of Thompson<sup>(2)</sup> and his collaborators in Harwell and later on in the University of Sussex on the focussed channeling of atoms in metals and ionic crystals. The major part of the investigation of radiation damage in solids has been confined to structure sensitive propertiesof solids since the damage is essentially caused in the crystalline lattice of a solid in the process of radiation.

The subject of colour centres, a class of radiation damage in ionic solids, is chosen for the following reasons. Firstly, their study is representative of the phenomenon outlined earlier and secondly, their most attractive feature is the utilization of variety of techniques and their combinations to extract the information of great importance. Some of these techniques were even treated as out of fashion and became unwelcome to physicists for some time.

A special feature of radiation damage in ionic crystaltis that lattice defects can be created in these materials by ionization only, without the need for collisions. Since most of the ionic crystals have a large window in the visible spectrum the first natural choice for the study is their optical properties. In fact, one of the most striking effects of the damage is that the materials often acquire a pronounced colour. NaCl, for example, turns brown whereas KCl become violet blue in colour. This is due to the creation of point defects by trapping electrons and holes in primary defects such as vacancy or a group of vacancies. These defects are therefore called colour centres. Before dealing with the details of the new experimental techniques recently used to study the centres, it would be proper to briefly outline basic concepts that have evolved through the past studies. This could best be done by choosing some of the simple centres in the alkali halides, since the conceptional contributions in this field stem from researches on this class of substances. Similar studies are now extended to materials belonging to the halides of the alkaline earth metals and their oxides.

The special aspects of the studies have been 1) to propose a model for the centre in question on the basis of the experimental data, (2) to construct a theoretical basis to explain the experimental data and the proposed model, (3) to construct a scheme or schemes for production of these defects on the basis of the model and the experimental evidence, (4) to study effects of the defects on the bulk properties of the material, e.g., density, hardness, etc. In this paper the first three aspects of the studies will only be considered. It should be mentioned here that the work covering the last aspect has also been done by using imaginative techniques.

#### 2. F - CENTRE :

The centre, called F-centre, is primarily responsible for the colour of irradiated alkali halides and gives a bell shaped optical absorption bands known as F-band. There is a definite relationship between the peaks of their absorption spectra and the lattice parameter of the crystals. This relation is known as Ivey's relation. Stockmann<sup>(3)</sup> made earlier attempts to explain the relation by assuming simple hydrogen atom model for an electron trapped in a potential box. The energy lovels are then given by

$$E_{k} = \frac{1}{8} \frac{b^{2} k^{2}}{m^{*} a^{2}}$$

where k is a quantum number, d, the lattice distance and m is the effective mass of the electron. The frequency of the optical transition between the ground state and the first excited state is given by

$$\gamma = \frac{3}{8} \frac{h}{m^* d^2}$$

This gives the following simple relation

 $\mathcal{V}d^2 = constant$ 

Although the theory agreed to the nearest value of the exponent 1.84 instead of 2, it says very little about the nature of the defect. De Boer<sup>(4)</sup> provided the necessary touches to this rather primitive model and brought in a definitive concept of defect. He proposed that the electron is trapped at the potential well produced by the polarization at the vacant site of a negative ion due to the charges of the positive neighbouring ions. (Fig. 1 a). This model has been the basis of the experimental and theoretical work so far done on the F-centre. We shall later see that it has been also used as a building block in order to construct models for the other centres in the alkali halides.

The optical absorption in the F-band shows a few remarkable properties. Firstly, as stated before, the peaks are dependent upon the lattice parameter. Secondly, the lines are Gaussian in shape and finally, their half-widths follow the relation

 $\left(\begin{array}{c} H(T) \\ H(0) \end{array}\right)^2 = \operatorname{ctgh} \frac{\hbar \omega_a}{kT}$ 

where H(T) is the half-width of the line at temperature T, H(O) is that at absolute zero, h and k have their usual meanings. ( $\omega_a$  is a characteristic frequency of a vibrational mode for which the neighbouring positive ions move in and out from the vacancy. This type for mode, called 'breathing model; is more effective since the motion of ions at right angles to the line joining an ion to the vacancy will have much less influence upon the energy than will the motion parallel to the line. The parameter that measures the displacement of ions from their equilibrium positions is called a 'configuration coordinate'. A plot of the potential energy of the ground state of a centre is called 'configuration coordinate diagram' and is shown in Fig. 2.

When the centre is excited by the absorption of a photon, the average electronic distribution is changed and after cufficient time the ions move to new equilibrium positions. This is given by the upper curve in the configuration coordinate diagram. It can be seen that the time for the transition is short, the ions are unable to move, the transition would take place with no change in the configuration coordinate of the ions. The photon of energy  $E_{\rm B}$ - $E_{\rm A}$  will therefore, be absorbed, but the excited centre loses energy till it comes to C on the diagram through lattice vibrations and then undergoes a transition which would correspond to luminescence. Since the luminescence involves lattice vibrations the emission spectra will be gaussian but of a half width determined by the characteristic breathing mode of the excited state. These predictions have been experimentally verified  $^{(5)}$ . The temperature dependence of the luminescence line is found to be similar to that of the absorption line as shown in Fig. 3.

The de Boer model, although it gives the necessary insight to the defect, really implies nothing about the actual electron distribution in the vicinity of the trapping vacant site. The technique of electron spin resonance is an ideal technique to answer this question. The magnetic hyperfine interaction of the unpaired trapped electron with the neighbouring nuclei of spin other than zero should give hyperfine structure to the resonance spectrum. The hyperfine constant which is given by the separation between the hyperfine components is given by the Fermi contact term  $a_{\rm H} = \frac{2}{3} \frac{g_{\rm e}}{2} \frac{\mu_{\rm B}}{2} \frac{g_{\rm N}}{2} \frac{\mu_{\rm N}}{2} \frac{\mu_{\rm N}}{2}$ 













PICK'S MODELS FOR ELECTRON TRAPPED CENTRES









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where  $\psi_N(0)$  is the electron density on nucleus N,  $g_e$  and  $g_N$  are the gyromagnetic ratics of electron and nucleus in question respectively and  $M_B$  and  $M_N$  are Bohr and nuclear magnetons respectively. It should be noted that  $a_H$  can be anisotropic in which case it gives information about the p character of the trapped electron<sup>(6)</sup>.

However, the experimental results on some alkali halides, e.g. KC1, the resonance lines are gaussian in shape and show no hyperfine structure whatsoever. This is due to the fact that the nuclei of high spin quantum number can give rise to number of lines which superimpose to give a gaussian line. In the case of low spin number neighbouring nuclei, hyperfine structure can be seen, e.g. LiF, RbCl. The cases for which no hyperfine structure is discernable, Feher<sup>(7, 8)</sup> has introduced an ingenious technique called ENDOR (Electron Nuclear Double Resonance) in which the electron spin is saturated with high microwave power so that their population in the magnetic levels are equalized. It is then disturbed by changing the spins of the nuclei with which the electron interacts. The nuclear spin transitions are induced by subjecting the nuclei to an R.F. field of frequency matching its Larmor frequency. These studies have given complete details about the distribution of the electron density in the vicinity of the vacancy. Fig. 4 shows the electron density as a function of lattice distance from the vacancy as measured by Seidel<sup>(9, 10)</sup>. It will be seen that about 95% of the density is ing the first shell and about 1% is in the next shell. Thus the model of de Boer for the F-centre has withstood some of the most demanding experimental tests.

The ESR analysis gives information about the ground state only. The methods outlined so far give very little insight to the nature of the excited state of the **F**-centre. Dexter<sup>(11)</sup> first pointed out that Faraday rotation would be fruitful method to study the excited p state of the F-centre. Luty and Mort<sup>(12)</sup> have recently done these experiments on the F-centre of KCl and a few other alkali halides. The experiment consists of observing rotation of the plane of polarisation of a plane polarized light wave upon traversing through the crystal in the direction of an applied magneticfield. The experimentally observed rotation is partly due to the background dispersion produced by the first exciton absorption and the remaining part is due to the F-centre. Theyhave succeeded in separating the F-centre contribution as shown in in Fig. 5.

The Faraday angle  $\theta$  is given in terms of the indices of refraction by the following expression

$$\theta = \frac{\omega}{2c} (n_r - n_1)1$$

where  $n_r$  and  $n_l$  are the indices of refraction for right and left circularly polarized components of light of angular frequency (1), 1 is the length of optical path in the crystal. In treating theoretically the experimental observations, Luty et al<sup>(13)</sup> assume simple alkali atom model and have used the gaussian shape of the F-band and



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Kramer-Kroning relation to calculate the difference in the two refractive indices. After applying proper population weight factors for the magnetic energy levels of the s state of the centre, they have been able to show that the maximum Faraday rotation for the F-centre is given by

$$\theta_{\max} = \left(\frac{\ln 2}{\pi}\right)^{\frac{1}{2}} \frac{\alpha_{\max}}{\frac{H_1}{2}} \cdot \frac{\beta}{\beta} \left(\frac{2m}{m} - \frac{\beta_1 \Delta}{kT}\right)$$

where

1

 $\alpha_{max}$  = the maximum absorption constant for the F-band,

- = optical path length in the sample,
- $\beta$  = Bohr magneton,

B = external magnetic field,

= effective mass of the electron in the excited state,

 $g_1 =$  Lande factor for the ground state,

 $\Lambda$  = spin orbit coupling constant of the excited state

Since  $\theta_{max}$  depends upon the population difference between right and left circularly polarized transitions between various magnetic levels of p and s states, the Faraday rotation is more pronounced at low temperature. The exact wavefunction for the excited state has also been worked out by Smith<sup>(14)</sup>. An advanced theoretical treatment for the effect is given by Slichter, Henry and Schnatterly<sup>(15)</sup>.

Another interesting espect of the work of Luty is the measurements of spin lattice relaxation time  $T_1$  of the ground state. Since the effect depends on the population difference between the magnetic levels of the ground the exponential rise of population on decreasing the temperature of the crystal would directly give  $T_1$ . The dependence of  $T_1$  on the magnetic field can be similarly studied.

3. PRODUCTION OF F-GENTRE :

The de Boer model, of course, brings in another basic issue to the forefront, namely, the mechanisms of production of the F-centres. The F-band colouration is known to increase rapidly in the initial stage of irradiation, however, it is found to be relatively slow in the later stages of irradiation. This suggests that in case of pure materials, the colouration proceeds through two distant stages.

The earlier stage is considered to be due to filling of the existing vacancies by electrons and therefore depends on the history of the crystal. For example, for a crystal which is preheated and quenched the rate of colouration is much higher than for an annealed one. This stage is faster for crystals containing divalent impurities because the presence of impurities helps to increase the concentration of vacancies.

The slow stage of colouration is due to the radiation induced vacancies. This stage is therefore of great interest to solid state physicists. The earlier attempts to explain the vacancy generation is due to Varley<sup>(16,17)</sup> and Seitz<sup>(18,19)</sup>. Varley suggested a mechanism by which a negative ion is further ionized to produce a positively charged halide ion. If the life time of that state is longer than the period of lattice vibration then the coloumb interaction between its positive charge and the neighbouring positive ions is strong enough to dislodge the halogen ion, thus producing a vacancy. The ion however drifts around in the lattice as an interstitial. The mechanism proposed by Seitz requires deposition of energy at a dislocation in the form of an exciton. This energy is assumed to be adequate to ionize an atom which would then move across the slip plane leaving a vacancy behind. The decay of second exciton in the immediate vicinity of the vacancy would provide enough energy for an ion on a normal site to slip in the site left by halogen atom. Thus a vacancy can be generated from a dislocation. The halogen atom subsequently captures an electron and occupies a normal halogen site along the dislocation line, thereby producing a dislocation climb. Dexter<sup>(20)</sup>, on the contrary argues that the Varley mechanism is not feasible because the holes that are formed on the hologon atom due to ionization would tend to separate unless the ionization takes place as from the innermost shells. He has calculated that it would take only 10<sup>-15</sup> seconds for the holes to move away in an initial field of 10<sup>8</sup> v/cm., the mobility of the holes being 1cm<sup>2</sup>/volt sec. In the case of inner shell ionization, the holes will be 'heavy' with smaller mobility and the period required for separation is comparable to the period of the lattice vibration. However, the experiments done by Sharma et al (21,22) support Varley's argument. Their experiments showed that the colourability of the alkali halides is high with X-rays having wavelengths shorter than the K ionization of chlorine atom. It, therefore, appears as Varley points out that the life time of the holes is not as short as Dexter has suggested. The main problem however is the mechanism of converting the ionization energy into kinetic energy of ions necessary to create a vacancy. The only reasonable explanation so far available is due to Howard (23) who has proposed that de-excitation collision between positively charged halogen atom end a negative ion would give a transfer of energy. This processewill take a period shorter than a lattice vibration and convert the electrostatic energy into kinetic energy. The collision which now takes place between the two atoms in 110 direction will initiate focussed channeling in that direction. Thompson has shown that 110 is a suitable direction for such displacements. These mechanisms do not take into consideration the sensitivity of impure crystals to colouration or its dependence on temperature (24). It is definitely useless for explaining intense colouration of alkali halides with ultra-violet light as found by Pooley<sup>(25,26)</sup>. Pooley has suggested electron-hole recombination model which can explain the influence of these parameters on colouration. The essential ingradient of the process is a formation of an electron-hole pair by the capture of electron by a hole at a  $V_{\rm b}$  centre which is essentially a hole self trapped by a large Jahn-Teller .

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distortion of the lattice (27,28,29). This pair comes to the ground state through radiationless transitions from its excitonic states, giving the energy to two halogen ions of the  $V_k$  centre. This energy is converted into kinetic energy since the two chlorine-ions are too close at the time of neutralization of the charge of the hole by the electron. This results in their momentum vectors lying along 110 direction. The energy need not be equally shared by both the ions owing to the interaction with the rest of the lattice. A more energetic ion then starts the replacement sequence. The role of impurities in this mechanism is to form recombination centres and thus reduce perfect lattice non-radiative recombination rate and, in turn increase the rate of production of F-centres. The calculated transition probabilities give good agreement with the experimental growth rates of F-centres for a number of alkali halides. Since the non radiative recombination rate is temperature dependent, the mechanism also explains the colouration rate dependence on the temperature of the crystal.

#### 4. AGGREGATE CENTRES:

Another area of interest in this branch of radiation damage is the study of aggregate centres. A single crystal of KCl when irradiated with X-rays at room temperature gives rise to number of absorption bands which are designated a M, N, N, R, R, hands. These bands can also be formed by bleaching F-band at room temperature. Since their growth is at the expense of the F-band, it was concluded that they are electron trapred centres. While the models were suggested and argued, certain interesting experimental data was emerging. Wallis and Wallis<sup>(30)</sup> showed that R, and R<sub>2</sub> bands are due to the same centre. Their experiment indicated that the ratio of R1 tp R2 absorption remains constant over a wide range of absorption intensities. It was also shown that  $N_1$  and  $N_2$  bands are also due to the same centre, now known as N centre. After sifting through the experimental evidence of Van Doorn and Haven<sup>(31,32)</sup>, Compton, Click and others (33, 34), Fick has finally given the most convincing models for these aggre-Fate centres (Fig.1, b.c.d.e). We will therefore consider some recent work on them since the time Fick's models have been accepted. The major efforts in these centres have gone in confirming Fick's models and their symmetries by using uniaxial stress and polarized light for measurements. The technique of ESR had a good measure of success in this area.

#### M-CENTRE:

This centre is now established as a centre formed by aggregation of two F-centres. It has axial symmetry along 110 direction. Van Doorn and Haven have studied the kinetics of formation of the M-centre after bleaching the F-centres in F-band. They found that the M-centre concentration is proportional to the square of the concentration of the F-centre. This second order kinetic rate indicates that two F-centres are required to form a M-centre. They also studied the dichroic behaviour of the centre and have confirmed its 110 symmetry. An indirect evidence for the two electron configuration of the centre is given by the absence of ESR absorption for the ground state of the centre. The final confirmation of this view comes from the ESR studies of the M-centre in its triplet state done by Seidel<sup>(35)</sup>. The M-centre was excited to its triplet state by irrediating the crystal with light of appropriate triplet transition. The lifetime of the state is long enough at low temperature to permit simultaneous ESR observations. He has shown that the triplet state has spin 1 and its g-value is 1.998. Seidel<sup>(36)</sup> has also made extensive studies of the triplet state using ENDOR and has measured the spin densities on the neighbouring nuclei.

#### R. AND N CENTRES

R-centre, according to Fick, consists of three F-centres lying in 111 planes. The centre, therefore, will have different optical transition moments in different directions, giving two distinctly separate bunds which are experimentally known as  $R_1$ and  $R_2$  bands.

Pick has extended the idea of aggregation to construct a model for N-centres. The N-centre according to him, will consist of four F-centres. He points out that for such an aggregation the cubic structure of the crystal can permit two models as shown in the Fig. 1,d,e. These would again give rise to two slightly different transitions experimentally known as N<sub>1</sub> and N<sub>2</sub> bands.

Krupka and Silebee (37) have made ESR measurements on the higher excited paramagnetic states of the R-centre and have confirmed that it consists of three electrons aggregate. Seidel (38) has again made its detailed ENDOR studies and measured the electron densities on the neighbouring nuclei.

An interesting outcome of the Pick models for the aggregate centres is that all of them have at least one optical transition which coincides with the F-band, The presence of such 'hidden' transitions was suspected since the experiments of Van Doorn and Haven<sup>(31)</sup> on the dichroic behaviour of the M-centre.

Throughout the studies we have been dealing so far, with broad and interesting absorption lines due to various centres. However, it was observed by Fitchen<sup>(39)</sup> and Pierce<sup>(40)</sup> that at low temperature some of the bands show a fine structure at the long wave length side of the band with roughly equally spaced broad lines towards the shorter wave length. This is an intermediate case of broad bands seen in solids and sharplines observed in atomic spectra. In this case the coupling between the electronic and vibrational states is weak enough to allow the purely electronic transitions to take place with relatively high probability. Table I shows the width of the sharp lines, also known as 'zero-phonon' line, observed in the alkali halides. Their existence has prompted some of the interesting experiments which have been done to find the symmetries of the aggregate centres. Kaplyanskii  $^{(41,42,43)}$  and Runciman and Huges  $^{(44)}$  have studied effects of uniaxial stress on the zero phonon line of R and N centres in IdF. They have observed that the line splits further with splittings depending upon the oriental and electronic degeneracy of the centre. The symmetries

of R and N centres are found to conform with the Pick's models for the centres. Highes has done similar experiments on N centre in NaCl and has shown the validity of the Pick's model.

#### CONCLUSION:

We have seen that in spite of the absence of accurate knowledge about the nature of forces involving the defects, an appreciable amount of information about the nature of radiation damage has been obtained through ingenious variations in the experimental techniques. It appears that this interplay of techniques is going to remain a modus vivendi in research on defects in solids for some time to come.

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## TABLE I

|      | Band Position | Zero Fhonom<br>Position | Halfwidth |
|------|---------------|-------------------------|-----------|
|      | 3785 A        | 3907 <b>A</b>           | 0.0024 eV |
| Naf  | 4330          | 4475                    | 0.0037    |
| NaC1 | 6025          | 6321                    | 0.0015    |
| RC1  | 7310          | 7417                    | 0.0009    |
| KBr  | 8000          | 8163                    | 0.0013    |

Zero Phonon Lines of R2 Bands in Alkali Halides at 4.2°K

DISCUSSION:

E.V.R. Sastry : What is the approximate extent of the splitting of zerophonon lines under stress?

A.V. Patankar : The work of Runciman and Hughes shows that the splitting is of about 5 Å to 10 Å for reasonable values of stress.

S.B. Karmohapatro :

You referred to the work of Thompson regarding the colour centre, which is pushed in the 110 axis by focussed collision? Will you clarify this point?

A.V. Patankar : This is due to Thompson.

A.S. Chakravarty :

In your Coth  $\frac{-\frac{1}{kT}}{kT}$  expression, I do not see any reason why only the breathing mode will contribute. I think the other vibrational modes will also contribute. I want your comments on this point.

A.V. Patankar :

I agree with you on this point. There would be contributions from the other modes. However, the effective mode of vibration is the one in which the motion is in the line joining the ion to the vacancy. Any motion perpendicular to this line will be less effective. The breathing mode in which all the six positive ions move in phase will therefore be the most effect tive.one and its contribution will be the one that would mainly decide the relation you have quoted.

#### MOLECULAR MOTIONS IN LIQUIDS

#### B.A. Dasannacharya Bhabha Atomic Research Centre, Trombay, Bombay-74.

The study of molecular motions in liquids is a subject in which interest has existed for several years and many different experimental techniques have been used to study these. For example, absorption as well as scattering of electromagnetic radiation over a large range of wavelengths has been in use for a long time. Dielectric and ultrasonic measurements and resonance experiments of various kinds have also given information on molecular dynamics. A comparatively recent technique, which has yielded interesting information, is that of neutron scattering. The results of the various measurements performed using different techniques have remained largely uncorrelated. Attempts towards correlating these have been made during recent years and it has been shown that this can be achieved elegantly if one approaches the analysis of these experiments from the point of view of correlation functions<sup>(1)</sup>. Using this approach, for example, it has been possible to correlate the experimental data from infrared, Raman, spin-lattice relaxation and (neutron measurements (2-5) - though only in very simple cases like CH4, CD4, CO, N2 etc. The situation is more complicated when analysing information from more complex molecules. Only qualitative comparisons based on models of molecular motion can be made in these cases.

A number of studies exist of neutron scattering (6,7), as well as of other techniques. Instead of reviewing the whole situation, we will take a couple of **examples** and see to what extent the relation between different techniques has been established and what information has been gained from these measurements with special emphasis on neutron measurements.

Let us start by looking at the scattering of cold neutrons from hydrogeneous substances where scattering is mostly due to protons and therefore incoherent. As is well known the motions of a molecule can be considered as made up of internal vibrations, rotations and the translations of the centre of mass. When using cold neutrons (specially at low temperatures), the vibrations, which involve comparatively large energies, are hardly ever excited and this part of the scattering need not be considered for the present purposes. The remaining part of the differential cross section for incoherent scattering per proton can be expressed as (8)

$$\frac{d^2\sigma}{d\Omega d\omega} = \frac{a^2}{2\pi} \cdot \frac{k}{k_0} \int dt \ e^{-i\omega t} \left\langle \exp\left[i\underline{q}\cdot\underline{r}(t)\right] \exp\left[-i\underline{q}\cdot\underline{r}(0)\right] \right\rangle \quad \dots \dots (1)$$

where the brackets represent an equilibrium statistical average and r's have to be interpreted in the Heisenberg sense. 'a' represents the incoherent scattering amplitude,  $k_0$  k and Q stand for the initial and final wave-vectors of the neutron and

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wave-vector transfer respectively and the denotes the energy change in the scattering. This form of writing the cross-section emphasises the fact that the measured intensity is the Fourier transform in time of a particular correlation function denoted by  $\langle \ldots \rangle$  in Eq. (1). This should be contrasted with the conventional way of writing the cross-section as a transition between an initial and a final level. The conventional form is not always the most convenient one. for one may come across a situation where a number of transitions lie in overlapping regions energy making it impossible for one to assign proper levels. Such circumstances almost always arise in the case of liquids and dense gases. It was first pointed out by Van Hove<sup>(9)</sup> in connection with neutron scattering that for these systems the form given by Eq. (1) is indeed the more convenient and useful one. This essentially changes the discussion from a domain of frequency to that of time. As a consequence, it has the additional advantage that in the case of systems approaching classical behaviour one can interpret the correlation functions conveniently in terms of time development of the molecular motions. Since Van Hove was dealing mainly with mono-atomic liquids his emphasis was on translational motions. The same facts were emphasised again by Gordon in connection with the theory of infrared absorption and Raman scattering applied to the study of moelcular rota $t_{ions}^{(2)}$ 

Now going to a step further and assuming that in simple liquids the rotations and translations are not strongly coupled and anisotropic forces are not strong compared to the isotropic  ${}^{(3)}$  one can simplify Eq. (1) as

$$\frac{d^{2}}{d\Omega d\omega} = \frac{a^{2}}{2\pi} \frac{k}{k_{0}} \int dt \ e^{-i\omega t} \left\langle \exp\left[iQ \cdot \underline{R}(t)\right] \exp\left[-iQ \cdot \underline{R}(0)\right] \right\rangle$$

$$x \left\langle \exp\left[iQ \cdot \underline{b}(t)\right] \exp\left[-iQ \cdot \underline{b}(0)\right] \right\rangle \qquad \dots \dots \dots (2a)$$

$$= \frac{a^{2}}{2\pi} \cdot \frac{k}{k_{0}} \int dt \ e^{-i\omega t} I_{T}(Q,t) I_{R}(Q,t) \qquad \dots \dots \dots (2b)$$

giving separate correlation functions  $L_T$  and  $I_R$  for the translational motion of the centre of gravity, <u>R</u>, and the rotatary motion of the vector <u>b</u> of an atom from the centre of mass of the molecule. The net cross section appears as a Fourier transform of a product of these. In other words the cross-section will be a convolution of scattering functions  $S_T(Q, \omega)$  and  $S_R(Q, \omega)$  for the translational and rotational motions:

$$\frac{d^{2}\sigma}{d\Omega d\omega} = \frac{a^{2}}{2\pi} \cdot \frac{k}{k_{o}} \int d\omega' s_{R}(\underline{Q}, \omega - \omega') s_{T}(Q, \omega') \qquad .....(3a)$$

$$= \frac{a^{2}}{2\pi} \cdot \frac{k}{k_{o}} \int d\omega' s_{T}(\underline{Q}, \omega - \omega') s_{R}(Q, \omega') \qquad .....(3b)$$

where

$$S_{R(or T)}(Q, \omega) = \frac{1}{2\pi} \int dt e^{-i\omega t} I_{R(or T)}(Q, t)$$
 ....(4)

Eq. (3a) shows us that the scattering due to rotations will be modified by translational effects. The opposite is also true as shown by Eq. (3b). An example of the first kind is given in Fig. (1) where we show a calculation of scattered neutron spectrum of liquid methane<sup>(10)</sup>. Diffusion has been assumed to occur following the Ficks law and rotations are free. The particular rotational levels involved are also shown. Under the assumption of free rotations these levels should be S-functions, but they are seen to have a finite width due to diffusion broadening. Similarly if rotational levels are not of free rotors the translational part (i.e., the scattering close to zero energy transfer, marked as quesi-elastic in Fig.(1)) will also get modified due to rotations. A separation of the quasi-elastic and inelastic parts is not always possible, a priori, but in most cases reasonable assumptions can be made. We shall from now be more interested in the rotational part of scattering.

As we said earlier we shall not review all the substances that have been studied but only take two examples. Our first choice is liquid methane<sup>(10)</sup> which is probably the simplest incoherently scattering molecule. The other example will be glycerol<sup>(11)</sup> which, in contrast with methane, is reasonably complicated, has strong bonds and a very high viscocity. We hope that these two examples will be able to bring out the salient features of neutron scattering as well as some features of the other techniques.

The experimental results of the scattering of cold neutrons by methane are given in Fig. 2; for three different angles of scattering. The predominent peak at the elastic position, referred to as the quasi-elastic peak, is broadened mainly due to translatory motions of the centre of gravity of the molecule. The broad inelastic scattering arises mainly from neutrons exchanging energy with rotational degrees of freedom.

In order to understand these let me remark here that me thanes is a spherical top molecule with weak intermolecular forces. Under these conditions it may be expected that the rotations may be rather free even in liquid methane. There was some evidence of this from earlier experiments. Keeping this in mind it is useful to look at the expression for the  $I_R(Q,t)$  for the case of free rotation. This has been derived earlier and one can show that<sup>(3)</sup>

$$I_{R}(Q,t) = \sum_{\substack{l=0 \\ l \neq 0}}^{\infty} (21 + 1) J_{e}^{2}(Qb_{p}) F_{1}(t) \qquad \dots \dots \dots (5)$$

where  $J_1(Qb_p)$  is a spherical bessel function of order 1 and  $b_p$  is the distance of the proton in the methane molecule from its centre of mass.  $F_1(t)$  is a correlation function, 1<sup>th</sup> in a series. It will also be referred to as the



Fig. 2

relaxation function. We shall come to the physical meaning of  $F_1(t)$ 's in a while but we shall content ourselves for the present by saying that the correlation functions can be rigorously calculated for free rotations and the nature of  $F_1(t)$  is shown in Fig. 3 with full lines, for a spherical top molecule. In case one is not dealing with free rotations, but with rotational diffusion, taking place as a result of a number of infinitesimal angular correlations, then the relaxation functions can be shown to be exponentials with different relational diffusion constants Fig. 3 <sup>(3)</sup>. The qualitative behaviour of higher functions is smaller<sup>(4)</sup>. Thus, knowing the relation functions,  $I_p(Q,t)$  can be calculated.

For  $I_T(Q,t)$  one again assumes that diffusion in liquids is taking place according to one or the other of the models. When one is doing experiments at small momentum transfers, (that is, involving large distances and hence large times) one can assume that a simple classical Fick's law of diffusion gives a reasonable description of the translations. This gives <sup>(6)</sup>

$$I_{T}(Q,t) = e^{-Q^{2}D|t|}$$
 .....(6)

where D is the translational diffusion coefficient.

Thus, knowing  $I_T(Q,t)$  and  $I_R(Q,t)$  one can calculate the scattered spectrum and compare it with experiment. A comparison of this type immediately shows that if free rotations do occur in liquid methane, then the quasi-elastic peak at 90° should be much larger than observed in experiments (3,4). Also the rotational peaks should be observable at very small angles of scattering, unlike that shown by experiments (10). Hence one concludes that the correlation functions,  $F_1(t)$ , must be properly modified to take care of the weak hindrance.

To see how this can be done let us examine the physical meaning of the correlation function. This can be shown to be given by  $\binom{2,3}{2}$ 

$$\mathbf{F}_{1}(t) = \langle \mathbf{P}_{1}(\cos \theta) \rangle_{T}$$
 .....(7)

where  $\Theta$  is the angle through which a vector fixed in the molecule rotates in time t. That is,

$$\mathbf{F}_{1}(t) = \langle \underline{\mathcal{U}}(0), \underline{\mathcal{U}}(t) \rangle \qquad \dots \dots \dots (8a)$$
  
$$\mathbf{F}_{2}(t) = \langle [\underline{\mathcal{U}}(0), \underline{\mathcal{U}}(t)]^{2} - 1 \rangle \qquad \dots \dots (8b)$$

and so on.

Thus, one can now interpret the  $F_1(t) = \langle u(0), u(t) \rangle$  as follows: If a vector in the molecule pointing in a particular direction at time t = 0, then the correlation function gives how, in an average way, this will be pointing at time t, or, in other words, it tells us how the rotational part of a system approaches

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had went





thermal equilibrium from a given initial condition.

As we marked earlier we can calculate these functions for special asymptotic cases of free rotation and rotational diffusion. The situation is in fact quite similar to that of calculating similar correlation functions in the translational case. One expects that at small times the behaviour would be that of free rotations but at very long times the rotational diffusion will set in. Thus, the actual relexation function would start off as shown by full lines in Fig. 3, but change over to an exponential behaviour at larger times. While it is possible to say this qualitatively one cannot calculate the detailed correlation from basic principles. The correlation functions, however, can be derived from the infrared and Raman experiments.

In an infrared experiment the scattering arises because of the change in the dipole moment and it has shown by  $Gordon^{(2)}$  that in those experiments the appropriate rotation-vibration line shape indeed is given by the time Fourier transforms of the correlation function:

$$I(\omega) = \frac{1}{2\pi} \int_{-1}^{0} \frac{dt}{dt} (t) dt \qquad \dots (9)$$

Thus,

$$\langle \underline{\mathfrak{U}}(0), \underline{\mathfrak{U}}(t) \rangle = \int I(\omega) e^{i\omega t} d\omega$$
 .....(10)

Hence, one gets  $F_1(t)$  by Fourier transforming the line shapes from infrared measurements. Similarly, one can get  $F_2(t)$  by taking the Fourier transform of the Raman line. The nuclear spin-relaxation experiments measure the area,  $\int_{0}^{\infty} \left\langle P_2[\underline{\mathcal{U}}(0), \underline{\mathcal{U}}(t)] \right\rangle dt$  under this correlation function<sup>(2)</sup>, and in that sense are not able to give information in as much detail as the Raman lines, but provide an independent check on the measurements.

Thus, both  $F_1(t)$  and  $F_2(t)$  can be deduced for linear or symmetry molecules from infrared and Raman spectra. These functions for the case of  $CH_4$  are given in Fig. 4 by the dots which were got by Fourier transforming the infrared and Raman data. It is clear that at very small times the relaxation function does behave as if the rotations were free. The behaviour changes over to that of rotational diffusion at large times. The situation can be qualitatively compared to that of the translatory motions in liquids, as found by neutron experiments<sup>(12)</sup>. The results for mean square displacement of argon atoms from their positions at time t= 0 are shown in Fig. 5. It is clearly seen that the behaviour is that expected for free gas motion at very small times but changes to that of diffusion at large times. (A close relation exists between mean square displacement and the correlation functions<sup>(5)</sup>).

There are no direct experimental methods to get information on  $F_3(t)$  and  $F_4(t)$ . Put for substances like CH<sub>4</sub> or CD<sub>4</sub> reasonable assumptions can be made. It is seen from the behaviour of  $F_1(t)$  and  $F_2(t)$  that the relaxation functions depart from the free gas behaviour at about 3 x 10<sup>-13</sup> secs. Since the higher functions drop faster





with time the contribution of the exponential part is less. One may expect, therefore, that a suitable form of  $F_3(t)$  and  $P_4(t)$  would be to take the free gas value and terminate it at a suitable time as shown in Fig. 4 by arrows.

Taking these one can calculate the cross section for neutron scattering which are shown in Fig. 2, with ful lines. The theory seems to give fair agreement with experiment, but there is room for improvement. The causes for the disagreement are two-fold. The translational motions have not been properly taken into account, since a simple diffusion approximation has been made in these calculations. Second, the experiments were not performed with a thin sample, and contain a multiple scattering component. Corrections for this have not been made.

Similar experiments were performed with liquid  $CD_4$  but with a thinner sample. The interpretation of results in that case gets somewhat complicated due to the presence of coherent scattering but generally it was possible to obtain better agreement in this case, due to smaller multiple scattering.

We have seen that in case of  $CH_4$  and  $CD_4$  the correlation functions start with a gas-like behaviour and change over to rotational diffusion at  $t \sim 3 \ge 10^{-13}$  sec. We have also noticed the similarity of this behaviour to that of translational case of liquid argon. It is possible to think of more complicated behaviour for the correlation functions depending on the exact nature of hindrance just as for translatory motions. For example, after the gaseous behaviour stops and before the exponential decay starts one can have a flat or an oscillatory region depending on the extent and nature of the hindrance. This possible behaviour is shown in Fig. 3 with dashed lines end may be expected to occur in many-liquids.

We shall now consider the second example glycerol, studied by the Swedish group  $^{(11)}$ . Unlike methane, glycerol is a highly-viscous liquid and the self diffusion coefficient is therefore small. The rotational motions are highly hindered unlike in methane. As a result the quasi-elastic peak is considerably affected by the rotational motions, as shown by Eq. (3b). This can be taken as a typical case on the opposite side of the spectrum as compared to methane for which the shape of the quasi-elastic peak is determined almost completely by the nature of translational motions. For glycerol, the shape, as we shall see, will be largely determined by the rotational motions. Therefore, we shall confine our attention to this peak, in particular, to its width. The full width at half maximum of the quasielastic peak in glycerol is plotted as a function of the square of momentum transfer,  $\hbar^2 q^2$ , for different temperatures in Fig. 6. In the temperature range shown, the viscocity of glycerol gives a very large variation from a few centipoise to a couple of hundred centipoise, as compared to a viscocity of less than a centipoise of methane.

Instead of the approach taken earlier in the case of methane, which has a simple structure, it was found more convenient to resort to model calculation in this case (13, 14). For these calculations Iarsson assumed that glycerol can be treated as a linear molecule with hydrogen and OH groups hooked on to it at various places.

s n





Fig. 7

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H = C = OH H = H

As was done earlier we again devide the motions into vibrations, rotations and translations. We shall, however, now give specific characteristics to these motions as shown in Fig. 7. The centre of mass motions will be assumed to be made up of two parts. For a certain time  $\tau_o'$  the centre of mass will be oscillating, and then it will be freely diffusing for time  $\tau'_1$ . For viscous liquids  $\tau'_0 > \tau'_1$ . For considering the rotations we assume that at time t = 0 the molecular orientation can be denoted by  $N_1$  in Fig. 7. The various hydrogen atoms are connected to this axis at different distances. This axis performs a rotational diffusion (while the protons are performing hindered rotations) for a time  $\zeta_0$ , due to small changes in orientation of the surrounding molecules. At the end of a time 7 the environment has changed sufficiently for the molecule to make a rotational jump in a short time over an average distance 1. This can be considered as a isomeric rotation. After  $(\zeta_{0} + \zeta_{1})$  the whole process is repeated. As the hindrance increases the number of jumps will become less and less and the hydrogen atoms will start performing torsional oscillations, of smaller amplitude. Each proton goes through the same precess and what one observes in cold neutron experiments is an average behaviour. As against breaking of one bond at the end of  $\tau_0$ , the period  $\tau_0'$  could be probably locked upon as the time over which all bonds are broken and so the whole molecule can start moving.

The cross section for the quasi-elastic scattering due to these process can be worked out in detail with a few more assumptions which can be reasonably justified. With these assumptions the full width at half maximum of the quasi-elastic line is given as:

$$\Delta \omega = 2 \left( \frac{1}{\zeta_{00}} + \frac{2}{3} D_{p} q^{2} \right) - \frac{1}{\zeta_{0}} e^{-2w_{1}} - 4w_{e} - \frac{1}{6} \left\langle 1^{2} \right\rangle q^{2} - \frac{1}{\zeta_{0}} \cdot \frac{e^{-4w_{1}} - 2w_{e}}{1 + D \zeta_{0} q^{2}} \qquad \dots \dots (11)$$

for linear molecule. The symbols have the following meanings:

 $\mathbb{D}_{\mathbf{p}}^{i}$ 

rent 2.

$$\frac{1}{\overline{\zeta}_{00}} = \frac{1}{\overline{\zeta}_0} + \frac{1}{\overline{\zeta}_0'}$$

Rotational diffusion coefficient of the molecular axis; takes place over time.

- $2w_i = \frac{1}{6} \langle r_i^2 \rangle q^2$  where  $\langle r_i^2 \rangle$  is the mean square radius of the thermal cloud set up by molecular protons relative to the centre of mass of the molecule, due to their hindered rotations.
- $2w_{e} = \frac{1}{6} \left\langle r_{e}^{2} \right\rangle q^{2} \text{ where } \left\langle r_{e}^{2} \right\rangle \text{ is the mean square radius of the thermal cloud of protons due to vibrations of the centre of gravity. Normally <math display="block">\left\langle r_{e}^{2} \right\rangle \left\langle \left\langle r_{i}^{2} \right\rangle \right\rangle \cdot$

Under asymptotic conditions of large and small wavevector transfers this reduces to

and

where D is macroscopic self diffusion coefficient.

Thus, one has  $D_p$ ,  $\zeta_0$ ,  $\zeta'_0$ ,  $\langle r_i^2 \rangle$  and  $\langle r_e^2 \rangle$  to be found from the neutron experiments.  $\langle r_i^2 \rangle$  is determined by finding intensity variation of the integrated quasi-elastic peak  $D_p$  and  $\zeta_{00}$  are uniquely determined from the widths at larger values of Q i.e., from Eq. (12). At lower temperatures  $\zeta_{00} \approx \zeta_0$ since  $\zeta'_0$  (the period for which the c.m. is bound) is much larger than  $\zeta_0$ . this can be seen from Fig. 8. If the same temperature dependence is assumed for  $\zeta_0$  over the whole temperature range;  $\zeta_0$  and  $\zeta'_0$  can be separately calculated. The only quantity to be determined now is  $\langle 1^2 \rangle$  which can be determined either from Eq. (11) or (13). The final results are tabulated in Table I.

It is interesting to find that the model is able to describe the data well over a rather large range of temperature and a fair range of Q. It is now possible also to consider the physical implications of these parameters. For example, Larsson compared his  $\zeta'_{o}$  value with the measurements on dielectric relaxation time<sup>(15)</sup> which are also plotted in Fig. 8. (including an extrapolation). The dielectric relaxation time has been interpretted as due to changes in molecular orientation because of breaking of all the OH bonds. When one remembers that  $\zeta'_{o}$  was introduced as the time for which the molecule remains bound to one place and then starts moving it seems not unreasonable to associate this also with time required for breaking all the bonds. The agreement therefore seem gratifying. The activation energy for this process is  $(10 \pm 3)$  Kcal/mole which seems to be a reasonable number of bonds. As against this,  $\overline{\zeta}_{o}$ , associated with an activation energy of  $(2.6 \pm 1)$  Kcal/mole, seems to be connected with breakage of one bond, as assumed in the model. The neutron times do not agree with the relaxation time



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measured by ultrasonic measurements which seem to be measuring some other process. One should, however, be careful in making these comparisons since a large extrapolation is often required before making a comparison. Further, not enough substances have yet been studied from this point of view and so these comparisons should be treated with some caution.

Apart from comparisons with other experimental data some interesting conclusions can be drawn because of the success of the model itself. It is, for example, seen that one requires rather large rotational jumps to explain the data. This seems a necessary part of the theory. This, in turn, means that the correlation function defined earlier again will not have an expontial form, but would rather start as a Gaussian and only later change its form to an exponential. In substance like glycerol the correlation will probably show a more complicated behaviour than in methane, before the exponential behaviour starts. This is schematically given in Fig. 3 with dashed lines.

In conclusion, these experiments show clearly the connection between the information that is obtained from infrared, Raman and neutron experiments, and it seems that a parallel study using all the techniques on the same substance should be able to give rather detailed information on the nature of hindering and the behaviour of correlation functions in these liquids.

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| <u>, , , , , , , , , , , , , , , , , , , </u> | 7,                      | τ.                      | Dp                                      | <1 <sup>2</sup> > | $\frac{1}{6}\langle r_1^2 \rangle$ | D                                       |
|---|-------------------------|-------------------------|---|-------------------|------------------------------------|---|
| TOK   | (10 <sup>-12</sup> sec) | (10 <sup>-12</sup> sec) | (10 <sup>-5</sup> сm <sup>2</sup> /вес) | <b>Å</b> 2        | ₿ <sup>2</sup>                     | (10 <sup>-5</sup> cm <sup>2</sup> /sec) |
| 266   | 33                      | :<br>. i                | 0.095                                   | 2.46              | 0.07                               |   |
| 293   | 22                      |                         | 0.18                                    | 2.79              | 0.08                               | 0.008                                   |
| 334 .   | 11.3                    |                         | 0.36                                    | 2.67              | 0.12                               | 0.013                                   |
| 369   | 9                       | 11.8                    | 0.89                                    | 2.40              | 0.14                               | 0.064                                   |
| 403   | 5.8                     | 3.2                     | 0.9                                     |                   | 0.16                               | 0.2                                     |
| 453   | 4.0                     | 0.9                     | 1.5                                     |                   | 0.20                               | 0.6                                     |
|   |                         |                         | Mean                                    | 2.6               |                                    |   |

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TABLE I

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#### DISCUSSION:

Anil Kumar :

Please explain what is jump rotation and how it differs from hindered rotation.

B.A. Dasannacharya :

Any motion which is not free like, say, in the gaseous state can be labelled "hindered". The extent of hindering may vary from small in liquid methans to large in glycerol. "Tump" rotation, however, would normally refer to a process in which a fairly large angular rotation takes place in a very short time ( $\sim 10^{-13}$  sec.), between two angular positions where the molecule would stay for comparatively longer times.

H.G. Devare :

You have mentioned the breaking of bonds and jump in rotational motion. Could you elaborate more on the nature of these bonds?

B.A. Dasannacharya :

At the present state of neutron experiments it is not possible to say which of the bonds are breaking. However, if one looks at the curve of  $\mathcal{T}_{00}$  versus the temperature it is seen that the curve can be fitted as a sum of two straight lines for  $\frac{1}{\mathcal{T}_{0}}$ and  $\frac{1}{\mathcal{T}_{0}}$ , the way it is plotted in the figure. The activation energy calculated from these are roughly 2.5 Kcal/mole and 10 Kcal/mole, which seem to correspond to the breaking of a single bond and a number of bonds respectively.

D.K. Ghosh :

Is it possible to study in detail the molecules having internal rotation like CH<sub>2</sub>OH and if so is it possible to calculate the potential barrier hindering internal motion in molecules?

B.A. Dasannacharya :

It is possible to study the rotations in CH<sub>0</sub>OH and the like just as the case of methane. However, getting numbers like barrier height may not always be possible depending on the relative effects of rotational and translational broadening of the peaks.

N.S. Satya Murthy ::

Do you think Mossbauer measurements on liquids can provide information on useful time scales which can supplement neutron scattering data?

B.A. Dasannacharya : Only to a rather limited degree, I think. This is because Mossbauer effect in liquids can be studied only for very highly viscous liquids. A.V. Nerasimhan :

Desennacharya, in his slides, has shown the relaxation time in glycerol to be of the order of  $10^{-13}$  sec. But the dielectric relaxation time (according to Debye ( $7_D = \frac{4\pi\gamma_B^3}{gT}$  where  $\gamma$  = shear viscocity, a = radius of the molecule) turns out to be of much larger magnitude, of the order of  $10^{-7}$  sec. How can this discrepancy be explained?

B.A. Daoannacharya : De

Debye's theory is derived essentially on macroscopic considerations, thus giving a behaviour only after a number of "collisions" have taken place. The equation gives an average behaviour. Neutron measurements, however, look at processes in the time range of  $10^{-13}$  to  $10^{-11}$  sec. and therefore describe "individual" processes. For more details I would like to refer you to work by Shimizu [J. Chem. Phys. 43, 2453 (1965)] and reference (2) of the above paper.

#### MOLECULAR FORCES IN PHYSICS AND BLOLOGY

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#### 1. INTRODUCTION

In this lecture I shall deal with some aspects, both qualitative as well as quantitative, of the nature of the intermolecular forces and the laws governing them which have a similar role both in the formation of molecular crystals as well as in the occurrence of particular conformations of V biological macromolecules. Our interest in this subject arose mainly from the second aspect, namely the nature of the folding that takes place in biological large molecules and the relation of this to their activity. These molecules belong to the class that is now-a-days called as high polymers, i.e. molecules which consist of a chain of units, all of which are identical or closely similar. All these polymers are organic in nature and in the synthetic field also, most of the polymers that have been synthesised are compounds containing carbon. The simplest of such polymers is polythene, or polymethylene, whose structure is shown in Fig. 1, It consists of repeating units of CH, or methylene groups, and these are joined together by C ---- C single bonds. The essential problem of conformation, as it is called in the biochemical literature, or configuration, as it is called in physical chemistry, becomes apparent even in this simplest example. In principle, there is a good amount of freedom of rotation about each of the C---- C single bonds - in actual practice this freedom is restricted to three possible relative orientations of the third neighbours (C(1) and C(4)) in the -C(1)-C(2)-C(3)-C(4)--- chain about the middle bond C(2)-C(3), backbone which are separated by a rotation of about 120° about this bond. Even this freedom is sufficient to produce a large number of possible conformations in a chain composed of, say, 20 carbon atoms and, if the chain consists of a larger number of atoms, the number of possibilities becomes astronomical. As a result, the theory of the conformations taken up by such a large chain become statistical in nature. Such theories are described in well known books on polymer chemistry.

Coming in particular to one class of polymers, namely proteins, with which I am particularly familiar, we meet with a very similar situation. In this case, the repeating unit is somewhat bigger. Without going into more details, about the chemistry of these groups, we may note that the repeating unit in a protein chain is what is known as the peptide group, or peptide unit, which is shown in Fig.2.

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# MOLECULAR CHAIN OF THE POLYMER POLYMETHYLENE.

FIG.1



DIAGRAM OF A PEPTIDE UNIT SHOWING THE DIMENSIONS OF, AND ANGLES BETWEEN, DIFFERENT BONDS.

FIG.2
All the atoms in this unit are planar to a good degree of approximation and, for practical purposes, we may take the chain to be composed of such planar peptide units linked at the so-called alpha-carbon atoms, and having a freedom of rotation about the two bonds  $N - C^{\infty}$  and  $C^{\infty} - C'$  which meet at this alpha-carbon atom (Fig. 3 (a)). Just as in the case of polymethylene which was mentioned earlier, in this case also, the first problem will be to work out the restrictions on the degree of freedom of rotation about these two single bonds. The determination of these immediately brings in considerations which are essentially physical in nature. For the sake of definiteness, we may describe the degree of freedom about the two bonds by two torsion angles of rotation, denoted by  $\emptyset$  and  $\Psi$  which are indicated in Fig. 3. Figure 3(a) shows one particular relative orientation of the two units, which, in a suitable notation, corresponds to  $\emptyset = \Psi = 0^{\circ}$  and Fig. 3(b) that corresponding to  $\emptyset = \Psi = 180^{\circ}$ . In both cases, the atoms shown in the diagram are in the same plane, but this need not be so for a general ( $\emptyset, \Psi$ ).

## 2. CONTACT CRITERIA

It will be seen that in the conformation corresponding to Fig. 3(b), two atoms, 0 of residue 1 and H of residue 2, are very close to each other, being only about 0.5 Å apart. This is impossible, for the atoms themselves have radii of the order of 1.0 to 1.5 Å, and the nearest distance of approach for the two atoms will be of the order of 2.2 Å. This shows how certain relative orientations of the two peptide units become forbidden because of impossible contact distances. Therefore, in order to get an idea of the allowed conformation, it is necessary to have a clear picture of the allowed contact distances. This aspect was considered by us during the years 1961 to 1963. The resulting map for a pair of peptide units containing also a carbon atom  $C^{\beta}$  attached to the  $C^{\alpha}$  atom in the so-called L-configuration (as shown in Fig. 3(a)) is given in Fig. 4. In obtaining this map, certain criteria had to be used as to what are the allowed contacts and what are the disallowed contacts. Although there are data available in the literature regarding the van der Waals radii, i.e. the normal contact distances in an equilibrium configuration, of various atoms, these distances are found to be too large for use as the criteria for distinguishing between 'allowed' and 'disallowed' contacts. Distances which are about 0.4 Å less than the sum of the van der Waals radii are often found to occur for contacts between atoms under special conditions, particularly if these are intramolecular and there is some other attractive force like a hydrogen bond in the neighbourhood, which makes these contacts necessary. The map shown in Fig. 4 was obtained by making use of an empirical set of limiting contact distances arrived at from a survey of the available literature on simple compounds such as amino acids and peptides, which are analogous to proteins. (the figure is the latest version (Ref. 2) of the map first proposed from our laboratory<sup>(1)</sup>.



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FIG-4

Although the method of contacts gives a good idea of the nature of limitations on the allowed conformations, it cannot tell us much about the nature of the conformations which are most favoured. For this purpose, it would be an advantage if the potential energy on the various conformations could be worked out, for one would naturally expect that the most favourable conformations are those corresponding to least energy. However, in order to calculate the total potential energy of a molecule corresponding to a particular conformation, it is necessary to know the types of interactions between the atoms which contribute to the energy and the exact formulae for these quantities. Obviously, information of this nature will have to come from physical studies of various types, namely theoretical studies, data on infrared spectra, microwave spectra, crystal lattice stability and so on.

Before considering these theoretical aspects in detail, we shall first discuss the nature of the conformations taken up by biopolymers and the types of interactions that enter into the picture in these. In the case of bioplymers, one talks of what are called primary, secondary and tertiary structures. By primary structure is meant the covalent interconnections between the various atoms in the polymer chain. In the case of a protein, this is given by a string of peptide units of the type shown in Fig. 2, which have in addition short side chains of atoms (corresponding to different types of organic groups) attached to the alpha-carbon atom of the backbone chain at the positions marked R in Fig. 2. As is well-known in the case of polymers in general, the primary structure does not uniquely fix the spatial configuration of all the atoms in the chain. In particular, there will be various bonds in the backbone which are single bonds, about which relative freedom of rotation is possible, as already discussed in the case of a pair of peptide units. In consequence, a variety of 'configurations' are possible for the polymer chain. This word configuration, which is used in many books on high polymers, is specifically denoted by the word 'conformation' in the field of biopolymers. The resulting structural form taken up by the chain is known by the name secondary structure. This may sometimes consist of helical segments, or short stretches of rigid straight segments, The tertiary structure, which is particularly relevant in the case and so on. of proteins having biological activity, is the folding up of the chain having definite secondary structure at the next higher level of organisation which, will be in the region of tens of Angstroms. As a consequence, the protein chain as a whole may have a compact, approximately spherical, outline and will be coiled inside this in a form reminiscent of the folding of the intestines inside the abdomen.

In our discussion to-day we shall be mainly concerned with the secondary structure of proteins and the laws governing this. To some extent, this can be predicted from the nature of the contact map for a pair of peptide units (as shown in Fig.4) and its extensions; but it would be desirable to have exact energy values, so that the conformation of minimum energy can be calculated.

## 4. POTENTIAL MAPS

Before discussing the theories of intermolecular interactions, we shall slightly anticipate the results and discuss a few examples of the potential energy contour maps in the (  $\emptyset, \psi$  )-plane. Figure 5 shows four such maps obtained using slightly different theoretical assumptions - by our laboratory<sup>(3)</sup>, by Flory and coworkers<sup>(4)</sup>, by Scheraga and coworkers<sup>(5)</sup> and by Liquori and coworkers<sup>(6)</sup>. Although it will be seen that all these potential maps are broadly similar and all of them are in general agreement with the contact map of Fig. 4, there are appreciable differences between one and the other, which indicates the need for obtaining more exact information regarding the quantitative formulae for the various interactions. The best sources for such precise information are the data and theories on crystal properties, because the atoms in a crystalline solid are in close contact with one another very much like the atoms in a folded polypeptide chain, in which they are tightly packed. The interatomic distances that occur in both these cases are of the same order, the types and nature of the forces between these atoms are also very similar and therefore information obtained from one field will be applicable to the theories in the other field. As will be shown below, it is not a one-way relationship - not only do the physical theories of the solid state provide excellent data for the study of biopolymers, but the results coming out of a theoretical study of biopolymers will also be helpful in developing further theories of crystal structures.

#### 5. TYPES OF INTERMOLECULAR INTERACTIONS

Since main field of work of our laboratory is biomolecular physics, we shall first list the types of intermolecular forces that are relevant for biomolecular conformations. Most of them are relevant also for a study of the stability of crystal structures and lattice vibrations, and we shall refer to these as and when necessary. A full description of these forces, with particular reference to protein structure, is given in a review from our laboratory under publication in Advances in Protein Chemistry<sup>(7)</sup>. In view of the fact that most of the references are available in this review, only the more important ones are specifically mentioned here. We shall now consider the different types of interactions one by one.

## (a) Non-bonded Interactions:

Since we are dealing mainly with <u>intermolecular</u> forces, we shall first assume that the molecule itself is rigid, i.e. that the bond lengths, angles, etc. in it are held fixed by covalent forces and that the molecule moves rigidly as a whole. Later we shall consider the possible distortion of the molecule, or molecular chain as in biopolymers. Some of these distortions, like those involving torsional



(a) OUR LABORATORY (b) FLORY AND COWORKERS (a) TO (d) POTENTIAL ENERGY CONTOUR MAP IN THE  $(\phi, \psi)$  - plane AS CALCULATED BY DIFFERENT WORKERS

FIG. 5.



FIG-5 (contd)

motions about single bonds, require very little energy, and the energies involved in them are of the same order as non-bonded energies. In view of this, such torsional distortions play a predominant role in biopolymer conformation. However, we shall consider these under the section on intramolecular interactions.

The most important type of force among the intermolecular interactions are the non-bonded interactions consisting of (i) an attractive part,  $V_a$ , known as van der Waals attraction and (ii) a repulsive part,  $V_r$ . The non-bonded potential energy is thus  $V_{nb} = V_a + V_r$ .

## (i) van der Waals Interaction:

This type of force arises from the spontaneous fluctuations of charges in the electron cloud of an atom leading to the creation of transient dipole moments. These then induce a polarisation in a neighbouring atom, which means that the two are attracted to each another. The theory, which was first given by London as early as 1937, has been applied in a semiempirical way and leads to a formula of the type  $V_{a} = -A/r^{6}$  where

 $\alpha'_{1}$ , and  $\alpha'_{2}$  are the atomic polarisability of the interacting pairs of atoms, N<sub>1</sub> and N<sub>2</sub> are the effective number of polarisable electrons on these atoms, and the other quantities are the usual fundamental constants (see Ref. 8). In applying these formula, data on  $\alpha'$ 's and N's are obtained from various sources such as measurements of refractivities, which are known to a fairly good degree of accuracy. Purely theoretical values obtained from quantum mechanics have also been given in the literature.(see for example Ref. 9). However, the agreement between the values obtained from different sources is not too good. - e.g. for the H...H interaction, one source (Ref.9) gives  $A = 88 \text{ kcal mole}^{-1} A^{-6}$ , while another (Ref. 3) uses a value of  $A = 46.8 \text{ kcal mole}^{-1} A^{-6}$ , which is in close agreement with that used by a number of workers on biopolymer structure.

(ii) <u>Repulsive Energy</u> V<sub>r</sub>:

The theoretical expression for  $V_r$  is somewhat empirical. Two forms are in common use, namely the exponential form which may be expressed by

 $V_r = B \exp - \mu r$  .....(2a)

or B exp -r/p

.....(2b)

and the inverse power form

Of these, the former has a better theoretical basis than the latter, although for small variations in the contact distance near about the equilibrium value, one form can effectively be replaced by the other by a suitable choice of constants.

Combining the expressions for  $V_a$  and  $V_r$ , we may write the non-bonded potential energy in the forms

$$V_{\rm nb} = -A/r^6 + B \exp - \mu r \qquad (4)$$

 $V_{nb} = -A/r^6 + B/r^n$  .....(5)

These two forms are respectively known by the names Buckingham potential for equation (4) and Lennard-Jones potential for Equation (5) with n = 12. Both of these forms have been widely used in studies on protein conformation.

If the functions shown in equations (4) and (5) are plotted, it will be seen that they have a variation of the type shown in Fig. 6 with a minimum at a value r = R, which is the equilibrium distance between the two atoms. Such equilibrium distances have been estimated from different sources - for example from the observed distances in crystals of rare gas solids and simple molecular crystals of elements.

The value of  $\mathcal{M}$  or  $\rho$  in the repulsive part of the Buckingham potential has been estimated from one or two different methods. One of them is from the data obtained in gaseous diffusion studies. These give a value of about 4.5 for  $\mathcal{M}$ He and Ne and a value which drops down to 4.3 for Ar and 2.9 for Kr. In view of these, a constant value of  $\mathcal{M} = 4.6$  has been suggested by Flory and coworkers for organic compounds consisting of C, N, O, H and this has been adopted by us in most of our studies. However, more recently, our attention has been drawn to studies on cohesive energies of  $\rho$  tail halides, which give a value of about 0.3 for  $\rho$ , which corresponds to  $\mathcal{M} = 3.3$ . Such data are available in Ref. 9. In a paper presented at this Symposium, Dr. R. Srinivasan of the I.I.T. Madras has shown that a value of  $\rho$  nearly equal to 0.3  $\hat{k}$  fits very well the data on the second and the third order elastic constants, the dielectric constant and the Raman frequency of diamond. On the other hand, it was found that if the inverse



 (a) TWO INTERACTING ATOMS, SCHEMATICALLY REPRESENTED BY TWO OPEN CIRCLES WITH CENTRES SEPERATED BY 2d, IN A MEDIUM COMPOSED OF ATOMS WHICH ARE REPRESENTED BY SHADED CIRCLES.
 (b) AN IDEALISED PICTURE OF THE ABOVE IN WHICH THE MEDIUM OCCURS OUTSIDE THE IONISED SPHERE OF RADIUS g. FIG.7 nth power law is used, the value of n came out to be exceedingly low, of the order of 3 to 4. Thus a value of  $\mathcal{M} \subset 3.5$  is indicated for C...C interactions also near the equilibrium configuration.

As already indicated, A can be obtained from theory. In the inverse nth power law, the value of B can be determined when the value of the equilibrium distance is known. This distance is obtained as the sum of the van der Waals radii of the individual atoms, tables for which are available (e.g. Ref. 11). In the case of the Buckingham potential, the value of B can be determined when the value of  $\mathcal{M}$  or  $\rho$  is known.

Incidentally, an empirical formula connecting the variation of  $\mathcal{M}$  with the n nature of the atoms taking part in the interactions has been given by Kitaigorodsky<sup>(16)</sup>, in which  $\mathcal{M}$  is taken to be proportional to the equilibrium distance between the two atoms, and  $\Psi_{nh}$  takes the empirical form

$$V_{nb} = 3.5 \ 8600 \ \exp(-13r/R) - 0.04R^6/r^6 \ \dots (6)$$

As will be seen from what has been said above, there is a considerable amount of variation in the parameters used for the repulsive potential and, even for the van der Waals interactions, the values of A are not precisely known. Therefore, there is a need for a thorough study of these quantities from different sources, particularly for the case of interactions between atoms in close contact, i.e. at distances of the order of 2.0 to 5.0 A.

(b) Electrostatic Interaction :

If the two interacting atoms have charges  $e_1$ ,  $e_2$ , then there will be an interaction energy which may expressed in the form

$$\mathbf{v}_{es} = \frac{\mathbf{e}_1 \mathbf{e}_2}{\mathbf{e}' \mathbf{r}} \qquad \dots \dots (7)$$

The symbol  $\epsilon'$  rather than  $\epsilon$  is used for the dielectric constant in this expression for reasons to be descussed below. The two quantities that enter into  $V_{es}$  are thus the magnitudes of the charges  $e_1$  and  $e_2$  and the value of the dielectric constant that is effective. We shall consider each of these in turn.

(i) Magnitude of Charges :

In ionic crystals, the charge on the atoms is in general that of a full electron (or a multiple of it) as in NaCl. In the highly symmetric povalent crystals, as in diamond, there we no net charges on the individual atoms. However, in general, there will be partial charges on the different atoms in the molecules. The magnitudes of these are best calculated from dipole moment data - in particular the values of bond moments, which are listed in books on dielectric constants and dipole moments. This method of using partial charges on the individual atoms is known as monopole method of expressing the charge distribution in the molecule and is a very good approximation. However, the values of the bond moments as reported in the literature vary appreciably (see for example Table XXIIIa of reference 7 for the atoms in the peptide unit). As a consequence, at the present state of knowledge, one could only expect to have an accuracy of about 10%. For instance, at this degree of accuracy, the charges associated with the various atoms in the peptide unit may be given as

 $C^{\alpha}$  (zero), C' (+0.4e), O(-0.4e), N(-0.3e) and H(+0.3e)

Where e is the charge on a free electron.

### (ii) Value of the Dielectric Constant:

We had used an effective dielectric constant E' rather than E in the expression for the electrostatic potential energy in Equation (7). This has been done because the interacting atoms that are most relevant in the consideration of conformations are close together and the medium which produces the dielectric constant only exists in a region outside of the two atoms, but not in between them. The situation may be schematically represented as in Fig. 7(a). Obviously, even assuming the medium to be continuous in the region outside the two atoms, one would not expect the electrostatic interaction  $e_1e_2/r$  between the atoms in this example, to be reduced by the full factor 1/c because of the presence of the medium. An idea of the extent to which the 'effective dielectric constant' differs from the true dielectric constant may be obtained from an idealised system shown in Fig. 7(b). In this model system, we calculate the interaction of a pair of point charges situated symmetrically at a distance 2d on a diameter in the inside of a spherical cavity of radius a. The theory of this was worked out at my suggestion by Dr. R. Srinivasan and the results calculated from his theory are shown in Table I. To compare these results with an actual example of two atoms in contact which interact electrostatically, we may reasonably take d/a = 0.5, as shown in Fig. 7(b). For this value of d/a, we get a limiting value of  $\mathcal{E}'=5.0$ for very large  $\in$  and a value  $\in \sim 4.5$  for water, with  $\in = 81$ . (For d/a = 0.7,  $\in'$  is of the order of 15 for large  $\in$ ) Foe small ( $\in\sim3$  to 5,  $\in'$  is nearer to 2 for d/a = 0.5. Therefore, if we calculate the electrostatic interaction between neighbouring atoms inside a solid protein, we may take  $\epsilon' \simeq 2$  without much loss of accuracy. On the other hand, if we wish to calculate the properties of the protein chain in water,  $\epsilon'$  may be put equal to 4.5 with reasonable accuracy. It is interesting that the workers in the field of protein conformation like

Scheraga<sup>(5)</sup> and Flory<sup>(4)</sup> have used values of 4 and 3.5 respectively for E' in the presence of the solvent. Although they did not work out the theory for these values, their intuition seems to have been right.

# (c) Value of Dielectric Constant for Covalent Forces and van der Waals Interactions :

In the last section, we considered the dielectric constant for the interaction of static charges and showed that the effective value of this (E'-1) is a small fraction of (E - 1). However, we assumed that E is equal to the static dielectric constant. Now, we know that all interatomic forces in a molecule are essentially electrical in nature. In fact, in calculating the energies of electrons in the field of a set of nuclei using the Schroedinger equation, the electrostatic potential is taken to be of the form  $e_1 e_2/r$  for a pair of interacting charges. No dielectric constant is used for this purpose and this is satisfactory when one considers an independent molecule. In this way, we can calculate the energy of covalent bonds and also the energy of the van der Waals interaction. The question now arises as to whether these interaction energies will also have to be reduced by a factor  ${\cal E}'$ in the presence of a medium. If the theory of the covalent and van der Waals forces in quantum mechanics is carefully examined, it will be found that the terms involved in them in the perturbation theory have a time dependence, which corresponds to a frequency of the order of the optical transitions, or the ionisation energy, of the atoms concerned. This frequency, in general, is in the ultraviolet and therefore it is clear that the value of the  $\epsilon$  which has to be used in connection with these forces is the optical dielectric constant, or the square of the refractive index, and not, the static dielectric constant. This quantity is generally of the order of 2. Consequently, the value of E' which is the effective dielectric constant, will be close to 1 and therefore, for practical purposes, one can say that the energy of a covalent bond or the van der Waals interaction will not be affected to a sensible extent by the surrounding medium. Here again, it is interesting that none of the workers in the field of protein conformation had used any dielectric constant for any of the interactions expect for the interaction between static charges. Although they had not specifically discussed this question, it is gratifying that a more careful examination leads to the result that  $\mathcal{E} \sim 1$  for these interactions. In view of this, we shall not mention the quantity  $\in I$  in connection with any of the other interaction energies which we shall consider below.

#### (d) Hydrogen Bond Energy

<sup>T</sup>he hydrogen bond is a special type of bond that is formed by a hydrogen atom which is covalently linked to an atom X, but can also be weakly bonded to another atom Y in the chain of atoms  $X - H \dots Y - Z$  where X and Y are electronegative elements. In particular, the case X==N and Y==0 is of particular interest in the structure of proteins. There are well-known books on the hydrogen bond and therefore we shall not consider this topic in much detail except to mention briefly the conditions of its formation and the order of magnitude of the energy involved. Taking in particular the hydrogen bond NH...O, which is the commonest one in protein structures, the distances between N and O has a mean value of 2.9 A, with a variation from 2.7 to 3.2 A. The bond direction NH generally points towards the oxygen atom, the angle between the direction N-H and N...O being in general less than 30°. Similar considerations hold for OH...O bonds, with a mean length of about 2.7 Å and an angle less than 20°. The attraction energy of these bonds is of the order of 3 to 8 kcal/mole, the straighter bonds being in general stronger than those that are bent. In comparison with the van der Waals attraction energy of less than 1 kcal/mole for the same two atoms at a distance of about 3.0 A, the hydrogen bond is distinctly a much stronger interaction. Consequently, it is given the name of a bond and is commonly known as a <u>secondary</u> valence bond, to distinguish it from the strong covalent bonds in the molecules, which are called as the primary bonds.

Several attempts have been made to obtain semi-empirical formulae to represent the variation of hydrogen bond energy with distance, angle and other parameters involwed; but they have not critically compared with observational data (see Ref. 7 for literature citations). It would therefore be of interest to make such a comparison with observational data which are available in plenty from crystal structure studies on organic molecules. In fact, almost every group of the type NH,  $NH_2$   $NH_3^+$  or OH is invariably found to be taking part in a hydrogen bond in the crystal structures of organic molecules containing such groups. Therefore, in any theory of the stability of molecular crystals of organic molecules, this secondary valence bonds would play a very important part whenever such bonds are possible. We shall call this energy by the symbol  $V_{hb}$ .

# (e) Hydrophobic Interactions:

This again is an interaction which is peculiar to proteins and other biopolymers and is particularly relevant for their conformation in solution in water. In a sense this interaction may be considered to be opposite to the hydrogen bonding which occurs extensively in liquid water between one molecule of  $H_2O$  and another. Most proteins having biological activity have a content of about 20 to 30% of nonpolar side chains. These groups have a low affinity for water and hence, in their immediate neighbourhood, there will be no attractive interactions between water and these groups. Therefore, these groups would tend to eliminate contact with water and come close to one another. The secondary structure of the protein chain would therefore be affected by the presence of such non-polar groups either in close proximity br in different parts of the chain. We shall not consider this interaction in detail, for a corresponding effect does not occur in the case of crystals which are composed of only the molecules out of which they are made.

# 6. INTRAMOLECULAR INTERACTIONS

In the last section we mentioned that intramolecular interaction energies have to be combined with the intermolecular ones to arrives at the stable conformations. The most important of the intramolecular interactions are the covalent bonds which bind an atom to its neighbours; but we shall not discuss these bonds, as we will be dealing mainly with conformations in which the covalent bonds are, by and large, unaffected. The very word conformation is used in correct chemical nomenclature to indicate this fact, namely that the covalent structure of the molecule is constant, but that rotations about some of the bonds can take place leading to different secondary structures. However, slight variations from the equilibrium values of the covalent bond lengths and bond angles are relevant, as deformations may produce more favourable intermolecular interactions and thus lead to a conformation of lower energy. We shall briefly list these intramolecular interactions ( more details may be obtained from Ref. 7) — in particular, we shall consider three types, namely bond length variation, bond angle distortion and variation of torsion angle.

## (a) Bond Length and Bond Angle Variation:

Denoting the various covalent bond lengths and angles by  $L_i$  and  $\mathcal{T}_i$ , these quantities will have a set of values for the free molecules. When the molecules are packed together in a solid, or a fibre, these values may undergo slight variations, namely  $\Delta Q_i$  and  $\Delta \mathcal{T}_i$ , from their equilibrium values. Then the form of the potential energy V is, for small variations,

$$V_{\ell} = \frac{1}{2} K_{\ell} (\Delta \ell)^2$$
 and  $V_{\tau} = \frac{1}{2} K_{\tau} (\Delta \tau)^2$  ....(8)

In organic molecules, the values of  $K_{L}$  vary according as the bond is a single bond or a double bond, from about 500 to 1,300 kcal/mole/ $A^2$ , so that a change of 0.1 Å leads to an increase in energy of the order of 5 kcal/mole. In view of this, deformations in bond lengths greater than 0.05 Å are very unlikely. This magnitude is small compared with the changes in interatomic distances produced by deformations of the type of torsional rotations which normally occur and therefore they can be mostly neglected.

The values of  $K_{\tau}$  for bonds at C, N and O atoms, which commonly occur in organic compounds, are of the order of 40 to 80 kcal/mole. From this, it will be seen that a change of 5° in bond angle produces only an increase in energy of about 0.3 kcal/mole and therefore deformations of this order are expected to occur.

# (b) <u>Torsional Distortion</u>:

As already mentioned, this is a distortion which has great freedom and, in some cases, a full  $360^{\circ}$  rotation about the single bond is permissible. However, in the case of C --- C single bonds, as in the ethane, there is a three-fold symmetry in the energy, with minima occurring at intervals of 120° and maxima in between, the energy barrier between two minima being of the order of 3 kcal/mole. On the other hand, if one of the two linked carbon atoms does not have three bonds attached to it, but only two, in addition to the bond to the other carbon atom. and the three bonds are planar, then the potential barrier is six-fold and its magnitude is often extremely small. Since such a situation occurs in the case of the rotations arphi and arphi for a polypeptide chain, these rotations have very low energy barriers of less than 1 kcal/mole. On the other hand, the bond between C and N in the peptide unit has a partial double bond character and rotation about this bond, which may be indicated by the symbol  $\omega$  , is highly restricted. There is only a two-fold symmetry for the potential and the energy barrier is high, of the order of 20 kcal/mole. The non-planar distortion  $\omega$  had been neglected for a long time in studies on the stereochemistry of polypeptide chains, but it is clear that a distortion  $\omega$  of 10<sup>0</sup> would only lead to an increase in energy of about 0.7 kcal/mole and this value is not unlikely to occur.

In addition to these torsional distortions which rotate one part of the molecule with respect to the other part, individual out of plane distortions of atoms can also occur, e.g. the atoms 0 and H in the peptide unit (Fig. 2). Such distortions often have very low force constants K and can therefore, occur readily.

#### (c) Evaluation of Force Constants for Intramolecular Distortions :

We had mentioned above various values for the force constants K involving different types of deformations. The best source for obtaining these constants, particularly for small deformations, are the data on infrared and Raman spectra which give the frequencies of molecular vibrations. The theory connecting the force constants with molecular frequencies is well-known<sup>(12)</sup> and the constants themselves have been worked out in a number of cases. The data which were mentioned earlier have been taken from such studies. In order to get better information about these forces in particular examples like proteins, nucleic acids, polysaccharides and so on, it would be desirable to make an analysis of the infrared spectra of model compounds related to these biopolymers, Infrared studies of this type are being undertaken now-a-days (for example by Dr. Miyazawa in Japan, Dr. Krimm in Michigan and so on) and the results coming cut of these will be extremely valuable for the prediction of protein conformation.

In the case of the torsional potential, the values of K for small distortions can also be obtained from low frequency infrared vibrations. However, the energy barriers are best obtained from NMR studies. So, here is another example where Physico-chemical methods can lead to valuable information for the understanding of biochemical phenomena.

## 7. APPLICATION OF POTENTIAL FUNCTIONS TO PROTEIN CONFORMATION

One of the most important of the applications of potential functions to the field of protein structure is the determination of the most suitable helical conformations of protein or polypeptide chains. It is readily seen that, if the backbone of a chain composed of peptide units has helical symmetry, then the values of (  $\phi_i$  ,  $\psi_i$  ) will be the same for all values of i in the helix. The energies of such helical conformations have been worked out by a number of authors  $(2, \overline{4} - 7)$ . Figure 8 shows the potential energy map in the (  $arphi,\,arphi$  )-plane for such a heli+ cal chain worked out in our laboratory. It will be seen from this that a region near about (120°, 130°) is particularly favourable with reference to non-bonded potential energy. Simple mathematics, using matrix theory, enables one to calculate the elements of the helices corresponding to a particular (  ${\mathscr G},\,{\mathscr V}$  ) and this shows that the above stable conformation is close to that of the alpha helix, which was postulated for proteins by Pauling and coworkers a number of years ago from stereochemical considerations. The alpha helix is further stabilized by the formation of a hydrogen bond between an NH group of a unit and the carbonyl oxygen atom of a unit three steps behind it and this makes the alpha helix a particularly common feature in the structure of many proteins and synthetic polypeptides. It is further found, as may be seen from Fig. 8, that, for L peptide units the right-handed alpha helix has a lower energy than the left-handed helix ( as was first shown in Ref. 6). In fact, only the right-handed helix has been observed in proteins and most polypeptides. The only exception is poly-  $\beta$ -benzyl-L-aspartate in which case a conformation similar to the left-handed alpha helix is observed, which has been explained<sup>(5)</sup> by electrostatic effects between the side chain and backbone atoms in this particular polymer.

Although the specific type of hydrogen bonding between units n + 4 and n was postulated by Fauling a long time ago and has been found to be of common occurrence, a systematic computer survey of such possible hydrogen bonds was undertaken only recently, in our laboratory. This led to the discovery that another type of helix, called the  $3_{10}$ -helix (first proposed by Bragg and others) which has hydrogen bonds

The amino acids and peptide units, out of which a protein chain is built up, have asymmetric carbon atoms, and the two possible absolute configurations at this atom are denoted by L and D respectively. Of these, only the L-configuration occurs in all the proteins that occur in living systems. between units n + 3 and n, is a reasonable structure<sup>(3)</sup>. It was also found that various other types of hydrogen bonded structures that have been proposed do not have favourable stabilising energies. The potential energy map (Fig. 8) shows a slightly lower energy for the conformation corresponding to the  $3_{10}$ -helix than for the alpha helix. On the other hand, the hydrogen bonds themselves are quite good for this helix. It is interesting that this  $3_{10}$ -helix has actually been observed to occur in the chain structure of the protein lysozyme.

The above facts, which form a cross section of some of the studies made in this field, indicate that the potential energy method can lead to very useful information regarding the likely stable protein conformations. In view of this success of the theory, it has been sought to be applied in various structures like cyclic peptides; both by others and in our own laboratory. We shall not discuss these in full, except to say that such studies have led to useful methods for working out the minimum energy conformation for systems represented by several variable parameters. Again, although we had discussed essentially protein and polypeptide conformations, the ideas regarding the potential functions which we have considered are also applicable to other types of polymers and biopolymers (13-15). They are also applicable to the conformation of simple melecules (i.e. the actual relative orientation teken up by the groups which are capable of taking free rotation in their most stable . state). Thus, the formulae discussed above have been applied in our laboratory for the study of polysaccharides and have been found to agree well with observation (14). In making the study, it was necessary to first obtain the most stable conformation of the sugar residue out of which the polysaccharide is built up and this led to a study of the stable conformation of various sugars by the potential energy method and this again has yielded results in agreement with observations (15). More recently, the same method has been applied to the amino acid molecule, whose residue forms the chemical building block of proteins (V.Sasisekharan and P.K. Ponnuswamy -Unpublished). In this case, certain generalisations had been arrived at earlier regarding the behaviour of various amino acids in the conformations that they take up (see Ref. 7 for details about the nature of these conformations), but these were empirical. However, they have now become understandable on the basis of potential energy calculations. '

## 8. APPLICATION TO CRYSTAL LATTICE STABLITY

Following the main theme of this lecture, we shall now indicate how the potential functions of the same type which have had success in the field of protein conformation have also been applied for the study of the stability of crystal structures. The most interesting of such studies have been that of Kitaigorodsky in  $Moscow^{(16)}$ . He examined the location and orientation of the molecules of naphthalene and anthracene in the unit cell of their respective crystal structures. These effects can be represented by two types of degrees of freedom, one translational and the other rotational,





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the later of which can be most readily represented by Eulerian angles. Kitaigorodsky used the potential functions given in Equation (6) and obtained a variation of the stabilizing energy with the values of the relevant parameters as shown in Fig.9. It will be seen the positions of minima agree fairly well with the actual values observed. More recently, a similar study has been made in hexamethylbenezene with success<sup>(17)</sup>.

Liquori and his collaborators<sup>(13)</sup> studied the structures of simple polymers and found that a suitable set of potential functions could give their chain structures very satisfactorily. They adopted the same function later for polypeptide chains (6) as already mentioned. In our laboratory, the crystal structure of silk, which is obtained by packing the chain of a polymer, which is effectively poly (glycyl-Lalanyl) has been studied in terms of non-bonded interactions (C.M. Venkatachalam. unpublished). In Bombyx mori silk, the two neighbouring chains are known to be antiparallel. On the other hand, in the structure of poly-L-alanine, they are believed to be parallel. Making use of this information, and the covalent bond lengths and angles of the peptide unit as shown in Fig. 2, the distance, a, between the two chains was varied and the variation of energy with distance was determined. It was found that the minimum occurred very near a value of a = 4.75 A, which corresponded to the actually determined values as determined by X-ray studies. Although the hydrogen bonding energy was neglected in this study, since the hydrogen bond is expected to be good for a  $\sim$  4.75 A, the fact that the non-bonded energy is a minimum for the observed value of a is significant. This shows that the method of minimisation of potential energy can give the crystal structure to a reasonably good degree of approximation.

Therefore, there is now a need for working more examples of organic crystals of both simple and small complex molecules, as well as ordered crystal structures of polymers and polypeptides, from the point of view of potential energy and comparing the stable conformations derived in this way with the actually observed ones. In this way, it should be possible to obtain the best set of potential functions which fit the variation of the energy of interaction between atoms which normally occur in organic molecules. I am focussing attention on organic molecules as we have been primarily interested in proteins and biopolymer structures and in the types of information which physical methods can give, and which would be of use in predicting the secondary structures of these polymers. Studies of the above type should preferably first be made on compounds which do not have hydrogen bonds, so that the electrostatic, non-honded and intramolecular potential functions may first be evaluated as a function of the distance and other parameters describing the molecular systems. Afterwards, if the same functions are applied to examples with hydrogen bonds, the formulae for hydrogen bonds may be rigorously tested. At present, semi-empirical formulae are available for hydrogen bonds, but their agreement with observation has It is well-known that in the field of inorganic crystals not been carefully tested. such as alkali halides, not only the data on crystal lattice dimensions and energy

of formation, but also those on elastic constants, compressibility and such other parameters, which depend on the variation of the stable structure with some physical quantity, have used for obtaining the best parameters for the potential functions. In a similar way, if data on elastic constants of organic crystals are obtained, these will give additional data on the variation of the potential functions near the equilibrium configurations.

The vibration spectra of simple inorganic crystals like alkali halides have also been used for obtaining information on the interatomic forces. However, such information is likely to be not convenient in the case of molecular crystals, since the vibration spectra of a molecule in the crystalline state will not differ very much from that of the free molecule. This is also because the force constants corresponding to vibrations are in the region of 1,000 cm<sup>-1</sup> and above, and these are much larger than those corresponding to intermolecular bonding. The one exception is the effect of hydrogen bonding on infrared frequencies. Significant variation in the frequencies have been observed and these have been used to obtain some information on the hydrogen bonding potentials. However, this line of study should be explored further and utilized to obtain more critical data on the forces involved in hydrogen bonding.

# 9. POSSIBLE APPLICATIONS OF FOTENTIAL FUNCTIONS IN OTHER FIELDS

A comparison with the contact map and the potential energy map of polypeptide chains, as seen in Figs. 4, 5 and  $\theta$  shows that when the contacts are unfavourable the potential energy rises very sharply by several kcal/mole. Therefore, by calculating the potential energy of conformations it should be possible to find out those conformations which are unlikely to occur for a molecule. This is likely to be more reliable than a mere examination of the contact distances. The same considerations can also be used for finding out whether a certain postulated structure is possible or not for an organic molecule. The organic chemists usually test such a question by making space-filling models of the molecules concerned and finding whether they are capable of being built. This method is obviously not very accurate, as many of the models have fixed bond angles and the relative freedom of the degree of rotation about single and double bonds are not correctly represented in the models. For instance, it would be very difficult to obtain a model having the partial double bond in a peptide unit, which normally leads to a planar conformation, but is yet flexible enough to have an appreciable non-planar distortion. In fact, precise data obtained from the potential energies of the type we have discussed could be for making more realistic models of molecules and polymers. On the other hand, they could be directly used in a computer program for working out the energies of different structures, or conformations, of molecules. These could then be used for predicting the possibility of forming such molecules. Thus, in some recent studies in our laboratory, it has been found that

the cyclic disulphide cysteinyl cysteine is a possible structure, which however, has to be built out of the so-called <u>cis</u> peptide units, which occur also in the cyclic dipeptides of other amino acids (diketopiperazines). The cyclic tripeptide cyclotriprolyl has also been found to be possible with <u>cis</u> peptide units. Theoretical considerations seem to indicate that, in this case, although cyclotriprolyl is possible, such a cyclic tripeptide is unlikely to exist in this form for other amino acids. On the other hand, cyclic tetrapeptides are expected to occur readily, since they can be easily built out, of trans peptide units, although a slight nonplanar distortion is required. The compound cyclotetraalanine has been reported in the literature. Thus the synthetic organic chemist will find much use for the types of potential functions discussed here in predicting whether a particular type of molecule can be built or not.

It is indeed rather surprising that essentially physical considerations like those we have indicated above have come to the forefront from the need for understanding the structure of compcunds of biochemical interest. Scientific research now-a-days is progressing in a direction in which there is a fusion of the standard disciplines such as Physics, Chemistry and Biology. The aim of this lecture has been to draw attention to the need for one more such inter-disciplinary interaction where it is felt that good progress can come by making use of the knowledge from one field, namely biopolymer conformation, in other, namely intermolecular forces and crystal lattice stability, and vice versa.

#### ACKNOWLEDGEMENT

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| VARIATIC          | N OF EFFECTI<br>BETWEEN TH | VE DIFLECTRIC<br>E CHARGES IN | A SPHERICAL CA   | WITH DIST  | ANCE                    |
|-------------------|----------------------------|-------------------------------|--|--|-------------------------|
|                   |                            |                               |  | ,<br>,<br>,  |                         |
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| 0.0<br>0.2<br>0.5 | 1.00<br>1.24<br>1.72       | 1.00<br>1.45<br>2.89          | 1.00<br>1.60<br>3.70   | 1.00<br>1.62<br>4.69   | 1.000<br>1.625<br>5.000 |

\* E = Dielectric Constant of medium outside the cavity, .

= d/a, where 2d = distance between the charge X

2a = diameter of cavity.

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# CONTRIBUTED PAPERS

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#### OCCURRENCE OF SUPERCONDUCTIVITY IN ELEMENTS

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# ABSTRACT

If the clear distance between two metal ions is plotted vs the nearest neighbour distance, an interesting fact is discovered that all the superconducting elements conglomerate in a certain region of the plot, called "the island of superconductivity". This simple empirical correlation suggests that : considering the ion core as a "hard core" in space for the conduction electrons, which participate in interactions leading to superconductivity, the conduction electron wave functions are modified and this leads to a correction to the coulomb and electron-phonon interaction matrix elements. A model calculation of superconducting state parameters, the effective electronphonon interection strength and coulomb pseudopotential, in which the ionic core is replaced by a 3-dimensional constant repulsive potential and conduction electron state is calculated in Wigner-Seitz approximation and first order perturbation theory is performed.

While previous attempts to develop a criterion of superconductivity, using retarded electron-phonon interaction and Green function approach, (e.g. Morel and Anderson) perdict all metals to be superconductors we find that (1) alkali and alkaline earth metals are perdicted to be nonsuperconductors definitely and (11) a better agreement than before is obtained between theoretically estimated and empirical parameters.

#### LATTICE THERMAL CONDUCTIVITIES OF ALLOYS AT LOW TEMPERATURES

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# INTRODUCTION:

In pure metals; electrons are the major carriers of heat and phonons contribute very little. But by suitably alloying a metal, the electronic part can be brought down to make it comparable to the lattice part of the conductivity. This sort of alloying also influences the phonon distribution as well as the phonon conductivity. So, to find the lattice conductivity of a metal, it is first necessary to investigate the mode of change of lattice thermal conductivities of alloys with the change of concentration of solutes. With this view we have studied the thermal conductivities of Cu+2% Zn, Cu+5% Zn, Ag+2% Zn and Ag+4.46% Zn in the temperature range  $16^{\circ}$  to  $90^{\circ}$ K.

#### EXPERIMENTAL RESULTS:

The samples are prepared from spectroscopically pure rod of copper, silver and zinc rod supplied by M/s. Johnson and Mathey Co. Itd., London. The alloys were rolled in rod forms and annealed in evacuated sealed glass tubes at about 400° C for six hours. They were mounted in position by means of copper formers to which the specimens are soft soldered. Our apparatus is designed with a view towards simultaneous measurement of electrical and thermal conductivities. The experimental substance is mounted horizontally to the liquid chamber with the help of a copper plug. The temperature difference is measured by helium gas thermometers connected a differential manometer filled with Butyl Pthalate of a compact differential cil and absolute manometer. To avoid electrical short circuit, both the thermometers are electrically insulated from the specimen but thermally well connected. This is done by covering the copper strips attached to the thermometers with a layer of nail polish, and cigaratte paper, baking and adding fresh polish and wrapping this copper foil and finally baking it to harden the polish.

Measurements were taken at liquid hydrogen, nitrogen and oxygen temperatures and by pumping them through Cartesian manostat  $\binom{1}{2}$  which keep the vapour pressure of the boiling liquid fairly constant.

#### RESULTS AND DISCUSSIONS:

The total thermal conductivity is

 $\mathbf{K} = \mathbf{K}_{o} + \mathbf{K}_{o}$ 

where K and K are electronic and lattice components. Also,

$$1/K_e = W_e = W_i + W_o$$

where W, and W, are ideal and residual thermal resistivities respectively.

.(2)

is given by  $W_{o} = \int_{0}^{0} / L_{c} T$ 

where  $P_0$  is the resisual electrical resistivity,  $L_0$ , the Lorenz number,  $P_0$  is determined by extrapolating the resistivity - temperature curve to absolute zero temperature. Since our temperature range  $W_i$  of the alloy cannot be measured, we have taken  $W_i$  of the alloy to be the same as that of pure metal. Fig. 1 shows the temperature variation of thermal conductivity of the alloys.

At temperature near and above  $\theta_D/5$ ,  $\theta_D$  being the Debye temperature, theoretically it can be shown<sup>(3)</sup> that scattering due to anharmonic interactions between lattice waves and scattering of lattice waves by point defects are major factors which cause thermal resistivities ( $W_u$  and  $W_p$  respectively), and both of them vary directly as temperature. Thus

.....(3)

The following tanles shows the electronic and lattice part separately. It is seen that  $\frac{W}{g}$  T remains practically constant in the region  $60^{\circ} - 90^{\circ}$ K for alloys of higher percentages. But for alloys of lower percentage slight deviation from the theory has been observed.

W has been further separated into W and W with the help of the theoretical expression of W given by Liebfried and Schlomenn<sup>(4)</sup>.

 $1/W_{\rm u} = 3.61 \ {\rm a} \ {\rm A} \ {\rm e}_{\rm D}^{3}/{\rm Y}^{2} {\rm T} \ {\rm watt} \ {\rm cm}^{-1} \ {\rm deg}^{-1}$  .....(5)

where a is lattice constant, A, the atomic weight,  $\Theta_D$ , Debye temperature, and  $\Upsilon$ , Gruneisen parameter.  $\Upsilon$  for copper and silver as calculated from expansion coefficients, specific heat and compressibility are 2.0 and 2.4 respectively.  $W_u/T$  from expression (5) comes out to be 0.169 and .0556 watt<sup>-1</sup> cm for Cu+5% Zn and Ag+4.46% Zn respectively. vely: This means that  $W_D/T$  in these cases are .0136 and .0213 respectively.

#### ACKNOWLEDGEMENTS

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#### DISCUSSION:

S.K. Sen : During preparation, the alloys were maintained at a temperature near their melting points for six to seven days and then annealed for about six hours at 400°C.





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|                  | Temp.<br>in<br>( <sup>°</sup> K) | Total<br>Conducti-<br>vity of<br>the alloy<br>watt cm <sup>-1</sup><br>deg <sup>-1</sup> | Residual<br>Resistivity<br>of the alloy<br><sup>W</sup> o<br>watt <sup>-1</sup> cm deg. | Electronic<br>Conductivity<br>Kg<br>watt cm <sup>-1</sup><br>dg <sup>-1</sup> | Lattice<br>Conducti-<br>ty Kg<br>watt cm-1<br>dg-1 | Iattice<br>Resisti-<br>vity/Tem-<br>perature<br>Wg/T<br>watt-1<br>cm |
|------------------|----------------------------------|--|---|---|--|--|
| Cu +<br>2% Zn    | 60                               | 2.64   | .30477  | 2.327   | •313   | •05 <b>33</b>  |
|                  | 70                               | 2.76   | .26123  | 2.352   | -408   | .0350  |
|                  | 80                               | 2.92   | .22858  | 2.397   | •523   | .0239  |
|                  | 90                               | 3.04   | .20318  | 2.404   | •636   | .0175  |
| Cu +<br>5% 2n    | 60                               | 1.72   | •709552   | 1.198   | .522   | .0319  |
|                  | 70                               | 1.76   | .60816  | 1.295   | •465   | •030 <b>7</b>  |
|                  | 80                               | 1.80   | .53214  | 1.387   | •413   | •030 <b>3</b>  |
|                  | 90                               | 1.84   | •47301  | 1.458   | •382   | .0291  |
| Ag +<br>2% Zn    | 60                               | 1.392  | 1.123   | •754  | .638   | .0261  |
|                  | 70                               | 1.512  | •962  | .833  | .679   | •02 <b>10</b>  |
|                  | 80                               | 1.632  | •842  | •921  | •711   | .0176  |
|                  | 90                               | 1.755  | •748  | 1.002   | •753   | .0148  |
| Ag +<br>4.46% Zn | 60                               | •690   | 2.357   | •390  | •300   | •0555  |
|                  | 70                               | •705   | 2.020   | •443  | •262   | •0545  |
|                  | 80                               | •720   | 1.768   | •497  | .223   | •0561  |
|                  | 90                               | .730   | 1.571   | •549  | .181   | .0614  |

TABLE I

MAGNETIC HYPERFINE INTERACTIONS OF <sup>119</sup>Sn IN GdSn<sub>3</sub> AND CeSn<sub>3</sub> AT 4.2°K

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#### INTRODUCTION:

The Mossbauer investigation of rare-earth alloys yileds very valuable information regarding the magnetic interactions in these materials. In this paper is described a study of <sup>119</sup>Sn hyperfine interactions using Mossbauer effect in the rare earth-tin alloys of Cu<sub>3</sub>Au type viz. GdSn<sub>3</sub>, EuSn<sub>3</sub> and CeSn<sub>3</sub> in the range of temperatures  $4^{\circ}$  - 300°K. In GdSn<sub>3</sub> and EuSn<sub>3</sub> the observed spectra have been interpreted as arising due to the long relaxation time of the rare-earth ions which might be expected from the fact that Gd<sup>3+</sup> and Eu<sup>2+</sup> are S-state (<sup>8</sup>S<sub>7/2</sub>) ions as revealed by their EPR spectra<sup>(2)</sup>. CeSn<sub>3</sub> shows interesting magnetic properties<sup>(1)</sup> and Mossbauer spectra resulting from the conversion of the normally trivalent Ce ions to the quadrivalent state and the onset of incipient ferromagnetism below 100°K.

## RESULTS:

(i)  $GdSn_3$  and  $EuSn_3$ : The spectrum of <sup>119</sup>Sn in  $EuSn_3$ , was taken at 80°K and 300°K while the spectrum in  $GdSn_3$  was taken at  $4.2^{\circ}K$  as well. At 300°K the Mossbauer spectra were simple quadrupole doublets. At 80°K the spectra (shown in Fig. 1 for  $GdSn_3$ ) are seen to be quite complicated in both the cases. The spectrum of <sup>119</sup>Sn in  $GdSn_3$  at  $4.2^{\circ}K$  shows clearly the smaller peaks on either side of a central absorption due to a distribution of hyperfine fields at the tin site.

(ii) CeSn<sub>3</sub>: At room temperature CeSn<sub>3</sub> shows a simple quadrupole-split spectrum. At  $80^{\circ}$ K, however, there appears four peaks in the Mossbauer spectrum corresponding persumably to the two portions of the alloy in which Ce ions are trivalent and quadrivalent respectively. The interesting spectrum at  $4.2^{\circ}$ K (Fig. 2) consists of a central quadrupole doublet corresponding to a non-magnetic phase and a six-line spectrum resulting from a magnetically ordered phase.

### DISCUSSION:

(i) GdSn<sub>3</sub> and EuSn<sub>3</sub>: The g-values of the RE ions were somewhat less than two, indicating a sizable conduction electron polarization resulting from the interaction between the rare-earth spins and the conduction electron spins. This interaction may be written in the form

 $\mathcal{H}_{ex} = -\mathcal{T}\vec{s} \cdot \vec{b}$  .....(1)

where  $\vec{s}$  and  $\vec{s}$  are the spins of the rare-earth ion and the conduction electron respectively and  $\vec{\tau}$  is the strength of the exchange coupling between them. This type of interaction leads to a spin polarization of the conduction electrons which is oscillatory in space and localized around the paramagnetic atom. In rare-earth alloys it is possible to obtain the sign and magnitude of the exchange coupling from EFR (gshift), NMR (Knight shift) and Mossbauer hyperfine structure studies. These effects





Gd Sn 3

300

RELATIVE COUNT RATE

90

are normally derived on the basis of the Ruderman-Kittel-Kasuya-Yosida (RKKY) theory<sup>(3)</sup>. The g-shift is given by

$$\Delta g = \frac{3Z}{4E_{\rm F}} \qquad \dots \dots (2)$$

where Z is the average number of conduction electrons per atom and  $E_{p}$  is the Fermi energy. The Knight shift k of the nucleus of a non-magnetic atom in a rare-earth is given by (4)

$$\mathbf{k} = \mathbf{k}_{0} \left[ 1 - \frac{3\pi z(\mathbf{g}_{J}-1)\Upsilon \mathbf{M}}{N\mathbf{g}_{J}\beta^{2}} \sum_{j} \mathbf{F}(2\mathbf{k}_{F}\mathbf{R}_{j}) \right] \qquad \dots \dots (3)$$

where  $g_j$  is the Lande g-factor of the rare-earth ion and  $F(x) = (x \cos x - \sin x)x^{-4}$ is a damped oscillatory function. The summation in Eq.(3) is over all the rare-earth ions whose distance from the resonant nucleus are  $R_j$ .  $k_0$  is the Knight shift in a non-magnetic rare-earth alloy (LaSn<sub>3</sub> in our case). In a similar fashion, the field  $H_{eff}$  in the ordered state is given by

$$H_{eff} = k_0 \left[ \frac{3\pi z}{\beta} \left( \sum_{j} \langle s_z \rangle \right) F(2k_F R_j) \right] \qquad \dots \dots (4)$$

The magnetic susceptibility of GdSn<sub>3</sub> measured by Tsuchida and Wallace<sup>(1)</sup> in the temperature range 1.2 -  $300^{\circ}$ K, did not reveal any magnetic ordering. It is therefore surmised by us that the Mossbauer spectra of <sup>119</sup>Sn in GdSn<sub>3</sub> at  $80^{\circ}$ K and  $4.2^{\circ}$ K and EuSn<sub>3</sub> at  $80^{\circ}$ K are due to the long relaxation times of the Gd<sup>3+</sup> ions. These alloys in which the rare-earth ions Gd<sup>3+</sup> and Eu<sup>2+</sup> occur in the S-state are indeed admirably suited to show such effects at low temperature.

The spin-lattice relaxation time  $T_1$  at low temperatures is given by the following equation.

Using the value of  $\Delta g$  obtained earlier from the EPR data<sup>(2)</sup> it is estimated that  $T_1 = 10^{-8}$  sec which is of the order of the Larmor period  $T_L \approx 10^{-8}$  sec of  $^{119}$ Sn nucleus in these alloys.

In the paramagnetic state with randomly relaxing  $\mathrm{Gd}^{3+}$  ions, it is obvious that the field at <sup>119</sup>Sn nucleus is not unique. The crystal field splitting of rare-earth S-state ions is less than  $0.1^{\circ}\mathrm{K}$  while the Zeeman splitting is at least a few  $^{\circ}\mathrm{K}$  in alloys like  $\mathrm{GdSn}_{3}$ . One can therefore neglect the former and consider only the Zeeman split manifold of 8 sub-levels of the  $^{8}\mathrm{S}_{7/2}$  ground state of  $\mathrm{Gd}^{3+}$ . To calculate the probabilities of various hyperfine fields at <sup>119</sup>Sn we consider for simplicity only the four nearest neighbours to each tin atom. Then from Eq.(4) it is obvious that the net hyperfine field at <sup>119</sup>Sn is proportional to the sum of the S<sub>z</sub> values at the four rare-earth neighbours. In this manner a theoretical spectrum is calculated and is shown in Fig. 1. Best agreement between experiment and theory is obtained for  $|\zeta| = 0.25$  eV. This may be compared with a value of  $\zeta = -0.28$  eV obtained from g-shift measurements on  $\operatorname{Gd}^{3+}$  and  $(=-0.3 \text{ eV} \text{ obtained from Knight shift measurements}^{(5)}$  on  $\operatorname{PrSn}_3$  and  $\operatorname{NdSn}_3$  - which are isostructural with  $\operatorname{GdSn}_3$  and  $\operatorname{EuSn}_3$ . (ii) CeSn<sub>3</sub>: The Mossbauer spectrum of <sup>119</sup>Sn in CeSn<sub>3</sub> at 4.2°K may be explained on the basis of susceptibility measurements of Tsuchida and Wallace<sup>(1)</sup>. Near and above 300°K the susceptibility follows a Curie-Weiss law with a free ion Ce<sup>3+</sup> moment. At lower temperature, there is a large decrease from the expected value with a minimum at 30°K after which it again increases sharply. This behaviour has been explained by supposing that at low temperatures a fraction of Ce<sup>3+</sup> ions become Ce<sup>4+</sup> which are non-magnetic. Below 30°K there arises a ferromagnetic phase presumably in the part of the material in which Ce is trivalent. Our results support this conclusion. The value of H<sub>int</sub> = 65 KOe is in good agreement with that (61 KOe) obtained from the Knight shift versus susceptibility data<sup>(5)</sup>.

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#### DISCUSSION:

A.N. Garg : 1. How did you make the alloys?

2. How many number of counts did you record to reduce the statistical error?

| .R.P.M. Rao : | 1. The constituent elements were taken in the stoichiometric |
|---------------|--|
|               | ratios in a silica tube and sealed off under vacuum and then |
|               | heated to the required temperature in an induction furnace.  |
|               | 2. I think it is shout $\mathbf{A} = 10^5$ counts.           |

S.K. Malik :  $f(2k_{\mu}R)$  is a sensitive function of  $k_{\mu}$ . It can change the value of  $\zeta$ . How did you take the proper value of  $k_{\mu}$ ?

K.R.P.M. Rao : The value of  $k_{\mathbf{p}}$  is so chosen as to get good agreement between the values of  $\mathcal{T}$  derived from the Knight shift data, the paramagnetic Curie temperature and the g-shift data.

A.S. Chakravarthy : Has anybody calculated the exchange integral from the theoretical standpoint and if so, how does it compare with your experimental observation?

R. Vijayaraghavan : I think Freeman and Watson have done such calculations.

LOW TETPERATURE ANOMALOUS PROPERTIES OF DILUTE MAGNETIC ALLOYS \*

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In recent years, the effects of magnetic element impurities in metals have been of considerable interest both from theoretical and experimental view points. The absence or presence of magnetic moments and associated electronic properties e.g. electronic transport<sup>(1)</sup>, magnetic susceptibility, low temperature specific heats, anomalous thermoelectric power  $\binom{2}{2}$  and the superconducting transition temperatures  $(3)(T_{2})$  have been extensively studied. In particular, It is found that dilute alloys containing paramagnetic impurities (e.g. Fe, Mn in Ag, Au, Cu etc.) exhibit a minimum in the resistance and very large values of thermoelectric power at a certain value of temperature. Kondo<sup>(4)</sup>, based on the assumption that these anomalies arise only when the impurities carry a net magnetic moment, proposed a theory making use of the usual s-d exchange interaction. However, there have been a few observations of resistance minima<sup>(5)</sup> in systems in which localized magnetic moments on the impurity centres do not seem to occur (e.g. Fe in Ti). Furthermore, it is experimentally found that the impurities carrying a net magnetic moment decrease the superconducting transition temperature of the host metal, whereas for certain systems namely solid solutions of Ti with Fe, Co, Cr, Mn, Ru etc. and Zr with Co, Rh, Ir etc. where no net localized magnetic moment has been observed experimentally. T is increased in the low concentration regions.

In what follows we propose an interaction mechanism which consists of a combination of potential scattering of conduction electrons by impurity ion cores and a generalised exchange and coulomb type interactions of the conduction electrons with the electrons of the impurity atoms.

## INTERACTION HAMILTONIAN :

We consider an alloy containing N<sub>I</sub> paramagnetic impurity atoms. Each impurity atom is assumed to contain two localized electrons, either in the singlet or triplet state. In addition to occupied localized states we assume localized empty states at an impurity atom located above the Fermi level of the host metal. The possible interactions between the conduction electrons and the impurity atoms considered here are the following. First, we have the potential scattering in which a conduction electron is scattered by the impurity potential. Then we take into account the generalized Coulomb and exchange type interactions, in which the conduction electrons are scattered with or without spin flip, together with the virtual orbital excitation and deexcitation of impurity electrons. Such processes involve orbital transition to empty impurity states.

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Thus the Hamiltonian for a dilute alloy containing N<sub>1</sub> impurity atoms can be written as:

where

$$H = H_{0} + H_{I}$$

$$H_{0} = \sum_{k\sigma} \in \sum_{k\sigma} C_{k\sigma} - C_{k\sigma} + \sum_{li\sigma} E_{li\sigma} C_{li\sigma}$$

$$H_{0} = \sum_{k\sigma} \in \sum_{k\sigma} C_{k\sigma} - C_{k\sigma} + \sum_{li\sigma} E_{li\sigma} C_{li\sigma}$$

$$H = H_{11} + H_{2}$$

$$H_{1} = \frac{1}{N} \sum_{l \neq k'} U_{k'}^{k'} (l) C_{k'\sigma}^{+} C_{k'\sigma}$$

$$H_{2} = \frac{1}{N} \sum_{\substack{k \neq 0 \\ li \neq k'}} \left[ U_{li \neq k}^{\lambda i \neq k'} C_{li\sigma}^{+} C_{li\sigma} + C_{k'\sigma} C_{k'\sigma} + h \cdot a \right]$$

$$H_{2} = \frac{1}{N} \sum_{\substack{k \neq 0 \\ li \neq k'}} \left[ U_{li \neq k'}^{\lambda i \neq k'} C_{li\sigma}^{+} C_{k'\sigma} + h \cdot a \right]$$

$$H_{2} = \frac{1}{N} \sum_{\substack{k \neq 0 \\ li \neq k'}} \left[ U_{li \neq k'}^{\lambda i \neq k'} C_{li\sigma}^{+} C_{k'\sigma} + h \cdot a \right]$$

$$H_{2} = \frac{1}{N} \sum_{\substack{k \neq 0 \\ li \neq k'}} \left[ U_{li \neq k'}^{\lambda i \neq k'} C_{li\sigma}^{+} C_{k'\sigma} + h \cdot a \right]$$

$$H_{2} = \frac{1}{N} \sum_{\substack{k \neq 0 \\ li \neq k'}} \left[ U_{li \neq k'}^{\lambda i \neq k'} C_{li\sigma}^{+} C_{k'\sigma} + h \cdot a \right]$$

$$H_{2} = \frac{1}{N} \sum_{\substack{k \neq 0 \\ li \neq k'}} \left[ U_{li \neq k'}^{\lambda i \neq k'} C_{li\sigma}^{+} C_{k'\sigma} + h \cdot a \right]$$

$$H_{2} = \frac{1}{N} \sum_{\substack{k \neq 0 \\ li \neq k'}} \left[ U_{li \neq k'}^{\lambda i \neq k'} C_{li\sigma} + C_{k'\sigma} + h \cdot a \right]$$

$$H_{2} = \frac{1}{N} \sum_{\substack{k \neq 0 \\ li \neq k'}} \left[ U_{li \neq k'}^{\lambda i \neq k'} C_{k'\sigma} + C_{k'\sigma} + h \cdot a \right]$$

$$H_{2} = \frac{1}{N} \sum_{\substack{k \neq 0 \\ li \neq k'}} \left[ U_{li \neq k'}^{\lambda i \neq k'} C_{k'\sigma} + C_{k'\sigma} + h \cdot a \right]$$

$$H_{2} = \frac{1}{N} \sum_{\substack{k \neq 0 \\ li \neq k'}} \left[ U_{li \neq k'}^{\lambda i \neq k'} C_{k'\sigma} + C_{k'\sigma} + h \cdot a \right]$$

$$H_{2} = \frac{1}{N} \sum_{\substack{k \neq 0 \\ li \neq k'}} \left[ U_{li \neq k'} + C_{k'\sigma} + h \cdot a \right]$$

$$H_{2} = \frac{1}{N} \sum_{\substack{k \neq 0 \\ li \neq k'}} \left[ U_{li \neq k'} + C_{k'\sigma} + h \cdot a \right]$$

$$H_{2} = \frac{1}{N} \sum_{\substack{k \neq 0 \\ li \neq k'}} \left[ U_{li \neq k'} + C_{k'\sigma} + h \cdot a \right]$$

$$H_{2} = \frac{1}{N} \sum_{\substack{k \neq 0 \\ li \neq k'}} \left[ U_{k'} + C_{k'\sigma} + C_{k'\sigma} + h \cdot a \right]$$

Here  $C_{\mathcal{A}}^{\dagger}$  and  $C_{\mathcal{A}}$  are the fermion creation and annihilation operators respectively corresponding to the state  $|\mathcal{A}\rangle$ ,  $\in_{KO}$  is the energy of the conduction electrons in the state  $|\mathcal{K}\rangle$  and  $E_{lio}$  denotes the energy of the impurity state  $|lio\rangle$  and

The matrix element in the first term of (4) is a hybrid Coulomb interaction and that in the second term represents a hybrid exchange interaction.  $\int_{i} \frac{1}{2} \operatorname{d} \lambda_{i}$  respectively refer to the occupied and empty levels on the i<sup>th</sup> impurity site. The term  $U_{\mathbf{k}}^{\mathbf{k}'}(1)$  in equation (3) represents the potential scattering of conduction tion electrons from the core potential of the impurity atoms.

In the Goulomb type interaction the Bloch electron gets scattered from the state  $|K\sigma\rangle$  to  $|K'\sigma\rangle$ . On the other hand, in the exchange process it is scattered to  $|K'\sigma\rangle$  because of the two body interaction  $V_{12}$ . Simultaneously, for the Coulomb or exchange processes the impurity electron makes a transition from the ground state  $|li\sigma\rangle$  to excited state  $|\lambda l\sigma\rangle$  or  $|\lambda l\sigma\rangle$  respectively.

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## RESISTIVITY AND THERMOPOWER :

Before coming to the scattering process responsible for the anomalous resistivity and thermopower, it is expedient to consider the diagonal matrix elements of the botal Hamiltonian (i) with respect to certain states of interest in the present problem. For simplicity we consider the case of three electron systems consisting of one conduction electron and two localized electrons at an impurity site. It can be then easily shown that the diagonal matrix elements of the two states which are conmected by a process involving spin flip of a conduction electron with simultaneous change in the Ms value of the impurity electrons, the S value of the combined state remaining the same, differ from each other by the s-d exchange intégral.

Let us consider the various scattering processes. The transition probability connecting the states  $|\rangle$  and  $|\rangle$  involving excitation to intermediate states  $|\rangle$  is given by<sup>(6)</sup>

$$\mathbf{w}(\alpha \rightarrow \beta) = \frac{2\pi}{k} \left\{ \langle \alpha | \mathbf{H}_{\mathbf{I}} | \beta \rangle \langle \beta | \mathbf{H}_{\mathbf{I}} | \alpha \rangle + \sum_{\mathbf{r}} \langle \alpha | \mathbf{H}_{\mathbf{I}} | \beta \rangle \langle \beta | \mathbf{H}_{\mathbf{I}} | \gamma \rangle \langle \gamma | \mathbf{H}_{\mathbf{I}} | \alpha \rangle \right\} \left\{ \delta(\mathbf{E} - \mathbf{E}_{\beta}) + \sum_{\mathbf{r}} \langle \alpha | \mathbf{H}_{\mathbf{I}} | \beta \rangle \langle \beta | \mathbf{H}_{\mathbf{I}} | \gamma \rangle \langle \gamma | \mathbf{H}_{\mathbf{I}} | \alpha \rangle \right\} \left\{ \delta(\mathbf{E} - \mathbf{E}_{\beta}) + \sum_{\mathbf{r}} \langle \alpha | \mathbf{H}_{\mathbf{I}} | \beta \rangle \langle \beta | \mathbf{H}_{\mathbf{I}} | \gamma \rangle \langle \gamma | \mathbf{H}_{\mathbf{I}} | \alpha \rangle \right\} \left\{ \delta(\mathbf{E} - \mathbf{E}_{\beta}) + \sum_{\mathbf{r}} \langle \alpha | \mathbf{H}_{\mathbf{I}} | \beta \rangle \langle \beta | \mathbf{H}_{\mathbf{I}} | \gamma \rangle \langle \gamma | \mathbf{H}_{\mathbf{I}} | \alpha \rangle \right\} \left\{ \delta(\mathbf{E} - \mathbf{E}_{\beta}) + \sum_{\mathbf{r}} \langle \alpha | \mathbf{H}_{\mathbf{I}} | \beta \rangle \langle \beta | \mathbf{H}_{\mathbf{I}} | \gamma \rangle \langle \gamma | \mathbf{H}_{\mathbf{I}} | \alpha \rangle \right\} \left\{ \delta(\mathbf{E} - \mathbf{E}_{\beta}) + \sum_{\mathbf{r}} \langle \alpha | \mathbf{H}_{\mathbf{I}} | \beta \rangle \langle \beta | \mathbf{H}_{\mathbf{I}} | \beta \rangle \langle \beta | \mathbf{H}_{\mathbf{I}} | \gamma \rangle \langle \gamma | \mathbf{H}_{\mathbf{I}} | \alpha \rangle \right\} \left\{ \delta(\mathbf{E} - \mathbf{E}_{\beta}) + \sum_{\mathbf{r}} \langle \alpha | \mathbf{H}_{\mathbf{I}} | \beta \rangle \langle \beta | \mathbf{H}_{\mathbf{I}} | \beta \rangle \langle \beta | \mathbf{H}_{\mathbf{I}} | \alpha \rangle \right\} \left\{ \delta(\mathbf{E} - \mathbf{E}_{\beta}) + \sum_{\mathbf{R}} \langle \beta | \mathbf{H}_{\mathbf{I}} | \beta \rangle \langle \beta | \mathbf{H}_{\mathbf{I}} | \beta \rangle \langle \beta | \mathbf{H}_{\mathbf{I}} | \alpha \rangle \right\} \right\}$$

The expression for the relaxation time can be thus calculated with the help of (1) and (7) and one obtains for the magnetic and non-magnetic cases the following expressions:

$$\frac{1}{T_{k}^{nnag}} = \sum_{K'} w^{(3)}(K \pm \rightarrow K' \pm)$$

$$= \frac{\delta \pi}{\hbar} \frac{Z}{\epsilon_{q}} s(s+1) \frac{cv^{2}}{N} \left[ \sum_{q} \frac{fq^{p}}{(\epsilon_{k} - \epsilon_{q})^{2} - \Delta^{2}} \int_{-3U\Delta} -v(\epsilon_{k} - \epsilon_{q}) \right]$$

$$\frac{1}{T_{k}^{non-i:ago}} = \frac{36z}{\epsilon_{f}} \frac{\pi}{\hbar} ou |v|^{2} |\Delta_{f\lambda}| \qquad \dots \dots (8)$$

$$x = \frac{1}{N} \sum_{q} \frac{f_{q}^{o}}{\Delta^{2}} -(\epsilon_{k} - \epsilon_{q})^{2}$$

$$\dots \dots (9)$$

The resistivity contribution due to scattering with impurity is given as (7)
$$\int_{\mathbf{s}}^{\text{mag.}} \mathbf{r} = \frac{\mathbf{r}^2}{ne^2} \frac{1}{12 \, \pi^3} \int_{\mathbf{T}_{\mathbf{K}}}^{\mathbf{T}_{\mathbf{K}}} \frac{df_{\mathbf{K}}}{d\mathcal{E}_{\mathbf{K}}} \frac{df_{\mathbf{K}}}{d\mathcal{E}_{\mathbf{K}}} d^3 \mathbf{K}$$
.....(10)

with the help of equations (8), (9) and (10) one obtains

and

Thus the total resistivity, which will include: ideal and residual resistivity and the resistivity due to impurity will show a minimum at a certain value of temperature.

### THERMOELECTRIC POWER:

С

The

where  $f(\epsilon)$  is the total resistivity treated as a function of Fermi energy. Thus, using the expression for resistivity due to impurity of the previous section and the formula (13) one obtains,

$$\mu = \frac{\pi^2 k_B^2 T}{3 |e|\epsilon_p} \left( 1 + \frac{\rho_B}{\rho} + \frac{c\Lambda_o J}{\epsilon_p^2 \rho} \dots \dots \dots (14) \right)$$

Calculated values of thermopower with the above formula compare very well with the experimental results.

### SUFERCONDUCTING TRANSITION TEMPERATURE :

Let us first consider  $H_0$  and  $H_2$  only as the effect of interaction represented by  $H_1$  and  $T_0$  has been already considered by Suhl and Matthias. The resulting interaction between the Berdeen, Cooper and Schrieffer (B.C.S.) pairs over and above the usual B.C.S. type interaction is obtained by making use of a suitable canonical transformation which eliminates two possible conduction electron impurity electron interaction terms in first order. Thus one obtains the transformed interaction<sup>(9)</sup> Hamiltonian

$$H_{int}^{T} = -c \times \sum_{KK} c_{KM}^{T} c_{KV}^{T} c_{KV} c_{KV} (15)$$

where W is a function of impurity parameters and a +ve real quantity. The overall change in T<sub>c</sub>, including the effect of H<sub>1</sub>, following B.C.S. can be written as,

The calculated variation of  $T_c$  with c for certain systems e.g. Fe in Ti, using formula (14) compares well with the experimental results.

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MOSSBAUER EFFECT FOR 57 Fe IN NICKEL SINGLE CRYSTAL

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We describe here an attempt to study the magneto-crystalline anisotropy of nickel by Mossbauer Effect.

The existence of preferred directions of magnetization in crystals may be expressed formally in terms of energy functions which have a minimum value in that direction. For cubic crystals the expression is

$$\mathbf{E}_{\vec{k}} = \mathbf{K}_{1} (\alpha_{1}^{2} \alpha_{2}^{2} + \alpha_{2}^{2} \alpha_{3}^{2} + \alpha_{3}^{2} \alpha_{1}^{2}) + \mathbf{K}_{2} \alpha_{1}^{2} \alpha_{2}^{2} \alpha_{3}^{2}$$

where the  $\propto$  's are the direction cosines of magnetization with respect to cubic axes.  $K_1$ ,  $K_2$  are called crystal anisotropy constants and have usually decreasing order of significance. Let us consider the  $E_2$ 's in certain directions

$$E \langle 111 \rangle = \frac{K_1}{3} + \frac{K_2}{27}$$

$$E \langle 110 \rangle = \frac{K_1}{4}$$

$$E \langle 100 \rangle = 0$$

For nickel the variation of  $K_1$  and  $K_2$  with temperature have been measured<sup>(1)</sup>. Around room temperature  $K_1$  is negative and large,  $E_{\langle 111 \rangle}$  is the lowest and hence  $\langle 111 \rangle$  is the direction of easy magnetization. As the temperature increases  $K_1$  decreases in significance and at about 80°C where  $K_2 > 2|K_1|$ ,  $E < 110 \rangle$ is lowest and so the becomes the soft direction. Again when  $K_1$  drops to zero,  $\langle 100 \rangle$  is the easy magnetization. This occures at about 100°C according to this simple picture.

On the other hand, measurements of initial and maximum permeabilities for nickel by various authors<sup>(1)</sup> show maxima at about 200° and this is attributed to the change at this temperature of the direction of easy magnetization from  $\langle 111 \rangle$  to  $\langle 110 \rangle$ .

One can see clearly that these are not consistent with one another. We thought that such changes in the easy directions of magnetization can be easily demonstrated by studying the Mossbauer spectro for <sup>57</sup>Fe in a single crystal of nickel. For <sup>57</sup>Fe in the presence of magnetic hfs, the relative intensities of the

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six components are given (2) as

$$I_{1} = I_{6} = 3(1 + \cos^{2} \phi)$$

$$I_{2} = I_{5} = 4 \sin^{2} \phi$$

$$I_{3} = I_{4} = (1 + \cos^{2} \phi)$$

where  $\oint$  is the angle between the direction of the internal magnetic field and the direction of the emission of the  $\mathcal{N}$ -ray. One observes the simplest pattern along the direction of internal magnetic field, i.e., when  $\oint = 0$  or  $180^{\circ}$ . The pattern consists of only four, instead of the six lines. The transition m = 0completely discppears.

Since the direction of the internal field is parallel or antiparallel to the magnetization direction, the study of the relative intensities of the absorption lines gives the information about domain orientation. Since they are very sensitive to the changes in the domain orientation such changes can be easily seen by following the relative intensities of the Mossbauer transitions at various conditions.

Going over to the experimental part,  $^{57}$ Co actively was electrodeposited on a single crystal of nickel cut along (110) plane and diffused at about 800°C in vacuum. As a routine check the internal field at  $^{57}$ Fe nucleus at room temperature was measured using an electro-mechanical transducer, recording the Mossbauer spectrum on a multi-channel analyser. The absorber was Potassium Ferrocynide. The velocity calibration was obtained from the Mossbauer spectrum of source in copper against an iron absorber enriched with  $^{57}$ Fe. The spectra are least square fitted to a sum of Lorentzians using our CDC 3600 Computer. The obtained value for  $H_{int}$  at room temperature is 272 KOe which agrees well with other existing measurements  $^{(3,4)}$ .

We then followed the intensity pattern of the Mossbauer spectra with the crystal plane viewed at grazing incidence (Plane almost at 5° to the horizontal) detecting the gamma rays along various crystal directions and at various temperatures from 20°C to 250°C. Viewing along one of the directions, say,  $\langle 111 \rangle$  we expected a change in the relative intensities of the Mossbauer lines when there was a change in the direction of easy magnetization. There are two  $\langle 111 \rangle$  directions in the plane of the crystal, one  $\langle 111 \rangle$  along one of the edges of the crystal and the other at an angle of 70° to this edge. These were determined from an x-ray photograph.

Defining the angle  $\Theta$  to be the angle between gamma detection direction and one of the edges of the crystal as shown in Fig. 1, spectra were taken for different values of  $\Theta$  ranging from  $O^{\circ}$  to  $90^{\circ}$  at various temperatures. New representative spectra are shown in Fig. 1.



Fig. 1

We see that viewing the gauma rays  $\operatorname{along}\langle 111\rangle$  ( $\theta = 90^{\circ}$ ) an easy direction of magnetization, the intensity pattern is as though it were a hard direction, the  $\Delta m = 0$  lines being quite prounced. In the case when the gamma rays were observed along a direction perpendicular to this  $\langle 111\rangle$ , the  $\Delta m = 0$  lines were very weak. Varying the temperature up to 250°C did not change this picture as also repeated annealing at 800°C.

All these are contrary to expectations. Probably, this might be due to nickel being greatly sensitive to stress. The crystalline anisotropy if nickel is so small (unlike cobalt and iron which are strongly anisotropic) that the condition for predominant strain anisotropy, i.e.,  $3/2 \lambda_s \mathcal{C} \times K$  ( $\lambda_s$  is the magneto-striction coefficient,  $\mathcal{O}$  is the internal stress and K the crystal anisotropy) is very readily brought about. Great care has to be taken in preparing the specimen and in subsequent handling of it to avoid strain or déformation.

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#### DISCUSSION:

P.K. Iyengar : Is it possible to study <sup>57</sup>Fe in Nickel as the absorber?

T.S. Radhakrishnan

In principle it can be done. But the question of ascertaining whether the <sup>57</sup>Fe atoms have been properly sited is still there as in the case of <sup>57</sup>Co in Nickel. For the particular problem which we are looking at I do not think it offers any advantages. In fact, it might increase considerably scattering and electronic absorption.

# ON THE DIRECTION OF MAGNETIZATION IN KFeF,

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In this paper we report the spin direction in the antiferromagnetic state of the compound  $\text{KPeF}_3$ . Mossbauer spectra of this compound show<sup>(1)</sup> a temperature dependent electric field gradient (EFG) of positive sign parallel to the magnetic field at the Fe site below  $T_{\text{H}}$  (Fig.1). The positive sign of the EFG enables one to fix up the direction of magnetization uniquely as a  $\langle 111 \rangle$  axis of the lattice.

Let us first understand the origin of this EFG which is appearing even though the ligand symmetry is cubic. KFeF<sub>3</sub> has a perfect perovskite structure at room temperature with Fe at the body centre and F's at the face centres. Fe is divalent in this compound and is put in a cubic crystal field. The spectroscopic state of the free Fe<sup>2+</sup> ion is <sup>5</sup>D and the cubic crystal field splits this into a ground orbital triplet (T<sub>2g</sub>) and an excited orbital doublet (E<sub>g</sub>) with a separation of about 10,000°K. Since the spin orbit and exchange perturbations involved are much smaller compared to this separation we shall ignore the mixing of E<sub>g</sub> states with the T<sub>2g</sub> states. These T<sub>2g</sub> states have an over all cubic symmetry and being degenerate these are equally populated. This therefore, results in a net zero EFG.

These degenerate  $T_{2g}$  states can sustain a non zero orbital angular momentum and behave like the components of angular momentum, L = 1. This gives rise to the spin-orbit interaction. Under this interaction the 15-fold degeneracy (including spin degeneracy) is partially lifted and we get three degenerate states corresponding to J = 3, 2 and 1 (L = 1, S = 2). The cubic symmetry of the each set of the three sets of states is still preserved and the EFG vanishes as before. This is in the paramagnetic state and is confirmed by the experiment.

However, below  $T_{N}$ , the exchange field is present and this lifts the degeneracy completely, apart from any accidental degeneracy. Now we get a non zero EFG, because the states are no longer equally populated. Thus we see that the EFG arises because of the interplay of L = S and exchange interactions. This is also seen from the fact that when there is spin ordering the symmetry is no longer cubic.

To see the sign of this EFG, which fixes the direction of magnetization, let us look at the Hamiltonian in the ordered state. The magnetic sublattice has been shown<sup>(2)</sup> to be cubic (type G) from neutron diffraction date. Therefore, we can write the Hamiltonian in the single ion molecular field approximation as,

 $H = -\lambda \underline{L} \cdot \underline{S} + 2zg \langle S_{zn} \rangle T S_{z}$  .....(1)





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 $\mathbb{C}$ 

Here z is the direction of magnetization with the thermal expectation positive along the positive z direction. This direction is so far undefined with respect to the crystal axes. We shall now show from symmetry considerations that the magnetization direction can be only either a  $\langle 100 \rangle$  or a  $\langle 111 \rangle$  axis.

It is evident from Eq. (1) that if energy is to be minimized in the ground state, the direction of  $\underline{L}$  should be the same as that of  $\underline{S}$ . That is, the ground state has a complex wave function  $\psi_{\mathcal{V}}$ , 'running round' the z - axis. On the other hand, before the magnetic interaction is introduced, the crystal field states must be expressible as real wave functions. It follows, that there must be a conjugate state  $\psi_{-\mathcal{V}}$ , of the same energy so that  $\psi_{\mathcal{V}} \pm \psi_{-\mathcal{V}}^{\dagger}$  are real. These wave functions must satisfy the symmetry of the point group. Thus, if the z-axis is a n -fold axis of symmetry, and  $C_n$  the operator which causes a rotation through an angle  $\frac{2\pi}{n}$  about it,  $\psi_{\mathcal{V}}$  must be an eigenfunction of  $C_n$  with the eigenvalues  $e^{i\omega}$ , since  $C_n^n =$ 1, it follows that  $\alpha = 2\pi m$ , where m is an integer. Identifying the label  $\nu$  of  $\psi_{\mathcal{V}}$  with m, we can write,

If  $\Psi_{\rm m}$  and  $\Psi_{-\rm m}$  are to be distinct, then the eigen values of  $C_{\rm n}$  for these two states must be distinct. For n = 1 or 2, this is not possible with any values of m. Thus a necessary requirement is that n >2. This mean that the only two possible directions of sublattice magnetization are a <111> or a <100> . For both these cases the only possible physically distinct value of m is m = 1. Thus we obtain the wave functions  $\Psi_1$ , and  $\Psi_{-1}$ , which together with the real wave function  $\Psi_0$  give the crystal field wave functions. In the ordered state, the electronic states are a mixture of these three states. Since the ground state must have a maximum orbital momentum, it will contain a large amount of  $\Psi_{-1}$ . In terms of deorbitals,  $\Psi_{-1}$  is given by

 $\Psi_{-1} = \sqrt{\frac{1}{3}} d_{-1} - \sqrt{\frac{2}{3}} d_2$  when  $\langle 111 \rangle$  is the direction of

magnetization (2a), and  $\psi_{-1} = d_1$  when  $\langle 100 \rangle$  is the direction of magnetization (2b).

The EFG calculated using (2a) gives a positive contribution as it is in the experiment, whereas the one using (2b) gives a negative contribution. Thus the direction of magnetization must be a  $\langle 111 \rangle$  direction. Complete calculation<sup>(3)</sup> taking a  $\langle 111 \rangle$  as the direction shows a good agreement with the experiment (Fig. 1).

This magnetization direction is indirectly confirmed by the observation <sup>(4)</sup> that below  $T_N$  there is a slight elogation of the crystal along a  $\langle 111 \rangle$  direction. It can be seen from geometrical consideration that electrostatic interactions between the magnetic orbitals and the ligands lead to such a distortion<sup>(5)</sup>. REFERENCES

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DISCUSSION:

P.T. Narasimhan : Would the introduction of Jahn-Teller effect alter your results substantially?

- R. Nagarajan : No. The expected pure Jahn-Teller distortion is small in this case because of the very weak overlap between the  $t_{2g}$  and ligand orbitals. Moreover, the observed crystal distortion is opposite to pure J-T distortions and is of L-S origin. Even this is only one sixth of one per cent at 77°K and the E.F.G. due to this will be much smaller than what is observed in the experiments.
- C.M. Srivastava : What is the strength and sign of the exchange constant that is obtained from this experiment and how well does it agree with the value of the exchange constant obtained by other methods?

R. Nagarajan : The sign of the exchange constant is negative, as it should be for antiferromagnetic interaction. Our molecular field calculation gives J/k as 5.4°K when L-S coupling is included and 4.8°K when it is neglected. The inclusion of L-S coupling thus increases the estimate of J/k by about  $0.6^{\circ}K$ . More exact calculations neglecting L-S coupling give (i) by B.P.W. method 6.0°K and (ii) by Rushbrooke-Woods method, 6.7°K. Thus roughly the best value of J/k when, I-S coupling is neglected seems to be around 6.4°K. Assuming that the change on introducing L-S coupling is about the same for the molecular field calculation, we may say that  $J/k \approx 7^{\circ}K$ .

# RELAXATION AND MAGNETIC STRUCTURE STUDIES OF Croos - Fegos System

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The Mossbauer spectra of a solid solution 0.965  $\operatorname{Cr}_2O_3 - 0.035 \operatorname{Fe}_2O_3$  have been studied with a view to investigate its magnetic behaviour. Both  $\operatorname{Cr}_2O_3$  and  $\operatorname{Fe}_2O_3$ possess rhombohedral corundum type of similar crystal structure<sup>(1)</sup>. However, they differ in their magnetic structures. In the case of  $\operatorname{Fe}_2O_3$  the spins within any (111) plane are parallel and adjacent planes are coupled antiferromagnetically, while in  $\operatorname{Cr}_2O_3$  the spins are aligned antiparallel within the (111) planes. The addition of  $\operatorname{Fe}_2O_3$  creates a cone spiral<sup>(1)</sup> within each sublattice, the cone axis lying along the hexagonal C-axis for  $X \leq 0.2$ .

The measurement of resonance spectra was carried out on a 512 channel analyser operated in velocity mode with the source ( ${}^{57}$ Co in copper) mounted on a sinusoidal drive. The absorber  $Cr_2O_3 - Fe_2O_3$  was attached to the cold finger of a suitable dewar. The temperature was varied by using a heater coil placed in between the absorber and the cold finger.

The Neel temperature of this solid solution was determined to be  $289^{\circ}$ K by the stationery absorber technique. The resonance spectra were recorded at  $10^{\circ}$ K,  $80^{\circ}$ K,  $101^{\circ}$ K,  $120.5^{\circ}$ K,  $144^{\circ}$ K,  $162^{\circ}$ K,  $178^{\circ}$ K,  $209^{\circ}$ K,  $230^{\circ}$ K,  $241^{\circ}$ K,  $248.5^{\circ}$ K,  $258.5^{\circ}$ K,  $263.5^{\circ}$ K and  $293^{\circ}$ K. A few of them are shown in Fig. 1. The study of these spectra has brought out three distinct features.

1. The Zeeman splitting of the Mossbauer spectra from 10<sup>°</sup>K onwards decreases with increasing temperature.

2. Above  $101^{\circ}$ K, as the temperature is increased, there is a relative enhancement in the intensity of the central part of the spectrum. The effect is more prominent above  $200^{\circ}$ K, where with the increasing temperature the six line pattern gradually changes into five lines, the intensity of central peak increases, the outer peaks become broader, decrease in height and finally fade away leaving only a central peak.

3. There is quadrupole interaction present along with the magnetic hyperfine splitting as the separation between lines 1 and 2 is observed to be different from that of 5 and 6. However, this difference disappeares in the spectrum at  $10^{\circ}$ K.

The variation of hyperfine field with temperature is indicated in Fig. 2. A plot of reduced effective magnetic field  $\frac{H(T)}{H(BO)}$  against the reduced temperature  $(T/T_N)$  is given here. The solid line represents the theoretical reduced magnetization curve for S= 3/2. It is clear in the figure that above 100°K, the hyperfine field calculated from the total splitting, shown by dots, is more than that





Fig. 2

from the ground state splitting, shown by squares. Also the experimental points do not follow the theoretical magnetization curve.

The enhancement in intensity of the central part of the spectrum with the changing temperature and the nonequality of the two hyperfine fields, obtained from the total splitting and the ground state splitting, are interpreted in terms of relaxation phenomena as discussed by Van der Wood and Dekker<sup>(2)</sup> in the molecular field approximation. The relaxation effect arises due to the fluctuation in the Fe<sup>3+</sup> spin caused mainly by the spin lattice and spin-spin interaction. At very low temperatures when the spin flip frequency is much smaller compared to the farmor frequency, a six finger pattern is maintained. As the temperature is increased the spin flip frequency increases and when it become equal to the splitting of the two inner most lines, they start merging into a single line. On further increase of temperature in a similar way first the lines 2 and 5 and finally the lines 1 and 6 merge and a broad dingle line is left in the spectrum. Van der Wood and Dekker<sup>(2)</sup> have used the theory of motional narrowing to explain this phenomena. Using their calculation for S = 5/2, which is actually the case in a ferric ion, the calculated<sup>(3)</sup> shape of the Mossbauer spectra in the case of Fe-alum is much similar to that observed by us.

The cone half angle @ i.e. the angle which the hyperfine field makes with the electric field gradient (defined completely by  $V_{ZZ}$  along the (111) axis due to three fold symmetry in the present case) is determined with the help of our spectra at various temperatures, using the analysis given by W. Kundig<sup>(4)</sup>. In the temperature range 80°K to 240°K @ varies from 40° to 30°. At about 10°K @ had the value 55°, which is the case of zero quadrupole splitting at that temperature. Thus the geometry of the cone spiral varies slowly with temperature.

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INTERNAL MAGNETIC FIELD ON 143 Pr IN GADOLINIUM METAL

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We have used the technique of perturbed angular correlations for the study of the hyperfine interactions on <sup>143</sup>Pr embedded in ferromagnetic Gd metal. The <sup>143</sup>Pr is formed in the beta decay of <sup>143</sup>Ce. We have used 292-57 keV gamma ray cascade. The unperturbed correlation in this case is obtained using  $\text{CeO}_2^{(1)}$ , which has cubic structure and the angular correlation coefficients are given by  $A_2 = 0.114 \pm 0.004$ and  $A_4 \approx 0$ . If the angular correlation is perturbed only due to randomly oriented magnetic hyperfine interaction in Gd metal, the angular correlation would be given by  $W(0) = 1 + G_2 A_2 P_2$  (cos 0). The attenuation coefficient  $G_2$  in this case has the form  $G_2 = \frac{1}{5} \sum_{N=0}^{1} \frac{1}{1+(N\omega_L T)^2}$ . Thus from the value of  $G_2$  for such a randomly oriented magnetic interaction, one gets the larmor frequency  $\omega_L$  as the mean life  $\tau$  of the state is known to be  $\tau = (6.06 \pm 0.10) \text{ns}^{(1,2)}$  and from the value of  $\omega_L$ , one can find the hiperfine magnetic field as the magnetic moment of the 57 keV state is known <sup>(1,2)</sup>.

In our experiment, we irradiated  $\sim 1$  mg of Ce metal for a day at pile factor  $\sim 100$  in CIRUS and alloyed it with  $\sim 25$  mg of Gd metal. Since Ce is highly reactive, it was handled under oil or in argon atsmosphere. Though it would be desirable to form a more dilute alloy, the requirements of source thickness, source size and source strength make it difficult to reduce the quantity of Ce. The alloy was then pressed at one ton pressure to make it thin so that the self absorption of the 57 keV gamma ray is reduced. The sample,  $\sim 4$  mm in diameter, was then annealed at  $700^{\circ}$ C in vacuum for three hours. The angular correlation was studied at any desired temperature between  $77^{\circ}$ K and  $340^{\circ}$ K in a liquid nitrogen cryostat having a cold finger and a heater arrangement. An automated angular correlation setup was used to record the coincidence counting rate successively at seven angles between  $90^{\circ}$  and  $180^{\circ}$ . The value of  $G_2A_2$  were obtained by least squares fit of the data for various temperatures and the corresponding attenuation coefficients calculated. The results are as follows:

Temperature $290^{\circ}K$  $195^{\circ}K$  $77^{\circ}K$  $G_2$ 0.441 ± 0.0550.487 ± 0.0760.205 ± 0.044

At  $77^{\circ}$ K the observed value of  $G_2$  is very close to the hard core value  $G_2 = 0.2$ . This is to be expected as the magnetic hyperfine interaction at such low temperature would be quite strong. The attenuation at  $290^{\circ}$ K is just below the Curie temperature

of Gadolinium metal seems to be too large to be due to magnetic interaction alone. Moreover, the attenuation at 195°K is less while one would expect a much higher attenuation due to the magnetic hyperfine interaction. These results suggest that the quadrupole interaction is not negligible. As <sup>143</sup>Pr is an old proton nucleus. one may expect the 57 keV state to have a considerable quadrupole moment. Actually. our previous work<sup>(1)</sup> has shown that in a liquid source there is considerable attemiation due to time dependent quadrupole interaction. In order to see the effect of the randomly oriented state quadrupole interaction in the present case the attenuation coefficient was measured well above the Curie temperature at 350°K. The value of  $G_2 = 0.49 + 0.044$  was obtained. The attenuation in such a case is given by (3) $G_2 = \sum_{n=0,1,2,3} S_{2n} = \frac{1}{1+(n\omega_0 T)^2}$ . The observed attenuation corresponds to a quadrupole frequency \_ = 27 mc/sec. In order to ascertain that the observed attenuation was indeed due to static quadrupole interaction, we made a differential measurement. For this, a time distribution of the coincidence counts was recorded at 90° and 180° with a time to amplitude convertor. One then gets the anisotropy as a function of time and hence  $G_2(t)$ . The attenuation in such a case is given by<sup>(3)</sup>

$$G_2(t) = \sum_{n = 0, 1, 2, 3} S_{2n} \cos(n \omega_0 t).$$

The observed  $G_2(t)$  at 330°K is shown in the figure along with the computed curves for  $\omega_0 = 30$  mc/sec. and  $\omega_0 = 35$  mc/sec. It is clear that quadrupole interaction is also present and one has to consider a combined magnetic and quadrupole interaction in analysing the results.

Now, in rare earths, the major contribution to the hyperfine quadrupole interaction arises from the 4f electrons which are partially aligned due to the crystal field and such a field gradient is correlated with the magnetization of the rareearth sublattice and has the symmetry axis parallel to  $H_{eff}^{(4)}$ . The quadrupole interaction is highly temperature dependent and follows a sort of Brillonin function<sup>(4)</sup>. Under the action of such combined magnetic dipole and electric quadrupole interactions which are collinear and randomly oriented, the attenuation is given by<sup>(5)</sup>

$$G_{2} = \frac{1}{2} \sum_{N=0,1,2} g_{k}^{nN} \frac{1}{1 + (N \omega_{L}^{+} n \omega_{o}^{-})^{2} T^{2}} + \frac{1}{1 + (N \omega_{L}^{-} n \omega_{o}^{-})^{2} T^{2}}$$

Thus when  $\mathbb{N}\omega_{\underline{L}} = n\omega_{o}$  one gets a sort of resonance and the value of  $G_2$  would increase. This may be the reason why our value of  $G_2$  at 195°K is much higher than what one would expect for pure magnetic hyperfine interaction. Evaluation of both  $\omega_{\underline{L}}$  and  $\omega_{o}$  can be done if one makes a differential measurement and finds  $G_2(t)$ . This  $G_2(t)$  can be computed as a function of  $\omega_{\underline{L}}^{T}$  for various value of  $\frac{\omega_{o}}{\omega_{\underline{L}}}$ . Work on these lines is in progress.





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THE MAGNETIC HYPERFINE FIBLD AT THE PALLADIUM NUCLEI IN IRON."

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and

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The magnetic hyperfine field at the palladium nuclei in a b.c.c. iron lattice has been determined to be  $B_{hf} = (600 \pm 10)$  KG at 4.2°K by the spin-scho NMR method<sup>(1)</sup>. Preliminary data on the hyperfine field measured with integral perturbed angular correlation technique<sup>(2)</sup> at room temperature using a polarising field of 3.4 KG lead to a result which is 13% lower than that observed with the spin-scho method. In this measurement the 624-512 keV cascade in the ground state decay of <sup>106</sup>Rh was used. The discrepancy between the two results could be due to (a) the 'g' factor of the 512 keV state in <sup>106</sup>Pd (b) source preparation (c) small polarising field (d) temperature dependence of  $B_{hf}$  and (e) difference in environments for nuclei in domain walls and in domains. All these suggrations are examined below:

The 'g' factor of the 512 keV state has been measured by Korner<sup>(3)</sup> et al. They obtain a value of  $g = +0.45 \pm 0.06$ . This value of 'g' was used to evaluate  $B_{\rm hf}$  in the preliminary work<sup>(2)</sup>. As a special investigation the 'g' factor of the 512 keV state was re-measured<sup>(4)</sup>. The value obtained was  $g = 0.38 \pm 0.05$ . The two measurements do not agree very well.

Sources were prepared by electroplating the  $^{106}$ Ru activity on a 0.2 mm thick iron foil, which was bent in the form of a tube with 4mm diameter. The activity was diffused in iron in an evacuated quartz capsule. The diffusion time was varied in order to find the minimum time needed. Different diffused sources were polarised at room temperature by applying an external magnetic field of 3.4 KG. Coincidences obtained in the sequence of field directions  $+ \dots ++ \dots ++$  etc. were combined in the expression<sup>(5)</sup>

$$\mathbf{P} = \frac{C_{13} + C_{14} + C_{23} + C_{24}}{C_{13} + C_{14} + C_{23} + C_{24} + C_$$

where  $C_{13}$  denotes the coincidences between detectors 1 and 3. The quantity P-1 is proportional to  $B_{eff}$  acting on the Pd nuclei. The measurements on different samples showed that a diffusion time of about 50 hours at about 1000 °C was needed. Further measurements were done using this source.

The influence of the applied field on the P values was then investigated. The applied field was varied from 1.2 KG to 32 KG at room temperature. We concluded that at least 10 KG is needed to polarise the hyperfine field completely. A cryostat

\* Work done at the Institute of Physics, Uppsala, Sweden.

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was used to investigate the temperature dependence of the hyperfine field between the liquid helium and room temperatures. For measurements above room temperature a special heating system was constructed and used along with a temperature stabilising circuit. Using a polarising field of 21.5 KG the angular frequency was determined at sixteen different temperatures from 4.2°K to 850°C.

relation between 
$$\omega \mathcal{T}(T)$$
 and  $B_{eff}(T)$  is  
 $B_{eff}(T) = \omega \mathcal{T}(T)$ .  $\frac{B_{ext}}{\omega \mathcal{T}_{ext}} = \omega \mathcal{T}(T)$ . (1)

where K is obtained from the liquid source measurement for the 'g' factor measurements. The effective field acting on the Pd nuclei can be expressed as the sum

$$B_{eff}(T) = B_{hf}(T) + B_{o} + (\frac{4\pi}{3} - D) H_{o} \cdot \frac{M_{T}}{M_{o}}$$
 .....(2)

where  $B_0$  is the applied field,  $M_0$  the spontaneous magnetization at  $0^{\circ}$ K, D the demagnetization factor and  $\frac{M_T}{M_0}$  the reduced magnetization at  $T^{\circ}$ K. Inserting the expression for  $B_{eff}(T)$  given by (1) and (2) and using  $B_0 = 21.5$  KG and  $M_0 = 1.74$ KG one gets

$$B_{hf}(T) = \omega T(T) \cdot K - 21.5 - 7.15 \frac{M_T}{M_0}$$
 ....(3)

Using  $K = (319 \pm 34) 10^2$  KG/rad from ref. 4 the result for the hyperfine field is  $B_{-}(4.2^{\circ}K) = -(584 + 63)$  KG.

which is in agreement with the spin echo value. If one uses 
$$K = (270 + 26)10^2$$

KG/rad from ref. 3 one obtains,

The

$$B_{h,p}(4.2^{\circ}K) = (499 \pm 49) KG$$

which differs from the spin echo value by 17%.

 $\{ \}_{j}$ 

The temperature dependence of  $B_{hf}$  is expressed by the ratio

$$R(T) = \frac{B_{hf}(T)}{B_{hf}(4.2^{\circ}K)}$$

Using the expression for  $B_{hf}(T)$  given by Eq. (3),  $\omega T(4.2) = -0.01739$  rad. Eq. (4) yields  $R(T) = -54.70 \ \omega T(T) + 0.0368 + 0.0123 \ MT/M_0$  .....(5) The reduced hyperfine field R(T) versus the reduced temperature is shown in Fig.1. in which the solid curve is the spontaneous magnetization for iron. Except for the region  $T/T_{c} \sim 0.04 - 0.6$  the temperature dependence of the hyperfine field is the same as that for the spontaneous magnetization. It is known that the reduced host lattice magnetization is dependent on the applied field<sup>(6)</sup> which explains the measured values above the Curie temperature.

A model explaining the temperature dependence of the local moment has been proposed by Jaccarino et al<sup>(7)</sup>. Rosenblum et al<sup>(8)</sup> have tried to include conduction electron spin polarisation in order to explain the temperature dependence. In ref.8 the reduced hyperfine field R(T) is given by



Fig. 1. The reduced magnetic hyperfine field as a function of reduced temperature.

$$R(T) = (1 - f) \frac{O_T}{O_0} + f \cdot B_J(y)$$
 .....(6)

where  $y = 5 \cdot \sigma_{T_{00}} \circ \sigma_{C/T}$  and  $B_{J}(y)$  is the Brillouin function. A least squares fit of f and S for different J in Eq. (6) to our experimental data was attempted but any reasonable result was not possible to obtain. The deviation from  $\sigma_{T_{00}}$  is much smaller than the one observed in the Ru - Ni alloy<sup>(8)</sup> which suggests that a considerable portion of the hyperfine field is non local in origin.

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#### DISCUSSION:

- P. Singh : Do you get the energy gap of magnetic field on the Pd nuclei?
- H.C. Jain : I do not know of any energy gap due to magnetic hyperfine field at the nucleus.
- E.S. Raja Gopal : The hyperfine field does not fall to zero even above the Curie temperature, would you comment on this?
  - H.C. Jain : It is known that the reduced host lettice magnetization is dependent upon the applied field which explains the measured values above the Curie temperature.

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# NUCLEAR QUADRUPOLE MOMENT OF 14.4 keV STATE OF Fe<sup>57m</sup> FROM MOSSBAUER DATA IN TRIVALENT IRON SALTS

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### INTRODUCTION:

The estimated values of  $Q(Fe^{57m})$  from Mossbauer data range from 0.1 to 0.46b; the values derived from Fe<sup>2+</sup> ion in various crystals, and the high value derived from Fe<sup>3+</sup> ion in Fe<sub>2</sub>O<sub>3</sub>. The variations in the values is mainly due to the difference in the calculated values of q, the EFG component in the Principal Axes system. Ingalls<sup>(1)</sup> in his recent analytic treatment, taking into account spin orbit coupling and covalency effects for the compound FeSiF<sub>6</sub>.6H<sub>2</sub>O has shown that his previous value of Q is to be raised from .15b to 0.29b. Sharma and Das<sup>(2)</sup> have computed the lattice sums in  $\chi$ -Fe<sub>2</sub>O<sub>3</sub> taking into account the contribution of 0-2 dipoles also and have evaluated the Q value as 0.277b, which shows an excellent agreement with Ingall's result. Later on Artman<sup>(3)</sup> carrying out an identical sum showed the value of Q to be 0.41b and thus bringing out in sharper focus the ferrous ferric anomaly. However, now Artman's Q value of 0.41b has been reduced to 0.3b more in accord with the previous data.

Nozik and Kaplan<sup>(4)</sup> have reviewed the lattice contributions to the EFG in various divalent salts and have shown that in contradiction to Ingall's analytical findings one can't in general assume the lattice contribution to be small and of opposite sign. Giving details in the case of  $\text{FeSi}_{6}.6\text{H}_2\text{O}$  and justifying the negligence of covalency effects in view of the essentially ionic character of  $\text{Fe}(\text{H}_2\text{O})_6^{++}$  complex, they have shown the value of Q to be 0.2b.

In view of the lack of correspondence between the ferrous and the ferric Q values and the importance of lattice contribution to the Mossbauer quadrupole splitting, we undertook to study in detail the lattice contribution on a point charge-point dipole model for the compounds  $2nFe_2O_4$ ,  $CuFeO_2$  and  $O(-Fe_2O_3)$ , all having iron in the Fe<sup>3+</sup> ionic state. Accurate crystallographic data<sup>(5-7)</sup> is available for all these compounds. Furthermore all the ions  $2n^{2+}$ ,  $Fe^{3+}$ ,  $O^{2-}$  and  $Cu^+$  have either half filled or completely filled outermost orbits and hence have S character. Therefore, such a calculation is quite appropriate.

## THE LATTICE SUM CALCULATION:

In contrast to the Fe<sup>2+</sup>(3d<sup>6</sup>, 5d<sub>4</sub>) where the major contribution to the EFG on the nucleus is due to the 6th uncompensated valency electron, the EFG produced in the case of the Fe<sup>3+</sup> salt is mainly due to the lattice charge distribution except for a factor  $(1 - \gamma_{en})$ , called the sternheimer anti-shielding factor which takes care of the polarization of the iron core i.e.,

$$q_{\rm Pe}^{3+} = q_{\rm lat}(1 - \gamma_{\rm co})$$

The g components of the EFG tensor were calculated by the formula

$$q_{ij} = \sum_{k} \frac{Z_{k} (3\gamma_{ik} \gamma_{jk} - \delta_{ij}\gamma_{k}^{2})}{\gamma_{k}^{5}} \text{ where } i, j, x, y, z$$

in an arbitrary orthogonal system, Z, is the charge at the k<sup>th</sup> site.

By a principal Axes transformation, the principal values of the EFG tensor and the direction conines (not reported here) of the Principal Axes with respect to the arbitrary orthogonal system are obtained. Using the experimental values of Q.S. and the more recent values of  $\gamma_{\infty}^{(8)}$  for Fe<sup>3+</sup>, the values of Q(Fe<sup>57m</sup>) are obtained from the following equation,

Q.S. = 
$$\frac{1}{2} e^2 q Q (1 + \frac{1}{3} \gamma^2)^{\frac{1}{2}}$$
, and are given in Table I.

### TABLE I

Calculated Values of Q(Fe<sup>57m</sup>) Prom the Experimental Values of Quadrupole Splittings.

| Compound             | Q.S. Experimental<br>(mm/sec) at 300°K | EFG in the PA<br>System (from<br>monopolies only)  | η Q(Fe <sup>57m</sup> ) |  |
|----------------------|--|--|-------------------------|--|
| ZnFe204              | (a)<br>0.36 ± 0.01                     | $q_{xx} \approx -0.050211$<br>$q_{yy} \approx -0.050210$<br>$q_{gg} \approx + 0.100421$      | 0 0.236b                |  |
| CuFeO2 (delafossite) | (b)<br>0.696 ± 0.015                   | q <sub>xx</sub> = - 0+108535<br>q <sub>yy</sub> = - 0•106526<br>q <sub>zz</sub> = + 0•217061 | 0 0.200Ъ                |  |
| d -Fe203             | (c)<br>0.539 <u>+</u> 0.083            | $q_{xx} = -0.029607$<br>$q_{yy} = -0.029593$<br>$q_{yy} = + 0.059200$                        | 0 0.299b                |  |

(a) Ref. No. 9; (b) Ref. No. 10; (c) Ref. No. 11.

#### DISCUSSION:

 $\operatorname{ZnFe}_{2}O_4$ : It is a normal spinel and the Fe<sup>3+</sup> ion which is at the B site is surrounded by six oxygen ions hearby octahedrally but the point symmetry is trigonal with its axis in the  $\langle 111 \rangle$  direction. Mizoguchi and Tanka<sup>(9)</sup> under the point charge model have computed the EFG, taking the trigonal axis as the principal axis and going upto the 4th nearest neighbours (a distance of  $\sim 10$  Å). Using the old value of  $\gamma_{\rm po}$  (-6.17), they concluded that there was a good qualitative agreement between the measured (0.36 mm/sec.) and the calculated value of 0.56 mm/sec. of Q.S. In our calculations we have included all charges in a sphere of 50 Å about an Fe<sup>3+</sup> ion. This yields Q(Fe<sup>57m</sup>) to be 0.236b.

CuFeO<sub>2</sub>: A lattice sum calculation of  $q_{zz}$  had been carried out<sup>(10)</sup> by using  $Q = +0.41b^{(3)}$ . The calculated value of Q.S. (0.70 mm/sec.) is higher by more than a factor of 2 than the measured value (0.328 ± 0.015 mm/sec.) Our calculations give the same value of  $q_{zz}$  and obviously yield the value of  $Q(Fe^{57m})$  to be 0.20b. (Table I).

 $(\chi'-Fe_2O_3)$ : It is antiferromagnetic and exhibits a weak parasitic ferromagnetism above the Morin temperature (200°K) where the electron spins align perpendicular to the 3-fold axis of rhombohedral structure (c-axis), due to the slightly canted spins nearly in the basal plane(c-plane), while the ferromagnetism disappears below this temperature where the spins align parallel to the c-axis. Burns<sup>(13)</sup> and Artman<sup>(3)</sup> obtained the Q(Fe<sup>57m</sup>) value from the measured values of Quadrupole coupling constant of 9.0 Mc/sec.<sup>(13)</sup> at 78°K and 9.7 ± 0.9 Mc/sec.<sup>(14)</sup> at 260°K respectively. However, we are not justified in employing the enriched sample results (<sup>13</sup>, <sup>14</sup>) while utilizing the results of the reagent grade sample X-ray analysis. Furthermore there is no justification in using the value<sup>(14)</sup> of  $\Delta E_Q$  at 260°K since the spin rotation transition is not very sharp. Using the measured value<sup>(11)</sup> of 0.539 ± 0.08 mm/sec. of quadrupole coupling constant at 300°K for a reagent grade sample, Q(Fe<sup>57m</sup>) is calculated to be 0.299b.

We are trying to calculate the dipolar contribution self consistently taking into account the contribution of Fe<sup>3+</sup> induced dipole also in addition to that of  $0^{2-}$  ions. This will further bring down this Q value towards~0.20b value of the other two compounds.

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MOSSBAUER SPECTRA OF ANHYDROUS FERROCYANIC ACID

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Fairly detailed studies have been made on the Mossbauer spectra of alkali metal group ferrocyanides (1-5). Spectra of ferrocyanic acid have also been reported (4,5). All these studies have revealed one line spectra, with no quadrupole splitting, for all these compounds, including the ferrocyanic acid. We report in this paper the results of our studies which show that in the Mossbauer spectra of anhydrous ferrocyanic acid there appear two absorption peaks (quadrupole splitting  $\Delta E_Q$ ) indicating an inhomogeneous electric field around the iron nucleus. This inhomogeniety apparently arises due to the presence of hydrogen bonding between some of the nitrogen atoms. Recent crystallographic (6,7) and infrared spectroscopic (8,9,10)investigations have already shown the existence of hydrogen bonding in anhydrous ferrocyanic acid. The present work is an improvement over the previous Mossbauer investigations in the sense that we have been able to resolve the quadrupole splitting, and also it illustrates the possibility of using Mossbauer technique for investigating hydrogen bonding.

Ferrocyanic acid was prepared as described in the literature <sup>(11)</sup>. The purity of the compound was checked by microanalysis of C,H, and N, and the characteristic infrared spectrum. Lithium ferrocyanide trihydrate was made by neutralising saturated acquous solution of ferrocyanic acid with lithium carbonate, keeping the solution over  $P_2O_5$  for several days, and drying the slurry in an oven at  $100^{\circ}C^{(12)}$ .

The Mossbauer spectra were recorded with a Nuclear Science and Engineering Corporation Model B analyzer fitted with a proportional counter and RIDL single channel analyzer. The source was 0.25 mc  $^{57}$ Co in palladium matrix and was supplied by NSEC. The source was kept always at room temperature. The absorbers were prepared by pressing finely divided 0.2 to 0.3 g solid samples between two 0.0025 cm aluminium foils and were held in ring of brass (3.0 cm diameter, 0.08 cm thick). For studies at liquid nitrogen temperature a metal dewar with windows of thin aluminium foil was made (13). It was evacuated and kept filled with liquid nitrogen during the experiment.

Ferrocyanide anion,  $Fe(CN)_{6}^{-4}$  has octahedral structure, with  $d^{2}sp^{3}$  hybridiasation. Though the cyano groups are linked to the central iron atom by  $\sigma$  bonds, partial  $\mathcal{N}$  -bonding due to back donation of electrons from the metal to the empty ligand orbitals has also been suggested <sup>(14)</sup>. The Mossbauer parameters for various compounds are given in Table I. Our results on  $K_{4}Fe(CN)_{6}\cdot 3H_{2}O$  and  $Na_{2}$  [Fe(CN)<sub>5</sub>NO]  $2H_{2}O$  are in agreement with those of Fluck et al<sup>(3)</sup>. We further note that the isomer shift ( $\delta$ ) decreases in going from the substituent cations K to H. For

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this series of compounds such trend has been shown earlier by Matasand Zemcik<sup>(4)</sup>. The s-electron charge density is largerst for most electronegative cation. An increase in the electronegativity of the cation decreases the effective number of 3d electrons in the iron atom. The s-electrons thus see less screening on the nuclear charge and therefore the net electron density around the iron nucleus increases <sup>(14)</sup>.

| TABLE | I |
|-------|---|
|       | - |

Mossbauer Parameters for Ferrocyanides

| Compound .   | Temp.              | $\delta_{(mm/sec)}$ | Relative                 | (mm/sec)* | $\Delta E_Q(mm/sec)$ |  |
|--|--------------------|---------------------|--------------------------|-----------|----------------------|--|
| Na <sub>2</sub> Fe(CN) <sub>5</sub> NO.2H <sub>2</sub> O | 298 <sup>0</sup> K | -0.44+0.02          | 0.00+(                   | 0.02      | 1.70+0.02            |  |
| K <sub>4</sub> Fe(CN) <sub>6</sub> .3H <sub>2</sub> O    | 298 <sup>0</sup> К | -0.22 <u>+</u> 0.02 | 0.22+0                   | 0.02      |                      |  |
| $Li_4 Fe(CN)_6 \cdot 3H_2O$                              | 292 <sup>0</sup> K | -0.26 <u>+</u> 0.02 | 0.18+0                   | 0.02      |                      |  |
| H <sub>4</sub> Fe(CN) <sub>6</sub>                       | 292 <sup>0</sup> K | -0.31+0.01          | 0 <b>.1</b> 3 <u>+</u> ( | 0.01      | 0.22+0.01            |  |
|  | 80 <sup>0</sup> K  | -0.28±0.02          | 0.16+0                   | 0.02      | 0.26+0.02            |  |
|  |                    |                     |                          |           |                      |  |

\* Relative to sodium nitropruside as standard.

For anhydrous ferrocyanic acid we have observed and have measured a definite quadrupole splitting bothst room temperature and at  $80^{\circ}$ K. We attribute this to the presence of intermolecular unsymmetrical hydrogen bonding in this compound (6-10) which results in a non-homogenous electric field around the iron nucleus. We are continuing more work along these lines and hope that such studies would provide more insight into the nature of hydrogen bonding.

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# DISCUSSION:

K.R.K. Easwaran

: Has neutron diffraction work been done on this compound?

A.N. Garg

: No, Neutron diffraction studieson this compound have not been done so far.

# NUCLEAR ELECTRIC FIELD GRADIENT DETERMINATION IN SINGLE CRYSTALS OF $Fe(NH_4SO_4)_2$ . $6H_2O$ AND $FeSO_4 \cdot 7H_2O$

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### ABSTRACT

Single crystal Mossbauer studies have been carried out on  $Fe(NH_4SO_4)_2 \cdot 6H_2O$ and  $FeSO_4 \cdot 7H_2O$  to determine the five independent parameters of the nuclear EFG tensor viz., its principal values, asymmetry parameter, coupling constant and the direction cosines of EFG azes with respect to crystal axes. Furthermore in view of the agreement of the observed and calculated values of the absorption peak areas ratios, the anisotropy of Lamb-Mossbauer function for both these cases, does not appear to be significant. It is concluded that in case of  $Fe(NH_4SO_4)_2 \cdot 6H_2O$  the principal axes of EFG tesnor are not coincident with those of the susceptibility tensor.

# INTERNAL QUADRUPOLE FIELD IN HfOCL,

Vikram Singh and I.M. Govil, Kurukshetra University, Kurukshetra, Haryana.

#### ABSTRACT

The quadrupole coupling due to internal electric field in HfOGl<sub>2</sub> crystals has been determined by perturbed angular correlation and it has been found that the electric field produced due to HfOCl<sub>2</sub> at the site of the Hf nuclei is nearly the same as present in Hf metal. The resultshave been verified by comparing the experimental curves with theory for a static combined magnetic dipole and electric quadrupole interaction.

# PARAMAGNETISM OF AN ELECTRON GAS IN METALS

# V.K. Saxena and D.L. Bhattacharya, Department of Physics, Banaras Hindu University, Varanasi-5.

In this paper we have tried to estimate the effect of the electron-static-lattice (E-L) and electron-phonon (E-Fh) interactions on the spin-paramagnetism of an electron gas in a metal. Since the ion-core electrons are tightly bound to the nucleus and move "adiabatically" with it, we can not neglect their contribution in the stucy of the electron-ion interactions. Therefore, we have used a more realistic Hellman-type pseudopotential in the present investigation, which is valid for sodium metal. This potential is given by  $\binom{1}{}$ .

The spin-paramagnetism susceptibility  $\chi$  of a metal is related to the change in the ground state energy per electron of the system, A, due to polarization by the relation:

$$\chi'/\chi_{0} = \Lambda_{\rm F}/\Lambda$$
 .....(2).

 $\mathcal{Y}_{0}$  is the Fauli susceptibility of the free electron gas. The quantity A can be written as

 $A_{F}^{,A_{ex}}$  and  $A_{L}$  represent changes in the kinetic, exchange and correlation energies respectively and have been taken from Silverstien<sup>(2)</sup>. We calculate the E-L and E-Ph contributions  $A_{L}$  and  $A_{e-ph}$  using the potential of Eq.(1) and following the method of Abe<sup>(3)</sup>. Thus we find for  $A_{T}^{,}$  to second order:

$$A_{\rm L} = -\frac{2r_{\rm g}^2}{9(12\pi^2)^{1/3}} \sum_{\vec{k}\neq 0} \frac{|\nabla(\vec{k})|^2}{x^2 - 1} \left\{ 1 - \frac{1 - x^2}{2x} \ln \left| \frac{1 + x}{1 - x} \right| \right\} \qquad \dots \dots \dots (4).$$

where  $V(\vec{k})$  is the Fourier coefficient of E-L (having the periodicity of the lattice) when expanded in terms of reciprocal lattice vectors  $\vec{k}$ . For V(r) of Eq. (1) this is

and  $x = k/2k_0$ , k being the Fermi momentum,

The main contribution to  $A_L$  (for alkali metals particularly) comes from reciprocal lattice points with smallest  $\vec{k}$  values<sup>(3)</sup>. We can thus evaluate  $A_L$  by taking only the terms corresponding to the smallest vectors  $k_{\min}$  ( $k_{\min} = 2\sqrt{2}\pi/a$ , a being the lattice constant). The value of  $A_L$  for sodium ( $r_g = 3.96$ ) is  $A_L = -0.022$  which in turn yields

the value of A = 0.217 and the susceptibility X = 0.94. The value is compared with other results in Table 1.

From the Table I it is clear that the present calculation shows an increase of about 10% over the value of Bohm and Pines<sup>(4)</sup> and Abe and observations suggest that a Hellman-type pseudopotential can be safely used in studying the effect of electronion interaction on different properties of sodium. It is desirable that such closed form of potentials be available for other alkali and monovalent metals, in order to simplify theoretical calculations.

We next estimate the EPh contribution  $A_{e-ph}$  by using the Frohlich's<sup>(5)</sup> lowest order term for E-Ph contribution to the ground state energy of the system. In this case we find,

$$A_{e-ph} = \frac{r_{e}^{2}}{9(12 \pi^{2})^{1}/3} \frac{1}{\pi^{3}} \int d^{3}q \frac{|v_{q}|^{2}}{2 \omega_{q}} \left[1 + \frac{u^{2}}{1 - u^{2}} \left\{1 + \frac{1}{1 - u^{2}}\right\}\right] \dots (6).$$
ith
$$u = \frac{(\omega_{q} + q^{2})}{2qk_{o}}$$

 $\omega_{q}$  is the phonon frequency;  $v_{q}^{1}$ , the electron-phonon matrix element is given by  $\left|v_{q}^{1}\right|^{2} = -\frac{v_{q}}{4} \Omega_{p}^{2} \left[2 - \frac{\beta q^{2}}{q_{1}^{2} + \lambda^{2}}\right]^{2} J_{1}^{2} (qr_{s}) \qquad \dots \dots (7).$ 

where  $\Omega_{p} = (8\pi N/M)^{\frac{1}{2}}$  is the ionic plasma frequency and  $3(\sin qr_{s} - qr_{s} \cos qr_{s})$ 

$$\mathbf{j}_{1}(\mathbf{qr}_{g}) = \frac{\mathbf{qr}_{g}}{(\mathbf{qr}_{g})^{3}}$$

For phonon frequencies we use the longwave approximation  $\omega_q^2 \rightarrow \Omega_q^2$  and also approximate  $j_1^2$  in the longwave limit by

$$j_1^2 = 1 - \frac{r_8^2}{5} q^2$$

With these approximations we have for  $A_{e-ph}$ :

$$A_{e-ph} \simeq -\frac{8r_{B}^{2}}{9\pi(12\pi_{c}^{2})^{1/3}} \int dq \ \Omega_{p} \left[2 - \frac{\beta q^{2}}{q^{2} + \pi^{2}}\right]^{2} \left[1 - \frac{r_{B}^{2}q^{2}}{5}\right] \left[1 + \frac{q^{2}}{2k_{o}}\right]$$
.....(8)

Because of the factor  $\sqrt{m/M}$  in  $\Omega_p$  this is clearly a term of order  $\sqrt{m/M}$  as compared to the coulomb contribution. Thus we find that in the longwave limit (which, in principle, is the main part of the phonon spectrum giving reasonable contribution to the E-Fh) the E-Fh contributes a term of order  $\sqrt{m/M}$  to the spin-paramagnetism. It can also be seen that it adds a term of in  $r_B^2$  in the perturbation expansion (although very small). In fact, by means of a straight calculation we have established the results of Migdal<sup>(7)</sup> and Quinn and Ferrell<sup>(8)</sup> that the spin susceptibility of an electron gas in a metal is not affected by E-Fh to order  $\sqrt{m/M}$ . A rough calculation shows that this contribution is of about 2% of the coulomb contribution, making it negligible.

#### ACKNOWLEDGEMENT

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# TABLE I

Comparison of Different Values of  $\chi$  for Sodium (r = 3.96).

| χ <mark>¢</mark> *<br>Ɓ₽ | ×Abc | $\chi_{_{ m HP}}$ ,         | $\chi_{exp}^{ 0}$ | $\chi^{p}_{g}$ |
|--------------------------|------|-----------------------------|-------------------|----------------|
| 9.04                     | 0.86 | 0•85<br>0•962 <sup>**</sup> | 1.09              | 0.948          |

- \*  $\chi^{p}_{\rm BP}$  is the value of  $\chi$  presently calculated with  $A_{c}$  taken from Brueckner and Sawada,  $\chi^{p}_{8}$  is that with  $A_{c}$  taken from Silvergetation. (Brueckner and Sawada, Phys. Rev. 112, 328 (1958)).
- @ R.T. Schumacher and W.E. Vehse, J. Phys. Soc. Jepan, 17, Supplement B-1, 460 (1962).
- \*\* This is the value of X calculated by taking A from Bohm and Pines and A from our calculations. This represents an enhancement of about 13%.

# DISCUSSION:

C.S. Warke :

Bruckner and Sawada have used a uniform charge distribution for ions to calculate the magnetic susceptibility. Have you subtracted it from your electron-ion interaction?

V.K. Saxena : Of course! Taking the periodicity of lattice into account in the electron-lattice part of the Hamiltonian we subtract the self energy of the positive charge in the uniform background of the negative charge which compensates the effect.

### POINT CHARGE CALCULATIONS OF CRYSTAL FIELD PARAMETERS FOR SOME RARE-EARTH COMPOUNDS

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### INTRODUCTION:

The magnetic properties of RX compounds (R = Tm, Xb, Pr and X = Ac, Sb, P, N)of NaCl type have been of much current interest<sup>(1)</sup>. These compounds have been fc min not to order till 2<sup>°</sup>K implying that exchange effects are small. The rare-earth ion experiences a cubic crystalline field. The crystal field split ground state is a singlet in Tm and Pr compounds and doublet in Yb compounds. The susceptibility data of these compounds has been explained<sup>(2)</sup> on the basis of a small exchange and predominantly fourth degree cubic crystal field splitting of the ground state of the rare-earth ion. We report here the calculations of crystal field parameters for these compounds based on a point charge model. According to this model<sup>(3)</sup> the surrounding ions are assumed as point charges that do not overlap the magnetic ion under consideration. Such a model is expected to work well specially for heavier rare-earth where the 4f orbitals are quite inside the atom and the overlap effects are really small.

### THEORY CALCULATIONS:

The electrostatic potential  $V(r, \theta, \emptyset)$  due to surrounding charges, at a point  $(r, \theta, \emptyset)$  near the origin is given by

$$F(\mathbf{r}, \boldsymbol{\Theta}, \boldsymbol{\emptyset}) = \sum_{j} \frac{q_{j}}{(R_{j} - r)} \qquad \dots \dots (1)$$

where  $q_j$  is the charge on the j<sup>th</sup> ion at a distance  $R_j$  from the origin and the sumation is over all the ions. The potential V is assumed to satisfy Laplace's equation so that it can be expanded in terms of spherical harmonics.

$$\forall (\mathbf{r}, \Theta, \phi) = \sum_{n} \sum_{m=-n}^{n} r^{n} \Upsilon_{nm} \Upsilon_{n}^{m} (\Theta, \phi) \qquad \dots \dots (2)$$

where 
$$\Upsilon_{nm} = \sum_{j} \frac{4\pi}{2n+1} \frac{q_{j}}{R_{1}^{n}+1} (-1)^{m} \chi_{n}^{-m} (e_{j}, \phi_{j})$$
 .....(3)

The Hamiltonian for a number of electrons, i, at  $(r_i, \theta_i, \phi_i)$  in the general potential  $V(r, \theta, \phi)$  is

$$H = -ie \left( \sum_{i} \forall (r_i, \theta_i, \phi_i) \right) \qquad \dots \dots (4)$$

Using Steven's 'Operator Equivalent' method we get

$$\mathbf{H} = \sum_{n,m} \mathbf{\Theta}_{\mathbf{n}} \mathbf{A}_{\mathbf{n}}^{\mathbf{m}} \boldsymbol{\langle} \mathbf{r}^{\mathbf{n}} \boldsymbol{\rangle} \mathbf{O}_{\mathbf{n}}^{\mathbf{m}} = \sum_{n,m} \mathbf{B}_{\mathbf{n}}^{\mathbf{m}} \mathbf{O}_{\mathbf{n}}^{\mathbf{m}} \qquad \dots \dots (5)$$

where  $O_n^m$  are spin operators and  $\Theta_n$  are usual Steven's multiplication constants,  $\Theta_2 = O_1; \Theta_4 = \beta_1; \Theta_6 = T_1$  and  $\langle r^n \rangle$  is the expectation value of  $r^n$  over 4f wave function. The strength of the orystal field is determined by  $B_n^m$ , s which are related to  $\mathcal{V}_{nm}$  of Eq. (3). For a crystal with cubic symmetry only  $B_4^O$  and  $B_6^O$ are non-zero. For convenience we define (4) W the absolute energy scaling factor and x a measure of ratio of fourth to sixth degree term in the potential in the following manner<sub>0</sub>

$$B_{4}^{0} F(4) = Wx$$

$$B_{6}^{0} F(6) = (1 - \{x\})$$
....(6)

where  $\mathbf{F}(4)$  and  $\mathbf{F}(6)$  are numerical factors tabulated for all rare-earths. We calculated the contributions to  $B_4^0$  and  $B_6^0$  from all the ions inside a sphere of 50 Å radius by summing over the corresponding expressions. The summations were done on CDC-3600 Computer and the sums were found to converge very rapidly.

### RESULTS AND DISCUSSION:

The rare-carth group V compounds are predominantly ionic. Assuming them to be completely ionic the calculated and observed values are given in Table I.

### TABLE I

| Compound | Iattice<br>Constant a<br>(in A <sup>0</sup> ) | (W in degree K) |               | <u>x</u>   |            |
|----------|---|-----------------|---------------|------------|------------|
|          |   | Calculated      | Observed      | Calculated | l Observed |
| TaSb     | 6.087   | - 0.752         | - 0.939       | - 0.94     | ~ - 1.0    |
| TnAs     | 5.716   | - 1.038         | - 1.141       | - 0.93     | ~ - 1.0    |
| TmP      | 5+575   | - 1+182         | - 1.25        | - 0.93     | ~ - 1.0    |
| TmN      | 4.807   | - 2.535         | - 3.47        | - 0.91     | ~ - 1.0    |
| YbAs     | 5.698   | 9.66            | 14.71 - 18.38 | - 0.97     | ~ - 0.8    |
| YbP      | 5.554   | 11.00           | 14.71 - 18.38 | - 0.97     | ~ - 0.8    |
| YDN      | 4.785   | 23.40           | 32.17         | - 0.96     | ~ ~ 0.8    |

Calculated and Observed Values of W and X for RX Compounds Assuming 3 Electronic Charges at X site. The free ion  $4f \langle r^4 \rangle$  and  $\langle r^6 \rangle$  values<sup>(5)</sup> have been used. For Tm compounds the agreement in magnitude and sign for both W and x is quite good. For Yb compounds also the signs of both W and x and magnitude of x are in good agreement while the order of magnitude of W also agrees with the observed values. The x values in all the compounds agree well with the observed values. This may be due to the fact that x is a ratic of two terms and is somewhat independent of the charge assumed at X sites.

The  $5s^2$  and  $5p^6$  electrons shield the 4f electrons from the effect of crystal field. The results given in Table I are without any shielding corrections. The problem of shielding is quite complex. Recently Freeman and Watson<sup>(6)</sup> have calculated shielding (antishielding) factors for  $Ce^{3+}$  and  $Tb^{3+}$  to  $Yb^{3+}$ . They find that for  $V_2^0$  terms shielding effects are larger in heavier rare-earths and become smaller as the 4f shell fills up from  $Tb^{3+}$  to  $Yb^{3+}$ . This is because distortion is given less freedom to act. Further they find that most rare-earth ions undergo a  $V_4^0$  linear enhancement. Our point charge calculations for Tm and Yb compounds are in conformity with the calculations of Freeman and Watson. The experimental results for Pr compounds given by Jones<sup>(7)</sup> and Busch et al<sup>(2)</sup> do not agree with each other and so we are unable to compare them with cur calculated values.

#### ACKNOWLEDGEMENTS

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#### PARAMAGNETIC SUSCEPTIBILITIES OF THE TRANSITION METAL OCTAHEDRAL COMPLEXES

# A.S. Chakravarty and V.P. Desei Saha Institute of Nuclear Physics, Calcutta-9.

# ABSTRACT

The temperature independent high-frequency contribution to paramagnetic susceptibility from outside the ground configuration i.e., from the first excited configuration has been estimated for the octahedral complexes of the transition metal ions.  $\overrightarrow{L}$  is a one-electron operator and therefore the only non-vanishing elements arise from

$$\left\langle \left( \begin{array}{c} t_{2g}^{m-1} e_{g}^{n+1} \right) \\ \psi_{n} \\ \psi_{$$

The strong-field wave functions for the ground and the excited configurations, which have been used here, have been derived by us using the method of tanabe and Sugano. The energy differences  $E_n - E_o$  are obtained from the absorption spectra of such complexes. The magnitude of this high frequency contribution depending on a particular ion and aparticular complex variesfrom 2% to 11.5% of the room temperature susceptibility value. Thismeans that the magnitudes of the crystalline field parameter.  $\Delta$ , the spin-orbit coupling constant in the crystal  $\mathcal{G}$  and the effective Lande' factors  $\alpha$  and  $\alpha'$  (Abragam and Pryce) usually obtained from the ground configuration alone will be appreciably altered in the temperature range 200°K to 300°K when this extra high-frequency contribution is also taken into account. This because the magnitude of susceptibility goes on increasing as the temperature decreases whereas this high-frequency contribution is temperature independent and therefore is constant at all temperatures.

#### DISCUSSION:

C.M. Srivastava

The high frequency contributions to paramagnetic susceptibility is temperature independent and varies linearly with the magnetic field. So if the contribution due to this is as high as 7% of the temperature dependent and H independent part, it should be possible to observe it experimentally. Have experiments been done in this direction?

A.S. Chakravarthy

The high frequency contribution to paramagnetic susceptibility does not vary with the magnetic field provided the magnitude of the applied magnetic field is not too great. This high frequency contribution has to be estimated from the magnetic susceptibility measurements at different temperatures. N.P. Sastry

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Can you please comment on (1) How good is the one ion approximation and (2) How good are the susceptibility measurements in the paramagnetic state in estimating the exchange integral?

A.S. Chakravarthy

Exchange integral is usually of negligible importance in complexes of sufficient magnetic dilution as is the case here. Only in the case of  $Cu^{2+}(3d^9)$  complexes, e.g., in copper acetates, it has been found by Bleaney and others, that since there are two  $Cu^{2+}$  ions in the unit cell, the exchange integral has to be taken into account in order to explain the magnetic behaviour in such complexes. One electron approximation is pretty good if you restrict yourself to ionic and not covalent complexes.

# MAGNETIC-DIPOLE TRANSITIONS IN THE OCTAHEDRAL COMPLEXES OF THE TRANSITION METAL IONS

# A.S. Chakravarty Saha Institute of Nuclear Physics, Calcutta-9.

# ABSTRACT

The oscillator strengths of the magnetic dipole transitions in the octahedral complexes of the transition metal ions have been calculated using the strong field wave functions. The agreement with the experiment is very reasonable. More experimental data are needed very badly in order to check the theory.

DISCUSSION:

B.K. Basu

1

A.S. Chakravarthy

Are there any other calculations of the transition probailities?

The electric dipole transition probabilities for the octahedral complexes of the transition metal ions using the model of vibronic interactions (proposed by us) have been worked out by me and it is in course of publication in J. Phys. Chem. (1968).

The electric quadrupole transitions for the above complexes have been published by me in Ind. J. Phys. (1967). Magnetic dipole transitions (the subject of this talk) are going to be published very soon. There is a series of papers by R. Engleman on charge transfer supectra of these complexes published in Mol. Phys. (1960-1963).

A.N. Garg

A.S. Chakravarthy

I am afraid, no. There is no regular variation of the oscillator strengths of the magnetic dipole transitions as we go from  $3d^{1}(\text{Ti}^{3+})$  to  $3d^{9}(\text{Cu}^{2+})$ . The values are rather hapazard and I do not think any useful information can be obtained by plotting them. The iron compound is  $\text{Fe}^{2+}(\text{H}_{2}0)_{6}$  and the oscillator strength found by us is  $0.1681 \times 10^{-5}$  in this case.

1) Was there any regular variation of magnetic dipole

value with the number of d electrons?

J.P. Srivastava

Could you mention the factors other than oscillator strengths which may explain the mechanism of a crystal field transition? A.S. Chakravarthy

These are all electronic transitions and they take place because of the splitting of the degeneracy of a particular ion due to the crystalline electric field surrounding the metal ion. Transitions may be of three types, as I said earlier; (1) the electric dipole coupled with odd vibrations of the ligands (2) the magnetic dipole transitions and (3) the electric quadrupole transitions. Third one has got negligible oscillator strength compared to mechanisms (1) and (2).

1

## SPIN POLARISATION DUE TO s-d INTERACTION

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In metals containing transition-metal impurities. Kondo<sup>(1)</sup> discovered a divergence in the electron scattering aplitude due to s-d interactions; since then, there have been many investigations as to the origin of this divergence (2). These calculations show that when the interaction is anti-ferromagnetic a bound state is formed below the Fermi level for temperatures below a critical temperature. It is predicted that below this temperature the magnitude of the localised moment decreases due to the formation of this bound state. It has been suggested that this bound state offers a link between the magnetic and nonmagnetic impurities<sup>(3)</sup>. In the present work we try to evaluate the spin polarisation and we find that there is a bound state formed below the bottom of the conduction band. Such states have been known to exist in the case of nonmagnetic impurities (4). The bound state is observed both for ferromagnetic and antiferromagnetic interaction.

The Hamiltonian for the problem in the Schrodinger picture is

$$H = \sum_{s} \int d\vec{r} \psi_{s}(r) \left(-\frac{\sqrt{2}}{2m}\right) \psi_{s}(r) - \frac{J}{N} \sum_{s,s'} \psi_{s}^{\dagger}(0) \langle s | \vec{s} \cdot \vec{\sigma} | s' \rangle \psi_{s'}(0)$$

Where  $\Psi(\gamma)$  and  $\Psi^{\intercal}(\gamma)$  satisfy the usual anti-commutation relations. The Green's function is defined as

$$G_{s's}(\overline{r}',\overline{r},t) = (-\lambda)\langle 0|T\{\psi_{s'}(\overline{r}',t)\psi_{s}^{+}(\overline{r},0)\}|0\rangle$$

The conduction electron spin polarisation can be calculated using the results

$$m_{1}(r) = \underset{\overrightarrow{r}' \rightarrow \overrightarrow{r}}{\text{lt}} (-\lambda) G_{1}(\overrightarrow{r}, \overrightarrow{r}, t) \text{ and } m_{1}(r) = \underset{\overrightarrow{r}' \rightarrow \overrightarrow{r}}{\text{lt}} (-\lambda) G_{1}(\overrightarrow{r}, \overrightarrow{r}, t)$$

We proceed to develop the perturbation expansion in the usual way by going over to the interaction picture. The Green's function in the interaction picutre becomes

$$(G_{\beta'\beta}(\bar{r}',\bar{r},t) = \frac{\langle S_{z}='_{2},0|T\psi_{\beta'}(\bar{r},t)\psi_{\beta}^{+}(\bar{r},0)S_{z}|S_{z}='_{2},0}{\langle S_{z}='_{2},0|S|S_{z}='_{2},0\rangle}$$

In the zeroth approximation we get  $\mathcal{N}^{(0)}_{\Lambda}(r) = \mathcal{N}^{(0)}_{V}(r) = \frac{k_{F}^{3}}{6\pi^{3}}$  $\mathcal{M}^{(i)}_{\uparrow}(r) = \frac{(+\lambda)J}{(2\pi)^{7}N} \langle \uparrow | S_{z}\sigma_{z} | \uparrow \rangle \oint d\omega \int d\bar{p}_{z} d\bar{p}_{z} G(\bar{p}, \omega) G(\bar{p}, \omega) e^{\lambda(\bar{p}_{z} - \bar{p}_{z}) \cdot \bar{\tau}}$ In the first approximation we have

This on integration gives exactly the same result as that of Yosida<sup>(5)</sup> i.e..

$$-\eta_{1}^{(1)}(r) = -\frac{mJ}{(2\pi)^{4}8N} \frac{(5in2k_{F}r - 2k_{F}r c_{s2}k_{F}r)}{r^{4}}, \quad \eta_{1}^{(1)}(r) = +\frac{mJ}{(2\pi)^{4}8N} \frac{(5in2k_{F}r - 2k_{F}r c_{s2}k_{F}r)}{r^{4}}$$

We notice that only  $\sum_{z \in Z} plays$  a role in this. Therefore we shall try to improve the result by keeping only the terms containing  $\sum_{z}$  but by going to higher orders in the perturbation approximation. The sum of all terms in the expansion can be written as 13 T ( ( - -

$$\mathcal{N}_{\mu}(r) = \mathcal{N}_{\mu}^{(0)}(r) + \mathcal{N}_{\mu}^{(1)} + \cdots = \frac{k_{F}}{6\pi^{2}} + \frac{J}{4N(2\pi)^{7}} \int d\omega d\mu d\mu_{2}$$

$$\begin{cases} G(\mu, \omega) G(\mu, \omega) e^{\lambda(\mu, -\mu_{2})} \overline{r} \left[1 - \frac{J}{4N(2\pi)^{3}}\right] d\mu_{3} G(\mu, \omega) + \cdots \end{cases}$$
Now if  $\mathcal{N}_{\mu}(\omega) = -\frac{J}{4N(2\pi)^{3}} \int d\mu_{3} G(\mu, \omega) d\mu d\mu_{3} (\mu_{3}, \omega) + \cdots \end{cases}$ 
Now if  $\mathcal{N}_{\mu}(\omega) = -\frac{J}{4N(2\pi)^{3}} \int d\mu_{3} G(\mu, \omega) d\mu d\mu_{3} (\mu_{3}, \omega) + \cdots$ 

$$\mathcal{N}_{\mu}(r) = \frac{\mu^{3}}{4N(2\pi)^{3}} + \frac{J}{4N(2\pi)^{3}} \int d\mu_{3} G(\mu, \omega) d\mu d\mu_{3} (\mu_{3}, \omega) + \cdots$$

$$\mathcal{N}_{\mu}(r) = \frac{\mu^{3}}{4N(2\pi)^{3}} + \frac{J}{4N(2\pi)^{3}} \int d\mu_{3} G(\mu, \omega) d\mu d\mu_{3} (\mu_{3}, \omega) + \cdots$$

In this equation we shall consider only the contribution coming from the roots of the equation  $(2\pi)^2 \int \frac{1}{(2\pi)^2} \int \frac{1}{(2\pi)^2} \frac$ 

 $1 - \chi_{i}(\omega) = 0$ 

We shall consider the roots for a square band with density of states  $\rho$  and width D. The root of interest is the one at the bottom of the band which has an energy  $\frac{-D}{e^4-1}$  where  $a = \frac{32\pi N}{|J|}$ . For J < 0 only the spin down electrons form a bound state and for J > 0 only the spin up electrons form a bound state. Bound states at the bottom of the band have been well known in the case of nonmagnetic impurities and have been discussed by Slater and Koster<sup>(4)</sup>. These are the analogues of the donor states in semiconductors.

The interest in the bound state below the conduction band is the following. Unlike the bound state that has been observed by Nagaoka and others<sup>(6)</sup> this need not vanish at higher temperatures. Therefore the question that arises is whether the observed magnetic moment of the impurity is the difference between the 'actual' moment and the contribution from this bound state.

The second possibility, which is more likely, is that when one does calculations beyond what has been done here, the bound state will be shifted near the fermi level. In this case a further link between magnetic and nonmagnetic impurities is the correspondence between Nagaoka bound state and the Slater-Koster bound states.

The Contribution to the spin polarisation due to this bound state goes as  $\frac{e^{qr}}{r^2}$  with q > o. This unphysical hature indicates that a more accurate calculation is needed for this contribution. The root near D contributes a term of the type  $\frac{\cos^2}{\sqrt{2m^2r}}$  which is always positive, unlike Yosida's result.

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1

# DISCUSSION:

| C. Ramasastry     | 1          | What is meant by saying that the magnetic moment of the iron ion extends upto 10 Å?   |  |
|-------------------|------------|---|--|
| C. Manohar        | ł          | It is not the magnetic moment of iron that extends to<br>10 Å but it is the conduction electron polarisation due<br>to s-d exchange which extends to 10 Å.  |  |
| P. Singh          | <b>1</b>   | How does this conduction electron polarisation arise physi-<br>cally? Is this due to R-K-K-Y mechanism?<br>Do you use some decouplin g procedure here to decouple<br>histor order Green functions?  |  |
| C. Manohar        | · <b>š</b> | Thispolarisation arises due to s-d interaction. The cal-<br>culations are done by perturbation theory by summing a<br>class of terms up to infinity.  |  |
| S.K. Dutta Roy    | <b>t</b>   | From your s-d exchange model if we calculate the magetic<br>susceptibility as a function of temperature, what type of<br>temperature variation should be expect?  |  |
| C. Manohar        | ŧ          | I have not calculated the susceptibility but I think it<br>will follow Curie-Weiss type law. I propose to calculate it.   |  |
| N.S. Satya Murthy | <b>\$</b>  | I think the dependence of susceptibility on temperature as<br>well as the spatial dependence of the spin density dis-<br>tribution when the moment does develop are interesting<br>features that should be calculated but difficult to do so.<br>The present calculation does not seem to attempt this. |  |
| 0. Manohar        | 1          | In this work spatial spin density has been calculated.<br>The susceptibility was not been calculated because of the<br>difficulties mentioned in the paper.   |  |
|                   |            |   |  |

ON NEXT NEAREST NEIGHBOUR INTERACTION IN LINEAR CHAIN

Chanchal K. Majumdar and Dipan K. Gosh, Tata Institute of Fundamental Research, Bombay -5.

The Heisenberg linear chain with the Hamiltonian

$$H = \frac{1}{2}J \sum_{i=1}^{N} O_{i} O_{i} + 1 \qquad \dots (1)$$

 $\begin{bmatrix} J < 0 & \text{ferromagnetic}; J > 0 & \text{antiferromagnetic} \end{bmatrix}$  has been investigated thoroughly, notably by Bethe<sup>(1)</sup> and Hulthen<sup>(2)</sup>, and its ground state energy has been determined. The Hamiltonian has been dritisized by many to be inadequate as it presupposes the isotropy of the interactions and because of its restriction to interaction between nearest neighbour alone. The question of existropy has been taken up in a slightly modified Hamiltonian.

$$\mathbf{H} = \frac{1}{2} \mathbf{J} \sum_{i=1}^{N} \left[ \sigma_{i}^{x} \sigma_{i+1}^{y} + \alpha (\sigma_{i}^{x} \sigma_{i+1}^{x} + \sigma_{i}^{y} \sigma_{i+1}^{y}) \right] \dots (2)$$

by various people and recently C.N. Yang and C.P. Yang (3) have offered a complete discussion. Focussing our attention on the other criticism we have studied the Hamiltonian with second neighbour interaction as well:

 $(N + 1 \equiv 1; N + 2 \equiv 2)$ . The parameter  $\propto$  which represents the relative strength of the second neighbour interaction has been allowed to run over all possible values between - 1 and + 1, in keeping with the recent experimental data<sup>(4)</sup> which show  $|\propto|$  may be as high as 0.6. The one dimensional chain may in fact have some importance for magnetically active chain like structures found in some crystals.

There are 4 different possibilities:

1)  $J \langle 0, \alpha \rangle 0$ , all interactions are ferromagnetic and the classcial ground state of aligned spins is expected to be stable.

2) J > 0,  $\alpha < 0$ , the nearest neighbours interact antiferromagnetically, while the next nearest neighbours tend to align themselves - again a stabilization of the accepted picture of <u>roughly</u> alternating up and down spins. 3)  $J < 0, \alpha < 0$ , the ferromagnetic state may no longer be the ground state and it is congectured that the ground state really belongs to the lowest possible spin 0 (N even) or  $\frac{1}{2}$  (N odd) with  $\alpha' = 0$  behaving as a singular point.

4) J > 0,  $\alpha > 0$ , the ground state has always spin 0 (N even) but its symmetry in arrangement may change.

A study of short chains of up to 8 spins arranged on a ring to have periodic boundry conditions substantiated the above picture. We shall describe results of even spins only. Note that the total spin  $\sum_{n=1}^{2}$  and its 2 component  $S_{z}$  are constant of motion. To get the complete picture of eigenvalues it suffices to study the  $S_{z} = 0$ subspace as all spin states (S = 0, 1, 2, ...) will have their representative in this subspace. The number of states in this subspace for N spin  $\frac{1}{2}$  particles is  $\binom{N}{N/2}$ . To obtain the total number of states belonging to a particular spin value S when mead take the difference between the number of states belonging to  $S_{z} = S + 1$  and  $S_{z} = S$  subspace.

Let  $\alpha$ ,  $\beta$  be the up and down spin states respectively. For 4 spins, there are 6 states with  $S_z = 0 \propto (1) \propto (2) \beta (3) \beta (4), \propto (1) \beta (2) \beta (3) \propto (4)$ etc., and the diagonalization of the matrix of the Hamiltonian is trivial. For higher numbers it is convenient to utilize elementary group and construct the basic states a la Hulthen from combinations of

$$[1,m] = \alpha (1)\beta (m) - \beta (1)\alpha (m)$$
  
$$[1,m] = \alpha (1)\beta (m) + \beta (1)\alpha (m)$$

for example [12] [34], [23][41] etc. for 4 spins. The Hamiltonian matrix can be constructed, using these relations

$$\frac{1}{2} (1 - \mathcal{T}_{1} \cdot \mathcal{T}_{m}) [1,m] = 2 [1,m]$$

$$\frac{1}{2} (1 - \mathcal{T}_{1} \cdot \mathcal{T}_{m}) [1,m] = 0$$

$$\frac{1}{2} (1 - \mathcal{T}_{1} \cdot \mathcal{T}_{m}) [k,1] \{m,n\} = -[1,m] \{k,n\}$$

$$\frac{1}{2} (1 - \mathcal{T}_{1} \cdot \mathcal{T}_{m}) [k,1] [m,n] = [1,m] [n,k]$$
.....(5)

**~..(4)** 

The resulting eigenvalues are shown in the slides.

We have been able to find upper and lower bounds for the ground state energy per

spin in the limit  $N \rightarrow \infty$ . If  $N \simeq F(\alpha', J)$  be the ground state energy (Z = coordination number), the different bounds are shown in Table I (for the linear chain).

Similar bounds can also be established for the square lattice for the corresponding problem<sup>(5)</sup>.

We have also started investigating the excited states of the linear chain  $(N \rightarrow \infty)$ , characterised by momentum vectors. For the Hamiltonian (1) Bethe considered 1,2,3 or more spin deviations from the fully aligned state, and was able to solve the resulting difference equations by his now famous (and proved correct<sup>(3)</sup>) ansatz. Thus for 1 spin deviation ( $\phi(m)$  has the up-spin at  $m^{\text{th}}$  site).

this gives the usual spin waves

$$\phi$$
 (m) = e<sup>ikm</sup>

For 2 spin deviations

$$\psi = \sum_{m < n} a(m,n) \psi(m,n)$$

$$a(m,n) = e^{ik_1m + ik_2n + \frac{1}{2}i} \phi_{+} e^{ik_1n + ik_2m - \frac{1}{2}i} \phi \qquad \dots \dots \dots \dots \dots \dots (6)$$

where  $\Psi(m,n)$  denotes the up spins at the m and nth sites. For each value of  $K = k_1 + k_2$  (K a constant of motion), Bethe found, besides the usual continuum a bound state of energy

 $\mathcal{E}_{\mathbf{B}} = J(1 - \cos \mathbf{k}) \quad (J \text{ positive})$ 

For our Hamiltonian, Eq. (3) works all right, and the spin waves are given by

The fully aligned state is unstable with respect to spin waves  $\propto \zeta = 0.25$ .

For two spin deviations Betbe's ansatz no longer does the trick. We have,

however, solved the spectrum by the Gman's function method and also by using the Schrodinger equation a la Wortis and Fukuda<sup>(6)</sup>. The bound state exists for  $\sqrt{20}(J \text{ ferromagnetic})$  only, and starts merging into the continuum at  $K = \pi$ .  $\alpha = 0.5$ . For higher  $\alpha$ , K becomes smaller.

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# DISCUSSION:

R. Nandy?:: 1) On which physical properties does the nature of  $\alpha$  depend?

> 2) How can the sign of  $\propto$  make a substance ferromagnetic or not, even when the exchange interaction J satisfies the necessary ferromagnetic condition?

D.K. Ghosh :

1)  $\alpha$  depends on the sistance between two second neighbours (range) and also on the strength of the coupling.

2) This is exactly what we are investigating and it is shown that this does crucially depend upon  $\propto$ . In other words, the presence of the next nearest neighbour interaction will change the ground state determined by taking into consideration the nearest neighbour interaction only.

P. Sah : 1) In view of the fact that you consider such short chains, these results will not be applicable to solids; at best they can be applied to molecules.

> 2a) What is the order of the matrix arising out of this problem and what is its nature?

> 2b) If it is a matrix with only two co-diagonals then there is a powerful method which could be used to consider long chains (of 8000 atoms say) whose behaviour approximates closely to that of infinite chains. These matrices of order 8000 have been diagonalized by Dean and the density of states calculated in connection with the frequency spectra of disordered linear chains.

#### D.K. Ghosh : 1

1) Experimentally a number of crystals are known, for example, copper tetramine sulphate monohydrate, in which the magnetic ions are arranged in chains with strong interactions within each chain but rather weak interaction between chains. Except at very low temperatures, the chains should be almost independent and theoretical values based on our model may be confronted directly with the experimental measurements. Furthermore, the experimental evidence on various Cupric Quinone Comples salts indicate the existence of independent 'finite' chains of 10 to 20 magnetic ions.

2a) In  $S_Z = 0$  subspace the Hamiltonian has a dimension  $\binom{N}{N/2}$  which is 20 in the case of 6 spins, 70 in the case of 8 spins, 210 in case of 10 spins and so on. For S = 0 subspace they are 5, 14 and 42. In the  $S_Z = 0$  space matrices are real symmetric and in S = 0 space they are real but unsymmetric.

2b) In view of above this is not of relevance here.

# TABLE 1 (Linear Chain)

| J                  | <0;d>            | 0  |              |
|--------------------|------------------|----|--------------|
| F(∝,J)≥ -          | $\frac{1}{4}$  J | (1 | <b>+</b> ≪() |
| $F(\alpha, J) > -$ | 1/13             | (1 | +A)          |

J<0; X < 0

 $F(\alpha, J) \ge - \frac{1}{4} |J||\alpha| (0.88629)$  $F(\alpha, J) \ge - \frac{1}{4} |J| + \frac{1}{4} |J||\alpha|$ 

# $J > 0; \alpha > 0$ $F(\alpha, J) > - \frac{1}{2}(0.88629)J(1+\alpha)$ $F(\alpha, J) > - \frac{1}{4}J + \frac{1}{4}J\alpha$

 $J > 0; \alpha < 0$ F( $\alpha, J$ )  $\Rightarrow -\frac{1}{2}(0.88629)J - \frac{1}{4}\alpha |J|$ 

 $F(\alpha',J) \leqslant - \frac{1}{4}J - \frac{1}{4}|\alpha'|J'$ 

# NONLINEAR ELECTROMAGNETIC RESPONSE OF SEMI-CONDUCTORS IN A MAGNETIC FIELD

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The study of linear and nonlinear<sup>(1)</sup> optical and magneto-optical properties of solids has been a main source of information concerning the band-structure of most 3-5 and 4-6 send conductors. The nonparabolic conduction and valence bands with very small effective mass in such substances have been<sup>(2)</sup> attributed to strong coupling of the conduction and valence bands. However, much of the theoretical work in this field has treated the carriers in these solids semiclassically i.e., using the relations

and

| c<br>× | #9 | F ext             |  |  | (1) |
|--------|----|-------------------|--|--|-----|
| *      | 19 | <u>der</u><br>dhr |  |  | (2) |

where k is the Hloch wave vector,  $\mathcal{E}_k$  the energy function in the given band, and  $\mathbf{F}_{ext}$  is the external force applied. The most important attempt to find a rigorous justification for such an approach is Wanniers<sup>(3)</sup> where it is realised that there are many difficulties in such justification, particularly when one considers the case of Hloch Electrons in a D.C. Magnetic field. Lut tinger and Kohn<sup>(4)</sup> approach to this problem is simpler for quantitative calculations but involves many approximations. Unfortunately, their final results do not account for higher powers than 2 in k in the energy  $\hat{\mathcal{E}}_k$  and hence cannot be used to discuss these semiconductors.

Recently, Jha and Warke<sup>(5)</sup> have worked out the linear and nonlinear current density induced in a solid due to a self-consistent electromagnetic field, in terms of the solutions of the unperturbed problem (i.e., without the inccident light beam). Apart from the general results, they showed that in one parabolic band model one has to replace electron mass m by effective mass  $m^{**}$  even in the interaction Hamiltonian to get same results as obtained in the semiclassical approach. It may be expected that this replacement of m by  $m^{**}$  may be justified by a detailed many band calculation. In the linear case such calculations have been done numerically for many of these semiconductors. However, these calculations do not throw much light on the semiclassical approach itself.

Following the work in reference(5) we have worked  $\binom{(6)}{}$  out the linear and nonlinear electromagnetic response of an inversion symmetric semiconductor with small band gap. We assume a two band model  $\binom{(2)}{}$  with isotropic inverse effective mass tensor, and always work in the long wave length limit. We find that our linear current proportional to the D.C. magnetic field is small by a factor  $\binom{\pi}{n}$  compared to the semiclassical expressions. However, in this regard it seems difficult to judge the correctness of our expressions from the available experiment data since the diference concerns the magnitude of the intensity observed at cyclotron resonance and not the position (frequency) of the resonance itself. The nonparabolacity of the conduction band modifies the observed cyclotron frequency to  $\omega_{c}$ ,

$$\omega_{c} \approx \omega_{o}^{*} \left(1 - \frac{\hbar \omega o \, \mathcal{E} \mathbf{F}}{\Delta^{2}}\right) \qquad \dots (3)$$

where  $\omega_{0}^{*} = \frac{eH^{0}}{m^{2}c}$ , m<sup>\*</sup> is the band edge effective mass, 2  $\Delta$  the band gap and  $\beta_{p}$  the fermi energy.

The bilinear current density vanishes in the dipole approximation. In the trilinear case for incident beam directed along H<sub>o</sub>, we obtain the trilinear current as

$$\mathbf{j}_{\mathbf{AAA}}(3\omega) = \frac{\mathbf{e}^{4}\mathbf{n}_{c}(\underline{a}^{(\omega)},\underline{a}^{(\omega)})}{\Delta \mathbf{m}^{*2} \mathbf{o}^{3}} \quad \frac{1}{2} \underline{a}^{(\omega)} + \left(\frac{\mathbf{m}^{*2}}{\mathbf{m}^{2}} - \frac{\Delta}{\hbar \omega_{c}}\right)$$
$$\omega_{c}^{2} \left(\omega_{c}^{2} + \omega^{2}\right) \quad \frac{2 \underline{a}^{(\omega)} \omega_{c}^{2} + 6 \mathbf{i} \omega \omega_{c} \underline{a}^{(\omega)}}{(\omega_{c}^{2} - 9\omega^{2})(\omega_{c}^{2} - 4\omega^{2})(\omega_{c}^{2} - \omega^{2})}$$
$$\dots \dots (4)$$

The corresponding tesult obtained from the semiclassical approach in our notation is (7)

$$J_{AAA}(3\omega) = \frac{e^{4}n_{o} a^{(\omega)}(\omega) \cdot a^{(\omega)}}{m^{2} o^{3}} (\frac{3\omega^{4}}{2}) \frac{(3\omega^{2} + \omega_{o}^{2})a^{(\omega)} + 4 i \omega(\omega \times a^{(\omega)})}{(\omega^{2} - \omega_{o}^{2})^{2} (9\omega^{2} - \omega_{o}^{2})} \dots (5)$$

The differences are apparent. The term proportional to  $\mathbb{H}^{0}$  in our case is smaller by a factor  $(m^{*2} \Delta / \frac{2}{m} \omega_{c})$  than in the semiclassical case. The difference in resonance denomenators is also significant. We, therefore, do not expect a sharp resonance in the third harmonic current at  $\omega = \omega_{c}^{\circ}$ , as was stated in reference (7). The experimental information is still lacking.

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## INVESTIGATIONS INTO THE CRYSTALLINE ELECTRIC FIELD IN RARE-EARTH METALS

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#### ABSTRACT

The origin of the crystalline electric field at the 4f electron site of rareearth metals has been investigated in the light of the experimental results of Mossbauer effect in Thulium metal. The contribution of the lattice of positive charges together with the shielding by the closed shells has been considered for calculation of the crystal field parameters in Praseodymium metal. In order to see how far it is justified to assume that the conduction electron contribution is small, the estimated crystal field parameters have been used to calculate the magnetic susceptibility pf the metal at low temperatures. The results on magnetic susceptibility thus obtained are considerably larger than the experimental ones. The effect of exchange interaction has been introduced in a phenomenological way. A. Kumar, A.K. Srivastava and G.S. Verma, Department of Physics, University of Allahabad, Allahabad.

The lattice thermal conductivity of alkali halides doped withmonoatomic and polyatomic ions is of considerable interest. Such observations coupled with infrared and specific heat measurements give information about the rotational energy levels of molecular ions in the host lattice. The study of thermal conductivity of doped alkali halides has revealed resonance scattering of phonons. Not only there is a marked reduction in the thermal conductivity but there are also distinct depressions or dips in the thermal conductivity versus temperature curve. For example. KCliCH system<sup>(1)</sup> there are depressions in the curves at 0.6 and 7°K which have been shown to correspond to the resonance scattering of phonons. The dip in the conductivity curve at 1.6  $\text{ cm}^{-1}$  (0.6 K) corresponds to the resonance absorption between the ground state  $A_{1g}$  (J = 0) and the level  $T_{1u}$  (1.4 cm<sup>-1</sup>, J = 1) or  $E_g(2.4$  cm<sup>-1</sup>, J = 2). Similarly the second dip at 18 cm<sup>-1</sup> corresponde to the resonance absorption between  $A_{1g}$  and  $T_{1u}$  (16.4 cm<sup>-1</sup>, J = 3) or  $T_{2u}$  (18.6 cm<sup>-1</sup>, J = 3) levels. Thus the presence of the rotational energy levels such as T<sub>10</sub> or E<sub>g</sub>, which could not be resolved by the infrared measurements, are confirmed by the resonance scattering of phonons as observed in the thermal conductivity measurements. The phonon conductivity measurements also reveal strong phonon coupling between the tunneling states and the rotational energy levels such as  $T_{1u}$  or  $T_{2u}$ , which lie close to the top of the barrier for the hindered rotations of the substitutional impurity CH ions.

The present problem of resonance scattering of phonons is similar to the resonance scattering of phonons by donor electrons in Ge as studied by Griffin and Carruthers  $\binom{2}{}$  and Kwok $\binom{3}{}$ , where phonons are scattered, as a result of virtual transitions of donor electrons between the singlet ground state and the first excited triplet state. Although the nature of the electron-phonon interaction responsible for the electronic transitions between the different rotational energy lovels of the molecular impurities in alkali halides is not known, it is considered desirable to investigate the frequency dependence of the relaxation rates of the resonance scattering of phonons in KCl : CN systems. With this aim in view the phenomenological expressions for the resonance scattering of phonons are used in the present work and these expressions have the same frequency dependence as obtained by Griffin and Carruthers and Kwok.

Griffin and Carruthers considered the deformation potential approximation and their expression for the resonance relaxation rate can be expressed as

$$\mathcal{C}_{\mathbf{r}}^{-1} = \frac{\mathrm{HMT}^{4} \mathbf{x}^{4}}{(1 + \delta \mathbf{T}^{2} \mathbf{x}^{2})^{8}} = \frac{(4 \Delta_{1})^{2}}{\left\{\mathbf{T}^{2} \mathbf{x}^{2} - \left(\frac{4 \Delta_{1}}{K}\right)^{2}\right\}^{2}} + \frac{(4 \Delta_{2})^{2}}{\left\{\frac{1}{\mathbf{T}^{2} \mathbf{x}^{2} - \left(\frac{4 \Delta_{2}}{K}\right)^{2}}\right\}^{2}}$$

where H is a constant, N is the impurity concentration,  $\mathbf{x} = \frac{\hbar}{\hbar} \omega / K_{\rm B} T$ ,  $S = \left(\frac{\mathbf{r}_0 K}{2\hbar}\right)^2$  $\mathbf{r}_0 = \mathbf{a}_0 K / (m^*/m)$ ,  $\mathbf{a}_0$  is the Bohr radius, K is the static dielectric constant,  $\mathbf{m}^*$  is the effective electron mass, m is the free electron mass and  $4\Delta$  is the energy difference betweem the two states responsible for the resonance absorption. Following the same perturbation approach Kwok also considered the inelastic scattering of phonons as well as the scattering of the first excited triplet state. His expression can be expressed as

$$\mathcal{T}_{\mathbf{r}^{-1}} = \frac{\mathrm{HR}(4\Delta_{1})^{2}}{(1+\delta_{\mathbf{x}}^{2}\mathrm{T}^{2})^{8}} \left[ \frac{x^{4}\mathrm{T}^{4}}{\left\{ \frac{x^{4}\mathrm{T}^{4}}{x^{2}\mathrm{T}^{2}-\left(\frac{4\Delta_{1}}{K_{B}}\right)^{2}\right\}^{2}} + e^{-\left(\frac{4\Delta_{1}}{K_{B}}\right)} \left\{ \frac{x^{2}\mathrm{T}^{2}}{\frac{4\Delta_{1}}{4\Delta_{1}}} + \frac{8\Delta_{1}}{K_{B}} \frac{x^{4}\mathrm{T}^{2}}{\frac{4\Delta_{1}}{\hbar_{c}}} \right\} \right]$$

$$\mathbf{F}\left(\frac{4\Delta_{1}}{\hbar_{c}}\right) \simeq \left[ 1 + \frac{1}{4} e^{\frac{x}{2}} \left[ 2\left(\frac{4\Delta_{1}}{\hbar_{c}}\right)^{2}\right]^{-2} \right]$$

A similar term can be added for another dip with  $4\Delta_1$  being replaced by  $4\Delta_2$ , at low temperatures, the first term dominates and the characteristic features of both these theories is the  $\omega^4$ -dependence of the resonance relaxation rate.

It is well known that for frequencies which are close to the resonance frequency the perturbation theory fails. Ewok has also used thermodynamic Green's function technique and obtained expressions for the resonance scattering of phonons. The frequency dependence of the resonance relaxation rate is given by

$$\mathcal{T}_{r}^{-1} = \mathbb{E} \left\{ \frac{H_{1} x^{2} r^{2}}{\left\{ \frac{T^{2} x^{2} - \left(\frac{4 \Delta 1}{K_{B}}\right)^{2} \right\}^{2}} + \frac{H_{2} x^{2} r^{2}}{\left\{ \frac{T^{2} x^{2} - \left(\frac{4 \Delta 2}{K_{B}}\right)^{2} \right\}^{2}} \right\}^{2} \right\}$$

Where H is proportional to level width of the excited state which is different for the resonance frequencies corresponding to  $4\Delta_1$ , and  $4\Delta_2$ .

It has been shown in the present work that the  $\omega^4$ -dependence of the resonance relaxation rate cannot explain the resonance dips in the observed phonon conductivity versus temperature curve. The results are, however, explained very well by the expressions obtained on the basis of Green's function.

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#### PHONON CONDUCTIVITY AND ACOUSTIC ATTENUATION IN SI

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Our earlier analysis(1) of the phonon conductivity data in Si in the framework of Callaway's formalism(2) has given information regarding different phonon scattering processes. It was found that normal phonon processes make a negligible contribution to phonon conductivity and point defect scattering makes an appreciable contribution towards thermal resistance below 200°K. The phenomenological expression for the phonon - phonon scattering relaxation time  $\gamma_{pp}^{-1} = (B_1 + B_2)$  $\omega^2 r^3$  in combination with other phonon scattering processes could explain very well the phonon conductivity in the entire temperature range. The value of the parameter  $(B_1 + B_2)$  which represents the scattering strength could not be checked in the absence of any exact theory of the phonon - phonon scattering. Recently Bateman and Mason(3) have modified Akhiezer's theory(4) and for  $\omega \mathcal{T}_{pp} \lt$  1 they have shown that  $\mathcal{T}_{pp}^{-1} = \omega^2 DE_0 / 3 d \rho V^3$  where  $\omega = 2\pi$  times the frequency at which acoustic attenuation  $\alpha$  is measured,  $\beta$  is the density, V is the phonon velocity, E is the total thermal energy per unit volume and D is a non-linearity constant which can be obtained from knowledge of the second and third order elastic consta-Thus if phonon-phonon scattering is responsible for the observed acoustic nts. attenuation, one can identify  $au_{\rm pp}$  (acoustic) with  $au_{\rm pp}$  (thermal). It is then possible to obtain the values of the parameter D from the phonon conductivity data in the temperature range where the relevant acoustic theory is valid.

The aim of the present paper is to obtain the values of non-linearity constant D from the phonon conductivity data in the presence of point defect scattering and to compare it with the theoretical value, obtained on the basis of Keating's theory which has been very successful in explaining the third order elastic constants of Si. Mason and Bateman have carried cut measurements of acoustic attenuation and phonon conductivity in the same Si crystal and in order to have some decisive results regarding the identification of acoustic and thermal phonon-phonon scatter---ing relaxation time, this system was considered most appropriate.. The results of calculation of the non-linearity constant D are given in Table I which also shows the values obtained by Mason and Bateman. TABLE I

Comparison of the experimental and theoretical values of the non-linearity constant D.

| Temperature.        | D <sub>Expt.</sub><br>(Our cal-<br>culation) | D<br>Expt.<br>(Mason<br>and<br>Bateman) | D (Mason and Bateman)<br>(On the basis of the<br>Experimental values<br>of third order elas-<br>tic constants. | D <sub>Theor</sub> : (Our calcu-<br>lation) (On the basis<br>of the theoretical<br>values of third order<br>elastic constants<br>due to Keating) |
|---------------------|--|---|--|--|
| 300 <sup>°</sup> K  | 4.0  | 4.4                                     | 3.38   | 5.48   |
| 250 <sup>0</sup> K  | 4.3  |   |  | ~,   |
| 500 <sub>0</sub> K  | 4.7  | 4<br>-                                  |  |  |
| 150 <sup>0</sup> K  | 3.8  |   |  |  |
| 100 <sup>°0</sup> K | 2.5  |   | -  |  |

The last column of Table I gives the values of D on the basis of Keating's theory. It may be seen from column 2 of Table I that the value of the D which one obtains following the present approach does not remain constant with temperature. In the range of  $300^{\circ}$  to  $200^{\circ}$ K,  $p_{exp}$  increases from 4.0 to 4.7 and then decreases from 4.7 to 2.5 in the range 200° to 100°K. This may be compared with  $D_{exp} = 4.4$ obtained by Mason and Bateman which is assumed to be the same for the entire range 100° to 300°K. The non-linearity constant D = 3.38 obtained on the basis of the experimental values of the third and second order elastic constants at room temperature is closer to the value of  $D_{exp} = 4.0$  at room temperature obtained by us. It may be noted that the previous workers have assumed that D is independent of temperature but this assumption is not borne out by the present investigations. Keating's theory, which has been very succesful in explaining the third and second order elastic constants of Si, overestimates the value of the non-linearity constant. It will be interesting if the measurements are carried out to study the temperature depenence of the third order elastic constants so that the temperature dependence of D observed in the present work could be checked experimentally.

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It is well known that high attenuation or loss of ultrasound in a ferromagnetic metal like Ni is due to the presence of domains in the material. There have been several proposals for this loss process, (1) micro eddy current loss due to rigid domain wall motion and domain rotation by  $Mason^{(1,2)}$ ; (2) micro eddy current losses due to domain wall motion by Levy and Truell<sup>(3)</sup>; (3) microhysteresis effect due to cylindrical wall deflection by  $Simon^{(4)}$ . None of these formulations, however, explain all the experimental facts. It, therefore, appears relevant to present here, some experimental observations which through light on the actual process occurring as a result of the propagation of ultrasound in the material. We have measured ultrasonic attenuation in Ni as a function of temperature for longitudinal wave propagation along  $\langle 111 \rangle$  and  $\langle 110 \rangle$  directions.

Standard Pulse-echo technique has been used. Low temperature measurements were taken in a vacuum cryostat and for temperatures above room temperature the crystal was heated in air. No undesirable effect was observed by following the latter procedure.

The figure shows the attenuation curves as a function of temperature. There is considerable difference between  $\langle 111 \rangle$  and  $\langle 110 \rangle$  curves. This difference can be accounted for, if we assume that a magnetization process is involved as a result of propagation of ultrasonic waves. We, therefore, rule out the possibility of stationary walls contributing to the loss process<sup>(5)</sup>. Further, we assume that there is more than one magnetization process which we attribute to domain wall motion and domain rotation.

On the basis of the above discussion we associate the abrupt changes in the attenuation curves at  $120^{\circ}$ C and  $170^{\circ}$ C with the changes in the direction of domain magnetization from  $\langle 111 \rangle$  to  $\langle 110 \rangle$  and  $\langle 110 \rangle$  to  $\langle 100 \rangle$  respectively. Such changes are known to take place in Ni in these temperature ranges. The change at  $240^{\circ}$ C is associated with the rapid change of the saturation magnetization which goes to zero at Curie temperature.

From the nature of the curves it is possible to obtain the magnitudes of the contribution to the loss by domain wall motion and domain rotation. In order to discuss these we make use of the consideration of magnetoelastic energies associated with domains under an applied stress. This magnetoelastic energy is  $\lambda_s \sigma \sin^2 \theta$  per unit volume where  $\lambda_s$  is the saturation magnetostriction,  $\sigma$  is the applied stress, and  $\theta$  is the angle between the directions of domain magnetization and of applied stress. Domain wall motion is possible between domains which have magnetoelastic energies and domain rotation is possible if  $\theta$  is not zero. We also find

NI SINGLE CRYSTAL



Fig. 1. Attenuation as a function of temperature in Ni for a longitudinal wave at 15 Mc/sec.

the following results: 1) if the process is domain rotation the magnetization is independent of the direction of applied stress. 2) if the process is domain wall motion, the effect of an applied stress is highest for the easy direction and least for the hard direction. Referring to this, we find that above  $170^{\circ}$ C when  $\langle 100 \rangle$ is the easy axis,  $\langle 111 \rangle$  has less attenuation than  $\langle 110 \rangle$ . In this temperature range no domain wall motion is possible for stress waves along  $\langle 111 \rangle$  since all the domains are equally oriented with respect to this axis. Thus the attenuation for  $\langle 111 \rangle$  is entirely due to domain rotation difference between  $\langle 110 \rangle$  and  $\langle \langle 111 \rangle$  is due to wall motion for wave propagation along  $\langle 110 \rangle$ .

A clear cut separation, as above, of the loss processes is not possible at other temperatures, but it is possible to observe that below  $100^{\circ}C$  both domain wall motion and domain rotation contribute to the loss processes.  $\langle 111 \rangle$  is the easy axis and it shows higher attenuation of the two. At room temperature a relative comparison of domain wall motion and domain rotation is some of interest. Assuming the attenuation along  $\langle 110 \rangle$  to be entirely due to domain rotation, we find,

 $\frac{O'(\text{domain rotation})}{O'(\text{domain well motion})} \approx 1.7 \text{ at 15 Mc. and} \approx 1.0 \text{ at 65 Mc., where O' is}$ the attenuation in db/ M sec. This of course gives the upper limit of the ratio.

The temperature variation of the curves can be explained if we assume that for a magnetization process, the attenuation should be of the form

According to Mason the situation should be the opposite.

$$\alpha = \frac{A}{\sqrt{\frac{1}{8}\sigma_1}} + \frac{1}{\frac{1}{8}\sigma_1}^2 + \frac{1}{\frac{1}{8}\sigma_1}^2$$

The first term gives the contribution due to domain wall motion and the second due to domain rotation. In the above equation  $I_g$  is the saturation magnetisation,  $\sigma_i$  is the internal stress,  $\lambda_g$  is the saturation magnetostriction,  $K_1$  is the first magnetocrystalline anisotropy constant. A and B should contain the frequency terms. From the variation of  $I_g$ ,  $\lambda_g$  and  $K_1$  with temperature, we expect that the temperature variation below 100°C will be essentially given by the second term, whereas at higher temperatures all three parameters will have to be taken into account. We find the temperature dependence below 100°C is of the form  $\frac{1}{K_1^3+C}$  where C is a constant.

The higher power dependence may be due to changes in domain width which is known to change with temperature.

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# DISCUSSION:

- S.B. Karmohäpatro : In the case of polycrystalline nickel are there similar data? If there are, will attenuation be more or less at a certain temperature and frequency?
  - P.P. Sethna : The temperature variation of the attenuation is available for lower frequencies (kc region) (see Bozorth 'Ferromagnetism'). The significant fact is in the frequency region we have investi-Ented the attenuation changes by a factor of approximately 80. At low frequencies this factor is~10.
  - R.P. Singh : What material do you use for the acoustic bonding?
  - P.P. Sethna : For low temperature, Nonag. Above room temperature we use Nonag + Silicone 710 fluid.
  - S.K. Joshi : Are there any measurements of ultrasonic attenuation in paramagnetic Ni?
  - P.P. Sethma : No measurement is available for paramagnetic Ni. The difficulty is performing the experiment at his high temperature (bonding trouble)

# LATTICE DYNAMICS AND BAND STRUCTURE OF BERYLLIUM USING PSEUDOPOTENTIAL AFPROACH

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## ABSTRACT

A first principle calculation of phonon dispersion relations in Beryllium using local pseudopotential approximation has been made. The results are only in qualitative agreement with experiments. We have therefore, inverted the experimental results to derive an 'empirical pseudopotential'. This pseudopotential has been used to compute the band structure of the metal. STUDY OF THE FERMI SURFACE OF NOBLE METALS

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# INTRODUCTION:

A systematic theoretical study of the band structure of all the noble metals is still lacking except some semi-quantitative approach of Cohen and Heine<sup>(1)</sup>. This is perhaps due to the difficulty in constructing a crystal potential for silver and gold. However, Ham<sup>(2)</sup> has shown that this difficulty in constructing a orystal potential can be svoided by the application of the quantum defect method and the cohessive energies of these metals can be calculated quite easily. In a later work, Ham<sup>(3)</sup> has also shown that the knowledge of the quantum defect data can be applied even to the rigorous calculations of band structure and other related properties. The present authors<sup>(4)</sup> have tried to use the quantum defect data to calculate the band structure of silver rigorously. In this paper, the same method is extended to copper and gold, the data for all the noble metals are compared with the estimated values of Cohen and Heine.

# QUANTUM DEFECT DATA FOR COPPER AND GOID:

The spectroscopic eigenvalues for both copper and gold have been taken from the National Bureau of Standards<sup>(5)</sup>. The core eigenvalues for Cu have been taken from the Hartree Fock solution of Cu<sup>+</sup> by Hartree and Hartree<sup>(6)</sup>. In the case of p levels, the term values show irregularities due to configuration interactions. We have taken the core 3p and unperturbed positions of 4p and 5p terms assigned by Whitelaw<sup>(7)</sup> for the interpolation and 4p, 5p, 8p for the extrapolation regions. Since Hartree-Fock solution of Au<sup>+</sup> is not available till now, we have taken the core eigenvalues from the x-ray values for 's' and 'p' states<sup>(6)</sup> and Stark effect for the d state. Moreover, there are not sufficient spectroscopic data for the p state in gold. Hence the  $\mathcal{N}_1$  defect could not be extrapolated upto third power series in  $(1/n^2)$  and is, only extrapolated as

$$\eta_1 = a + b(\frac{1}{n^2}) + c(\frac{1}{n^2})^2$$

This is unavoidable and affects only slightly the  $X_p$  and  $L_p$  levels in gold.

For d radial wave functions  $I_1(\epsilon, r)$  is negative throughout the extrapolation range in copper and gold just as in eilver and  $\eta_2$  has been extrapolated graphically as prescribed by  $\operatorname{Ham}^{(2)}$  (Fig.1).

#### RESULTS AND DISCUSSION:

We have calculated the energy values at the symmetry points  $\Gamma$ , X and L of the Brillouin zone by the composite wave variational method as discussed in Ref.1. Since we have followed Cohen and Hein's treatment for the study of distortion of the Fermi surface mear the Brillouin zone the secular determinant has been solved for a level at  $\Gamma$ , and s and p levels at the zone faces X and L. In Table I and II we represent the results of calculations along with those of Cohen and Heine to facilitate comparison.





# TABLE I

Energy Values in Rydbergs.

| Motals | States         | Energy   | States               | Energy               | States                           | Energy               |
|--------|----------------|----------|----------------------|----------------------|----------------------------------|----------------------|
| Copper | ۲ <sub>s</sub> | - 0.9195 | X <sub>3</sub><br>Xp | - 0.0763<br>- 0.1722 | Le<br>Ly                         | - 0.3729<br>- 0.4241 |
| Silver | Γ.             | - 0.8740 | Xs<br>Xp             | - 0.1201<br>- 0.2632 | Le<br>Lp                         | - 0.3873<br>- 0.4226 |
| Gold   | Гв             | - 1.0122 | X.<br>Xp             | - 0.3278<br>- 0.3636 | L <sub>B</sub><br>L <sub>p</sub> | - 0.5857<br>- 0.4409 |

TABLE II

|                                   | Copper | Silver | Gold   |
|-----------------------------------|--------|--------|--------|
| Ea - En in e.v.                   | 0.70   | 0.49   | - 1.97 |
| Es - En in e.v. (Cohen and Heine) | 1.42   | 0.10   | - 0.75 |
| d                                 | 0.25   | 0.19   | - 0.73 |
| d (Cohen and Heine)               | 0.40   | 0.04   | - 0.27 |
| Big                               | 1.22   | 1.07   | 1.00   |
| m <sup>**</sup> (Cohen and Heine) | 1.08   | 1.01   | 0.95   |
| mo (Optical Constants)            | 1.45   | 0.97   | 0.98   |

 $E_6 - E_p$  is the band gap at L; d, the distortion parameter and m<sup>\*</sup> the effective mass as defined by Cohen and Heine(1).

The above results show that in copper and silver E lies below E but in gold  $E_p > E_p$ . Except for the difference in the absolute values our results are consistent with Cohen and Heine's estimations because  $E_g = E_p$  shows a simple trend of decrease with the increase of atomic number. The magnitude of d is a measure of distortion of the Fermi surface. It shows that the Fermi surface is distorted in copper, less distorted in silver and most distorted in gold, but no contact with the Brillouin zone is indicated in any of the metals. The values of the effective mass are more consistent with the experimental values obtained from optical constants than those of Cohen and Heine.

#### ACKNOWLEDGEMENTS

The authors are grateful to Prof. B.N. Srivastava for his keen interest in the problem.

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## HOLE BANDS IN BISMUTH

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# INTRODUCTION:

Recently attention has been given to establish the structure of the valence and conduction band in Bismuth<sup>(1-8)</sup>. It has a rhombohedral crystal structure and cleaves readily along trigonal planes perpendicular to the trigonal axis. The Fermi surface for electrons of a set of three ellipsoids about the trigonal axis even though six, rather three, ellipsoids for the light electrons (effective mass 0,005) have also been reported.<sup>(5)</sup>. Evidence has also been presented for heavier electrons in a different ellipsoid<sup>(5)</sup>. The picture has also been presented for heavier electrons in a Hole carriers have been associated with one or two ellipsoids of revolution lying on the trigonal axis itself with effective masses of 0.01 and 0.1, respectively<sup>(2)</sup>. For instance. the observed low temperature specific heat has been explained assuming both light and heavy holes (9). The multiplicity of the light hole ellipsoide also has not been fully established. Recently the observations of very large variation of Hall coefficient and magnetoresistance for holes with varying magnetic field have been interpreted in terms of two band conduction-the light hole band is considered to be located directly below the conduction band in momentum space (k-space) and plays an important role on transport in acceptor doped Bi (10). Such bands have also been predicted from theory<sup>(11)</sup>.

Measurement of galvanomagnetic tensor components is one of the direct methods of obtaining carrier concentrations and their mobilities. From these data and the data of Hall coefficient and resistivity vs temperature, deduction can be made about ellipsoid multiplicity, effect of relaxation time anisotropy and the existence of different sets of carriers. If there are several sets of ellipsoids, the observed variation of magnetoresistence,  $\Delta l'/c$ , will have an appearance which is composite of the effect due to individual symmetry elements.

The reported carrier concentration in Bi is  $\sim 3 \ge 10^{17}$  /cc. <sup>(1,6,7)</sup>. Hence the presence of impurity atoms  $\sim 1-10$  parts per million, specially in Bi, would be sufficient to affect the concentration of carriers leading to erroneous conclusions about its band structure. It is useful to note that the Fermi level may be conveniently changed by addition of acceptors such as Pb or Sn without appreciably affecting the crystal potential <sup>(1, 12, 13)</sup>. This fact can be utilized to control the Fermi level and draw unambiguous conclusion about the hole band structure. On theoretical grounds one would suppose that Sn or Pb should accept one electron per stom if they are acceptors. Experiments have recently been reported on 0.2 (at.%) tin doped Bi exhibiting a predominantly hole type conduction (10, 13). However, Shoenberg and Uddin (1) state that it takes 150 ppm of Sn to reduce electron ellipsoid extremal cross section to 2/3 of that in pure Bi; in contrast, 450 ppm of Pb is needed to produce the same effect. Goetz (12) finds that Sn is three times as effective as Pb in changing the steady magnetic susceptibility of Bi. It was therefore, felt to be of interest to add small amount of Pb in Bi thus producing still smaller anticipated changes in the Fermi surface. Magnetoresistance measurements on such crystals could be expected to provide evidence in favour of or against the picture of Bi walence band proposed by Morimoto and Takamira (10). Several samples of Bi doped with Sn were also prepared to find if the earlier results (10) could be reproduced.

## EXPERIMENTAL:

Bridgemen technique was used for growing single crystal of Bi with 0.2 - 0.4 atomic % of Pb or Sn. Crystal sample of suitable orientation was mounted so that it was placed coaxially into a rotating magnetic field. Standard d.c. potentiometric method was used after checking that superious thermcelectric voltages were always lower than 1 microvolt.

#### RESULTS AND DISCUSSIONS:

Complete measurement of four samples with Pb or Sn impurity were made at nitrogen temperature and room temperature (Table I). At high temperature large number of conduction electrons gets excited from the hole bands and give Hall coefficient and resistivity as in intrinsic semiconductors. At 77°K there is conduction only in the hole band and Hall coefficient and resistivity would show normal behaviour due to The Hell coefficient at room temperature is found to be negative which is holes. due to the higher mobility of electrons than that of holes. These electrons are senerated by intrinsic thermal excitation and their number is comparable to that of holes due to acceptor impurities present in the samples. At 77°K all the samples have positive Hall coefficient and indicate a hole concentration of  $\sim 10^{20}/cc.$ which is close to the number of impurity atoms added in each of these samples. The relative direction of current, magnetic field and crystal orientation for sample geometry which provides the most striking observation were as follows: the sample length and the direction of current are along the trigonal axis, Z, the magnetic field lies in the trigonal plane (X-Y) and rotates completely around the trigonal axis at intervals of 5°. The measured value of magnetoresistance,  $\Delta \rho/\rho$ , is plotted in polar plots for the purpose of deducing information on the hole allipsoids.

The variation of magnetoresistance shows a clear three-fold symmetry around the trigonal axis (Fig. 1 and 2) thus supporting the picture of three ellipsoids







Fig.2 Angular dependence of  $\frac{\delta f}{f}$  for sample: Bi-3n-4 at H=5000 Gauss and 77°K. H is in X-Y plane.

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for the holes, centered around the trigonal axis. As evidence for the tilt of these ellipsoids from the trigonal plane ( $\sim 15^{\circ}$ ) reference is made to Fig. 11 and 10 of Morimoto<sup>(10)</sup>. The Hall data of the Pb doped samples, so far, indicate similar acceptor contribution from Pb and Sn. It is not clear why the observations of earlier workers have such large difference, a factor of three, in the relative contribution of holes due to these impurities.

A comparison of magnetoresistance vs  $H^2$  and variation of Hall coefficient with H and also the temperature dependence of Hall coefficient and resistivity indicates that the sample behaviour is quite consistent with the observations and analysis of Morimoto<sup>(10)</sup>, based on a heavy hole ellipsoid and three light hole ellipsoids. Detailed analysis of the lead doped samples would be reported elsewhere.

There is a considerable variation between the magnitude of  $\Delta \rho / \rho$  in different directions. (Fig.1). At present, it is not possible to make any definite statement except that it could be due to accidental error in alignment while the samples were cut.

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# DISCUSSION:

P. Singh : How do these light and heavy holes arise?

V.K. Chopra :

The variation of the Hall coefficient with magnetic field and magnetoresistance with magnetic field of the investigated samples can be explained only if we assume the existence of both light and heavy holes. B.V.R. Chowdari : What measurements have you made to make sure that the impurity has gone into the lattice uniformly?

V.K. Chopra : Samples were taken from different portions of the single crystal (excluding the ends) and the measurements were repeated. The similarity of the observations on these samples show that the impurity has gone into the lattice uniformly.

# TABLE I

|          |           | 300                                | °K                              | 78 <sup>°</sup> K                  |                                 |
|----------|-----------|------------------------------------|---------------------------------|------------------------------------|---------------------------------|
| Impurity | Sample No | R x 100<br>(cm <sup>3</sup> /coul) | J x 10 <sup>5</sup><br>(ohm.cm) | R x 100<br>(cm <sup>3</sup> /coul) | G x 10 <sup>6</sup><br>(ohm.cm) |
| Bi -Pb   | 1         | - 3.2                              | 179                             | + 7.2                              | 154                             |
| Ri Pb    | 2         | - 1.5                              | 240                             | + 7.0                              | 158                             |
| Bi-Sn    | 3         | - 5.7                              | 329                             | + 5.6                              | 185                             |
| Ri –Sn   | 4         | - 6.7                              | 384                             | + 5.2                              | . 137                           |

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# DYNAMICS OF WATER MOLECULES IN CRYSTALS

A. Sequeira, C.L.Thaper, R. Chidambaram, B.A. Dasannacharya and P.K. Iyengar, Hhabha Atomic Research Centre, Trombay, Bombay-74.

We have been interested in trying to understand the role played by the water molecule in hydrated crystals. With this view in mind, neutron diffraction investigations were carried out to determine the structure and coordination of the water molecule in some simple hydrates (1, 2). The dynamical aspects of the water molecule of these hydrates, have now been investigated using a filter detector neutron spectrometer. Crystals containing one non-equivalent water molecule should give rise to three librational modes designated as twisting, rocking and waving modes. These have been studied earlier by optical methods and the cold neutron time-of-flight technique. The optical methods observe only two of these modes because of limitations imposed by On the other hand, the neutron energy gain experiments (3) performed selection rules. so far have not often been able to resolve these frequencies. Our experiments have elearly resolved two of the librational modes in  $K_2 C_2 O_4 H_2 O$  and  $Ba(ClO_3)_2 H_2 O_5$  The position of the third frequency is not clear. These frequencies have also been derived from crystal energy calculations based on two different charge distributions on the water molecule.

The spectra of the inelastically scattered neutrons from analytically pure powder samples at liquid nitrogen temperature were measured using the Trombay filter detector spectrometer<sup>(4)</sup>, with BeO as the filter. In this spectrometer one observes the energy loss processes and the resolution in the relevant energy range is generally better than cold neutron time-of-flight experiments. The background corrected spectra are shown in Fig. 1. Librational frequencies are clearly seen at 740 and 640 cm<sup>-1</sup> in  $K_2C_2O_4$ oH<sub>2</sub>O and at 469 and 395 cm<sup>-1</sup> in Ba(ClO<sub>3</sub>)<sub>2</sub>oH<sub>2</sub>O. The values quoted by Prask and Boutin(3) are in reasonable agreement with our results, though their assignment is made on unresolved peaks. We have not clearly seen the position of the third peak in both these cases.

The librational frequencies have been derived theoretically for  $K_2C_2O_4 \cdot H_2O_4$ . For this purpose the lattice energy was calculated as a function of rotation of the water molecule about its three principal axes, considering electrostatic and Van der Waals type of interactions. The electrostatic energy was calculated by Ewald's method as modified by Bertaut<sup>(5)</sup> using the charge distribution on water molecule as given by Pauling<sup>(6)</sup>. The Van der Waals contribution estimated from L-J potential functions, which are mainly electrostatic, are found to be parabolic for small angular displacements. The librational frequencies derived using the harmonic approximation come out to be 532, 500 and 540 cm<sup>-1</sup> respectively for twisting, rocking and waving modes. To see if we can bring these frequencies closer to the experimentally observed ones calculations were performed using Rowlinson's model<sup>(7)</sup> for the charge distribution on the water molecule. The results were not significantly different.

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Thus the models considered above seem to be inadequate with the present charge allocations. While there is need for a better model for the description of the role of the water molecule in crystals, accurate measurements on more hydrates would be useful. Such measurements should be performed by filter detector method rather than the cold neutron time-of-flight technique hitherto used.

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## DISCUSSION:

G.N. Ramachandran : I am happy to see that the authors have used the technique of neutron scattering for accurate studies of the problem of hydrogen bonding in crystals.

> I note that the librational frequencies of the water molecules in  $K_2C_2O_4$ .H<sub>2</sub>O and  $Ba(ClO_3)_2$ .H<sub>2</sub>O are quite different. Is this obvious from their structures?

C.L. Thaper :

Knowing the strength of the hydrogen bonds in the two crystals one can perhaps make some qualitative estimates of the librational frequencies. Quantitative values can be derived only from a calculation of the potential functions (on the basis of some model) for the various librational motions.

# EXCHANGE CHARGE MODEL FOR THE THIRD ORDER ELASTIC CONSTANTS OF GERMANIUM AND SILLCON

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#### ABSTRACT

The nearest neighbour shell model of Cohran is unable to explain the measured third order elastic constants of germanium and silicon. A new model, the exchange charge model, has been worked out for these crystals to take into account the concentration of charge at the centre of each covalent bond. This exchange charge is assumed to decrease exponentially as the distance between the atoms of forming the bond increases. In addition to the coulomb interaction, central overlap interaction between the first and second neighbour atoms is also considered. The overlap interaction between the first neighbours is assumed to act through the exchange charge. The second order parameters of this model are obtained by fitting theoretical expressions for the second order elastic constants, the Raman active frequency, and the dielectric constant. The third order elastic constants can be obtained in reasonable agreement with experiment by assuming the nearest neighbour interaction to be of the Born-Mayor type and adjusting only the third order parameter of the second neighbour overlap interaction. The success of this model in accounting for the third order elastic constants on sufficiently encouraging to attempt to apply the model to get the dispersion relations and anharmonic properties like thermal expansion of these crystals.

#### DISCUSSION:

P.K. Iyengar :

To my knowledge, this model applied to Diamond does not fit the dispersion relations.

R. Srinivasan :

asan : This model has not been applied so far by any one. In fact, this exchange charge model is very complicated and has not yet been published.

W. Koch : I would like to ask about the nature of the concept of the 'Exchange chanrge' model: is it based on the negative charge density which exists between two atoms in such a crystal associated to the respective wave functions and on the fact that the forces acting on the charges are electrostatic in nature?

.R. Srinivasan : Yes, The distribution of negative charge is replaced in this model with a point charge at the centre of the bond. This point charge interacts electrostatically with the other charges in the crystal.

Work carried out at Materials Research Lab., Pennsylvania State University U.S.A.
# THE GREENIAN METHOD FOR ENERGY BANDS IN DISORDERED ALLOYS

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The band structure of an ordered alloy can be determined by a generalisation of the KR method<sup>(1)</sup> to complex lattice<sup>(2)</sup>, but for a dosordered alloy, the lack of a Bloch condition calls for certain radical changes in the formulation. The simplest treatment of the disordered alloy band structure probelm invokes the virtual crystal approximation<sup>(3)</sup> in conjunction with the KR method. We propose here a more realistic method for calculating the band structure of a disordered alloy, taking account of the short range order that may be present.

A disordered alloy differs from a liquid metal, treated by  $Ziman^{(4)}$ , in that while in the former the disorder is because the spheres located at the different lattice sites are not identical, in the katter it is because of the absence of a lattice structure. A binary alloy is regarded as an assembly of two types of ion cores A and B, imbedded in medium of electrons. Because of their mutual repulsion, the ion cores do not overlap and the potential at any point may be built up as a superposition of these potentials, corrected for screening, i.e.,

where  $\underline{x}_j$  is the position of the j<sup>th</sup> ion which carries the potential  $U(\underline{r}) \cdot V(\underline{r})$  is approximated by a muffin tin potential.

Our problem is to solve the Schrodinger equation

where  $\chi^2$  is the energy of the electron state being considered. The integral form of Eq. (2) is

where

$$(\underline{r} - \underline{r}') = -\frac{1}{4\pi} \qquad \frac{\exp(\mathbf{i} \times |\underline{r} - \underline{r}'|)}{|\underline{r} - \underline{r}'|}$$

We now introduce a variable of defined by

I

$$= \underline{x}_j + \underline{P}$$

and denote 
$$\Psi(\underline{r}) = \Psi(\underline{x}_j + \underline{f}), \text{ by } \Psi_j(\underline{f}).$$

With the help of Eq. (1), Eq. (3). may be written as

where  $\sum'$  denotes that the summation is carried over A atoms only and  $\sum''$  means that this summation is over B atoms only.

Let  $\langle \psi_j (\underline{\rho}) \rangle_{A(B)}$  the configurational average for A(B) at  $\underline{x}_j$ . It can then be shown in a manner similar to that of Ziman, that

$$\left\langle \Psi_{j}\left(\underline{f}\right)\right\rangle_{A} = \exp\left\{i\underline{k}\cdot\left(\underline{x}_{j}-\underline{x}_{j}\right)\right\}\left\langle \Psi_{j}\left(\underline{f}\right)\right\rangle_{A}$$

$$\left\langle \Psi_{j}\left(\underline{f}\right)\right\rangle_{B} = \exp\left\{-i\underline{k}\cdot\left(\underline{x}_{j}-\underline{x}_{j}\right)\right\}\left\langle \Psi_{j}\left(\underline{f}\right)\right\rangle_{B} \dots \dots \dots (6)$$

and

Using these configurational averages and the Bloch type relations (Eq. 6) between them and following a treatment parallel to that of Ziman we are led to the conditions

$$\sum_{L'} \sum_{j'} \left\{ \mathcal{B}_{LL'}^{(jj)} + \chi_{(cot} \chi_{\ell}^{(j)} - 1) \delta_{LL'} \delta_{jj'} \right\} \alpha_{L'}^{(j')} = 0.$$

Here, the structure constants  $\mathcal{B}_{\mu}$  depend on E and <u>k</u> and the phase shifts  $\gamma_{\ell}^{(j)}$  are functions of the energy. These equations thus yield an implicit relationship between the energy and the wave vector.

# EVALUATION OF BLL'S

The structure constants  $\mathcal{B}_{L'}$  arise from the expansions of the Greenians in spherical harmonics and Bessel functions, but they can be expressed in terms of a smaller number of constants  $D_{1,\eta}$ , by the relation

$$\mathcal{B}_{LL'}^{(jj')} = 4\pi \sum_{L'} c_{LL'L''} D_{L''}^{(jj')}$$

where

L denotes the pair of angular momentum quantum numbers 1, m and j is an index to denote the type if atom which may be either A or B. The constants  $C_{LL'L'}$  can be expressed in terms of Clebsch Gordon coefficients and  $P^{jj'}(\underline{r}_s)$  is a pair correlation function which denotes the probability that there is an atom of the j<sup>th</sup> type at a distance  $\underline{r}_s$  from an atom of the j<sup>th</sup> type.

# CONFIGURATIONAL AVERAGE OF THE WAVE FUNCTION:

If  $\oint_i$  denotes the probabability that i<sup>th</sup> neighbour of a B atom, and  $\underline{r}_{\mathcal{H}}$  denotes the positions of the varios lattice sites referred to the B site under consideration as origin, then the average potential at a point  $\underline{r}$  within a B cell is,

$$\overline{\overline{v}}_{B}(\underline{r}) = \overline{v}_{B}(\underline{r}) + \sum_{\alpha} \left[ p_{1} \overline{v}_{A}(\underline{r} - \underline{r}) + (1 - p_{1})\overline{v}_{B}(\underline{r} - \underline{r}_{\alpha}) \right]$$

a similar expression can be obtained for  $\overline{U}_{A}(\mathbf{r})$ .

The  $\gamma_l^{(j)}$  are to be taken as the solution of the Schrödinger equation for these potentials. A knowledge of the  $p_i$ 's can be had from X-ray, electron or neutron diffraction measurements and these are related to the Cowley parameters by the relation

$$\alpha_i = 1 - pi / m_A$$
.

#### CONCLUDING REMARKS:

The method outlined above appears to be a significant improvement over that using the virtual crystal approximation. This is all the more true of  $\beta$ -brass type allowys, which show a correlation between neighboursupto quite a large distance as pointed out be neutron diffraction results. We therefore intend to carry out detailed calculations by the above method for disordered  $\beta$ -brass and Cu<sub>3</sub>Au. The choice was guided by the fact that a lot of experimental information is available for these alloys and calculations have been made for the band structure of their ordered phases.

#### ACKNOWLEDGENE NTS

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THE ANHARMONIC CONSTANTS OF SILICON AND GERMANIUM

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#### ABSTRACT

The method of homogeneous deformation is used to obtain expressions for the third order elastic constants of diamond-type crystals, taking the structural symmetry into account. Numerical results are given, for Si and Ge, in different cases. SLOW NEUTRON SCATTERING BY LIQUIDS : DIFFUSING OSCILLATOR MODEL

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Physics Department, University of Rajasthan, Jaipur-4. The second seco

$$\frac{d^{2}\sigma_{inc}}{d\Omega d\omega} = N \frac{k}{k_{0}} \frac{a^{2} ins}{2\pi} \iint \exp\left[-i(\chi \cdot r - \omega t)\right]$$

$$\int_{g_{s}(r,t) drdt}$$

where the symbols have their usual meaning.

In the Gaussian approximation<sup>(2)</sup> for the self-correlation function, the width function f(t) which gives  $g_{is}(r,t)$  in the form

$$\mathcal{G}_{\mathbf{g}}(\mathbf{r},\mathbf{t}) = \left[4\pi \rho(\mathbf{t})^{-3/2} \exp\left(-\frac{r^2}{4\rho(\mathbf{t})}\right)\right],$$

is described by the velocity autocorrelation function

$$\Phi(t) = \langle V(0), V(t) \rangle \quad T / \langle v \rangle$$

(T stands for the thermal averaging)

by the relation

$$f(t) = \frac{k_{\rm B}T}{M} \int f(\omega) \left(\frac{1-\cos\omega t}{2}\right) d\omega,$$

 $\mathcal{T}(\omega)$  is the frequency spectrum defined by the Fourier Transform

$$f(w) = \frac{2}{\pi} \int_{0}^{\infty} \Phi(t) \cos(\omega t) dt$$

In the present note an attempt is made to calculate this frequency spectrum  $\mathcal{F}(\omega)$  in liqud Argon at 94°K and compared with the digital computational calculations of Rahman<sup>(3)</sup>.

The basic idea is that in a monatomic liquid atoms of the liquid are making oscillations about their mean position of oscillation and during the course of time they are also diffusing in the bulk of the liquid. Eglestaff<sup>(4)</sup> has pointed out that the diffusion phenomenon in simple liquids like monatomic inert liquids, is

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primarily of the continuous type and the jump diffusion being only a secondary process. This view point has been employed in the present calculations. The parameters occuring in the model are derived from the microscopic properties of the liquid.

The oscillatory motion of atoms is governed by the equation of the type

$$\frac{d^2 u_0(t)}{d t^2} + \int \frac{d u_0(t)}{dt} + \langle \omega^2 \rangle av u_0(t) = F_0(t) \quad (a)$$

where

u, is the displacement of the atom

 $\mathcal{C}$  is the friction constant of the motion

 $\langle \omega \rangle$  is the average square frequency of oscillation given by the equation

 $\langle \psi \rangle_{av}^2 = (1/3 M) \int_{g(r)} \nabla^2 \phi(r) dr$ , and  $F_o(t)$  is the stochastic force causing the oscillations.

On the other hand, the diffusive motion which is taken to be of the continuous .type, is governed by Langevin equation of motion

$$\frac{d^2 u d(t)}{d t^2} + \int u_d(t) = F_d(t)$$
 (b)

Since the diffusive type of motion is continuousone, it is not correct to say that the force  $F_d(t)$  causing the diffusion will be a completely random function of time but instead, it should have a simple correlation in its values. We have, however, assumed an exponential type of correlation as a simplest correlation for  $F_d(t)$ . A use of this fact then, brings out that  $\langle F_{d\alpha}(o) F_{d\beta}(t) \rangle$  will be directly related to  $\delta_{\alpha\beta} \exp(-\frac{t}{\zeta_D})$  where  $\zeta_D$  is a certain relaxation time characteristic of the liquid specifying the capacity of the atoms of the liquid to remember its prior condition.

The solution of equations (a) and (b) coupled with the above consideration gives the frequency spectrum f() in the form:

$$\frac{\widehat{f}(\omega)}{\widehat{f}(\omega_{0})} = \begin{bmatrix} \underbrace{(\xi^{2}/\zeta_{D}^{2})}_{(\omega^{2} + \xi^{2}) + (\omega^{2} + \frac{1}{\zeta_{D}^{2}})}_{(\omega^{2} - \langle \omega^{2} \rangle_{av})^{2} + \xi^{2} \omega^{2}} \end{bmatrix}$$
with 
$$\widehat{f}(o) = \frac{2MD}{\pi k_{B}^{T}} \qquad \dots \dots \dots (o)$$

where

D is the self diffusion coefficient T is the absolute temperature.

and

 $\zeta_{o}$  is another relaxation time for the oscillatory motion which weights the oscillatory component.

The friction constant G, F and the relaxation times  $T_o$  and  $T_D$  are to be derived from the microscopic behaviour of the liquid through the statistical theory. The results will be reported elsewhere. However, in the present attempt they are being adjusted to give the best fit with the computational calculations of Rahman and fulfilling the normalization relation,

$$\int_{0}^{\infty} f(w) \, \mathrm{d}w = 1$$

In the figure the calculated values of  $\mathcal{F}(\omega) / \mathcal{F}(0)$  for Argon are shown where Rahman's curve isalso given. The values of the parameters yielding the best fit are as:

 $G = 0.82 \times 10^{13} \text{ sec}^{-1}$   $T = 0.128 \times 10^{-12} \text{ sec}.$   $G = 0.42 \times 10^{13} \text{ sec}^{-1}$   $T = 0.243 \times 10^{-12} \text{ sec}$ 

The value of  $\langle \omega^2 \rangle$  av is 15.2 x 10<sup>24</sup> sec<sup>-2</sup> calculated with the help of the miscroscopic parameters given in reference (5).

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## EFFECT OF PARAMAGNETIC IMOURITY ON THE LONG LIFETIME OF POSITRON

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and

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It has been known for quite some time that the two quantum annihilation spectra of positrons in many liquids and gases show a long lived  $\mathcal{T}_2$  component (~10<sup>-8</sup> sec) and this lifetime is affected appreciably by the presence of paramagnetic impurities. Any process whereby the two photon annihilation replaces the longer lived three photon annihilation and contributes to the  $\mathcal{T}_2$  - component is called quenching. Various types of processes may be involved: unpaired electron exchange, angular momentum reorientation, chemical compound formation, pick-off and spin reversal. The explanation of paramagnetic quenching is as follows : orthopositronium (triplet) is formed first and is subsequently converted by electron exchange collisions in the medium to parapositronium (singlet), which then decays promptly. The paramagnetic impurity introduced into the medium provides extra electrons that can be easily exchanged with the electron in positronium (Ps).

We have tried, partly in collaboration with Dr. C.S. Warke, to calculate the quenching cross-section of paramagnetic impurities  $^{(1)}$ . The pioneering calculation is by Massey and Mohr $^{(2)}$  on the simplest possible situation, namely hydrogen atom. It is clear that the calculation will be similar and the outermost electron exchange will be dominant in analogous situation such as Li or Na in liquid ammonia. So we describe the method for H first and indicate the modifications later.

The Hamiltonian describing the positronium-H collision is (1, 2 denote the two electrons, the proton is supposed fixed).

$$H = \frac{p^2}{2m} + \frac{p^2}{2m} + \frac{p^2}{2m} + \frac{e^2}{r} + \frac{e^2}{r} - \frac{e^2}{r_1} - \frac{e^2}{r_2} - \frac{e^2}{|r-r_1|} - \frac{e^2}{|r-r_2|} + \frac{e^2}{|r-r_2|}$$
(1)

The incident channel with electron 2 in the H atom has the decomposition

$$H = K_{a} + V \qquad \dots (2)$$

$$K_{a} = \frac{p^{2}}{2m} - \frac{e^{2}}{r_{2}} + (\frac{p^{2}}{2m} + \frac{p^{2}}{2m} - \frac{e^{2}}{r_{1}r - r_{1}}) \qquad \dots (3)$$

$$\mathbf{v} = -\frac{\mathbf{e}^2}{\mathbf{r}_1} + \frac{\mathbf{e}^2}{\mathbf{r}} - \frac{\mathbf{e}^2}{|\mathbf{r} - \mathbf{r}_2|} + \frac{\mathbf{e}^2}{|\mathbf{r}_1 - \mathbf{r}_2|} \qquad \dots (4)$$

We shall use the Born approximation. Hence we write the incident channel wavefunction as

$$\chi_{a} = \frac{\exp\left[ik.(r+r_{1})/2\right]}{(2\pi)^{3/2}} \frac{\overline{\phi}}{1s} \left(|r-r_{1}|\right)^{3} \chi_{M}(1) \phi_{1s}(r_{2})^{2} \chi_{s}(2) \dots (5)$$

 $\phi_{18}$  is the ground state wave function of hydrogen; the bar distinguishes that of Ps. If P<sub>12</sub> denote the exchange of the two electrons, the antisymmetrized wavefunction is

$$\chi_{A[a]} = \frac{1}{\sqrt{2}} \left[ \chi_{a} - P_{12} \chi_{a} \right]$$
 .....(6)

The outgoing channel wavefunction  $\mathcal{K}_{A[1]}$  is similar to (5), (6) except the spin function is singlet,  $\mathcal{K}_{0}$ . The scattering amplitude can be calculated easily.

The first term is the direct term and is easily shown to be zero. Hence (7) reduces to the calculation of the integral,

$$I = \int \exp \left[ -\frac{ik!}{m} \cdot \frac{(r+r_2)}{2} \right] \bar{\phi}_{18} \left( \left| \frac{r}{m} - \frac{r_2}{2} \right| \right) \phi_{18}(r_1) \nabla (r, r_1, r_2)$$

$$\exp \left[ \frac{ik!}{m} \cdot \frac{(r+r_1)}{2} \right] \bar{\phi}_{18}(\left| \frac{r}{m} - \frac{r_1}{m} \right| \right) \phi_{18}(r_2) dr dr_{m1} dr_{m2}$$
......(8)

We assume that the PS has essentially thermal energies and so a good approximation is to put  $k \approx k' = 0$ . The calculation is now straightforward with the usual spin sume for the final spin states and spin averages over the initial states. We get,

$$I = -2\pi 1^2 a_2^2 \cdot 3.75$$

$$d\sigma/ds = 14 \cdot 1 a_0^2$$
,  $\sigma_q = 56.4 a_0^2$  .....(9)

The calculation for Li is similar, but we have now to consider Slater determinants for Li. The scattering amplitude is

$$\langle A[1]|V| A[a] \rangle = \langle \chi_1 |V| \chi_a \rangle - \sum_{i=1}^{3} \langle P_{4i} \chi_1 |V| \chi_a \rangle$$
.....(10)

and

For the three electrons in Li we get equal contributions. The dominant contribution comes from the exchange of the 2s electron. There are small corrections due to the screening of the 1s electrons and the interchange of the is electrons with that in Ps. These are found to be small. The overall result is

 $\sigma_{q}$  (Id) = 5.9 x 10<sup>-14</sup> cm<sup>2</sup> .....(11).

r 2

Similarly for Na  $G_q$  (Na) = 7.2 x 10<sup>-14</sup> cm<sup>2</sup>.

The actual experiment in Id-NH<sub>3</sub> requires some more careful considerations, bécause of complications in chemistry. It is known at extreme dilution the Id electron is solvated, Id  $\rightarrow$  Id<sup>+</sup>+ e<sup>-</sup>, and at the opposite extreme of high concentration the metallic behaviour of Id presents Ps from formation. Only at intermediate concentration (about a Id/NH<sub>3</sub> ratio of 10<sup>-5</sup>) the above model of neutral Id atom applies. This seems to be the experimental situation<sup>(3)</sup>.

The paramagnetic quenching cross-section of  $O_2$  molecule can also be handled along the same line <sup>(4)</sup>. Here the main difficulty comes from the enormously complicated ground state wavefunction of  $O_2$  involving configuration interaction. Fortunately we can avoid the complexity by a variational argument. It is well known in variational principles of scattering theory, such as the one of Kohn<sup>(5)</sup> that the scattering amplitude of complicated systems is, to the first order indipendent of the error in the internal wavefunctions. Hence we shall use the simple molecular orbitals, given by Meckler<sup>(6)</sup>, of the two outermost electrons for calculating the scattering amplitude:

~ -

$$\langle \mathbf{r}_{12} \, \chi_{b} \, | \, \mathbf{v} \, | \chi_{a} \rangle = \int \phi \, \left( |\mathbf{r} - \mathbf{r}_{2}| \right) \psi^{+} \left( \mathbf{r}_{1} \cdot \mathbf{r}_{3} \right) \sum_{i=1}^{2} \left| \frac{\mathbf{e}^{2}}{|\mathbf{r} - \mathbf{r}_{1}|} - \frac{\mathbf{e}^{2}}{|\mathbf{r}_{1} - \mathbf{r}_{1}|} \right) = \int \phi \, \left( |\mathbf{r} - \mathbf{r}_{2}| \right) \psi^{+} \left( \mathbf{r}_{1} \cdot \mathbf{r}_{3} \right) \sum_{i=1}^{2} \left| \frac{\mathbf{e}^{2}}{|\mathbf{r} - \mathbf{r}_{1}|} - \frac{\mathbf{e}^{2}}{|\mathbf{r}_{1} - \mathbf{r}_{1}|} \right) = \int \phi \, \left( |\mathbf{r} - \mathbf{r}_{1}| \right) \psi^{+} \left( \mathbf{r}_{2} \cdot \mathbf{r}_{3} \right) d\mathbf{r}_{1} \, d\mathbf{r}_{1} \, d\mathbf{r}_{2} \, d\mathbf{r}_{3} \quad (12)$$

$$\begin{array}{l} \begin{array}{c} R_{1,2} \\ \text{denote the nuclear positions. The oxygen orbitals used are} \\ & \psi(\mathbf{r}_{1},\mathbf{r}_{3}) = \frac{1}{\sqrt{2}} \left[ \psi_{+}(\mathbf{r}_{1}) \ \psi_{-}(\mathbf{r}_{3}) \psi_{+}(\mathbf{r}_{3}) \ \psi_{-}(\mathbf{r}_{1}) \right] \\ & \psi_{\pm} = (\mathbf{k}/\sqrt{2})(\mathbf{p}_{\pm} - \mathbf{p}' \pm), \\ P_{\pm} = (2\mathbf{b})^{\frac{1}{2}} (\pi/2\mathbf{b})^{-3/4} (\mathbf{x} \pm 1\mathbf{y}) \exp\left[ -\mathbf{b} \left| \mathbf{r}_{-} - \frac{1}{2} \frac{\mathbf{R}}{\mathbf{k}} \right|^{2} \right] \\ P_{\pm} = (2\mathbf{b})^{\frac{1}{2}} (-2\mathbf{b})^{-3/4} (\mathbf{x} \pm 1\mathbf{y}) \exp\left[ -\mathbf{b} \left| \mathbf{r}_{-} + \frac{1}{2} \frac{\mathbf{R}}{\mathbf{k}} \right|^{2} \right] \\ p_{\pm} = (2\mathbf{b})^{\frac{1}{2}} (-2\mathbf{b})^{-3/4} (\mathbf{x} \pm 1\mathbf{y}) \exp\left[ -\mathbf{b} \left| \mathbf{r}_{-} + \frac{1}{2} \frac{\mathbf{R}}{\mathbf{k}} \right|^{2} \right] \\ p_{\pm} = (2\mathbf{b})^{\frac{1}{2}} (-2\mathbf{b})^{-3/4} (\mathbf{x} \pm 1\mathbf{y}) \exp\left[ -\mathbf{b} \left| \mathbf{r}_{-} + \frac{1}{2} \frac{\mathbf{R}}{\mathbf{k}} \right|^{2} \right] \\ p_{\pm} = 0_{0}\mathbf{8}, \ \left| \frac{\mathbf{R}}{\mathbf{k}} \right| = \left| \frac{\mathbf{R}}{\mathbf{n}} - \frac{\mathbf{R}}{\mathbf{n}} \right| = 2.2\mathbf{8}, \ \mathbf{K}^{2} = 1.142\mathbf{8}. \end{array}$$

Actually for calculating the many centre integrals we replace  $\phi$  also by a gaussian, invoking the variational argument again. We find in the limit k \$\$\$

$$\sigma_{q}^{-}(0_{2}) = 3.56 \times 10^{-16} \text{ cm}^{2}$$
 .....(14)

The experimental data in oxygen are rather confusing. It may be summarized by saying that at very low concentration the cross-section is  $\sim 10^{-16}$  cm<sup>2</sup> and decreases by a factor of 1000 at higher concentrations<sup>(7)</sup>. Our calculation should be valid at low concentration and agrees fairly well. The problem of the diminution is not properly understood. A tentative explanation is the possibility of strong short range correlation of  $0_{2}$  molecules to have a zero spin  $0_{4}$  configuration. Such  $0_{4}$ objects are actually known<sup>(8)</sup> to be present under high pressures and so high concentration.

Further work along this line and calculation of the cross-section at finite momentum transfer is in progress.

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#### DISCUSSION:

B.V. Thosar : 1. How do experimental values of guenching compare with your theoretical values for H atom and for Li?

> 2. For O<sub>2</sub>, could you extend your theoretical treatment to interaction of positronium with several oxygen molecules surrounding it? What is the experimental situation regarding variation of quenching with pressure?

M.G. Bhide : 1. For H atom no experiment has been done so far. For Li/NHz solution, at intermediate concentrations the experimental value is qualitatively in agreement and quantitatively it is of the right order of magnitudes - more than that is not expected.

2. This can be done, but we have to calculate the oxygen  $(0_4$  molecules, if you like) wave functions first-this is a big job. The experimental data are not clear, and the change by a factor of 1000 is not known to be sudden or gradual. We suspect it is gradual.

P. Sen : As you said that in some cases quenching by oxygen is less effective than that by nitric oxide, I would like to know any typical example where this is true.

M.G. Ehide : At high partial pressure of  $0_2$  in argon (background gas) has a quenching cross-section of  $10^{-19}$  cm<sup>2</sup> - lower than nitric oxide with a crosssection of  $10^{-16}$  cm<sup>2</sup>.

A.N. Garg : Has anybody studied the effect of diamagnetic impurity on the long lifetime of positronium?

M.G. Ehide : Nothing interesting happens here, so it has been not studied.

S.K. Joshi : Would you please comment on the validity of Born approximation for this problem? Is there a variational calculation of the positronhydrogen scattering? If yes, how do variational and Born-approximation calculations compare?

M.G. Enide : The Born approximation result will be higher than the true value. There is also some complication about the covergence of the Born series with rearrangement collisions. There does exist a variational calculation for positronium-hydrogen scattering, by Fraser, which gives a result of  $\sigma \sim 48\pi a_o^2$  as a compared with  $56\pi a_o^2$  in the Born approximation.

# POSITRON ANNIHILATION IN RHODIUM AND NIOBIUM

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#### ABSTRACT

A two photon angular correlation apparatus of angular resolution 1.0 milliradian has been used to measure electron momentum distribution in polycrystalline sheets of rhodium and niobium. The tail part of correlation curve in rhodium is similar to that in nickel andother transition metals. The results of Fermi momentum calculation will be presented.

#### POSITRON ANNIHILATION IN METALS

# J.C. Garg and B.L. Saraf, Department of Physics, University of Rajasthan, Jaipur.

The theory of positron anihilation in metals is essentially annihilation in the electron gas<sup>(1)</sup>. Simple calculations of positron interacting with one electron wave function<sup>(2-5)</sup> have been successful in giving momentum distributions of the annihilated electrons, in fair agreement with those measured by two photon angular correlation experiment. The same one electron model however gives too small annihilation rates, since it neglects the effect of electron positron correlations. Methods of many body problem taking full account of  $e^- e^+$ ,  $e^- e^-$  forces and Pauli principle have been used in different forms<sup>(6-9)</sup>. However, these calculations do not cover the physical processes in the low electron density region.

In this note we report the results of semi-empirical calculations of annihilation rates in an electron gas, based on simple one electron Sommerfield model, and have included the effects of positron-electron correlations. The model appears to be applicable in all density region.

The partial annihilation rate  $R_v$  due to valence electrons in an electron gas may be written as  $R_v = R_0 + \sum R_n (r_n)$  .....(1)

Where  $R_0 \approx 12 r_g^{-3}$ , is the Sommerfield rate,  $\sum R_n$  represents the rate due to positron-electron correlations in electron gas density  $n = \frac{4}{3}\pi r_{ga0}^{3}$ ;  $r_g$  is a dimensionless parameter, and  $a_n$  is the Bohr atomic radius.

The rigorous theoretical calculations<sup>(6)</sup> and recent experimental results <sup>(10)</sup> suggest that  $R_{\psi}$ , for nearly-free-electron metals approaches a value close to  $R_{pos}$ , the spin averaged positronium rate at low electron densities (large  $r_{g}$  values). Thus we have

 $\left|\sum_{n} R_{n}(\mathbf{r}_{s})\right|_{\mathbf{r}_{s} \to \infty} = R_{pos}$ 

It follows from above that a part of  $\sum R_n$  is independent of  $r_s$ . Keeping in view the identity of electrons,  $\sum R_n$  may be written as a sum of two terms, viz.,

$$\sum R_n = R_{nos} + BR_0 \qquad \dots \dots (3)$$

Where B is some arbitrary constant. Combining Eq. (1) and (3) we get,

$$R_{v} = R_{pos} + (1 + B) R_{o}$$
 .....(4)

On substituting  $R_{y} = 5.02 \times 10^{9} \text{ sec}^{-1}$  for  $\operatorname{aluminium}^{(10)}$ , in which nearly all the annihilation takes place via valence electrons<sup>(6)</sup>, we find B = 1 and thus,

The Eq.(5) however, overestimates  $R_v$  values for we have assumed in the foregoing discussion that  $R_v$  approches  $R_{pos}$  for infinite values of  $r_g$  and that in aluminium core annihilation part is negligible. The same is therefore modified as below

$$R_v = R_{pos} + 2R_o(1 - \frac{r^3 s}{x^3})$$
 .....(6)

where x can take any value  $\geq 6$ ; obviously, Eq.(6) reduces to Eq.(5) for  $x = \infty$ . On rewriting Eq.(6) in the form

$$R_{v} = \left\{ \frac{R_{pos}}{R_{o}} + 2 \left( 1 - \frac{r^{2}}{s^{3}} \right) \right\} R_{o} = E_{v}R_{o} \qquad \dots \dots (7)$$

Here E, is called "valence enhancement factor".

If  $R_c = R_c R_c$ , represents the core annihilation rate where  $E_c$  is the "core ennancement factor" and  $R_c$ , is the observed total annihilation rate then

$$E_{c} = \frac{R_{e}}{R_{o}} - E_{v} \qquad \dots \dots (8)$$

#### RESULTS AND DISCUSSION:

Fig. 1 depicts our  $R_v$  values against  $r_g$  for limiting values of x = and x = 6 and are labelled A and B. A comparison of these with the existing many body calculations of annihilation rates reveals that both curves fall slightly below the curve of Kahana<sup>(6)</sup> and are in good agreement with that of Carbotte<sup>(9)</sup>. The observed annihilation rates of Weisberg<sup>(7)</sup> are also shown in figure for the sake of comparison. The valence values assumed in calculating  $r_g$  were as below: 1 for alkali and transition metals; 2 for Be, Mg and Cd; 3 for Al and Ge; 4 for Si, Ge, Sn and Pb and 5 for Bi. It can be seen that both curves almost pass through the experimental points corresponding to free-electron-metals Bi, Mg, Ge, Si and Be.

| valence. and E | Vore enhanceme:                                  | at factor of mets<br>E   | 18  | E <sub>o</sub> /E <sub>v</sub>                          |  |
|----------------|--|--|---|---|--|
| Terrell et al  | This work  | Terrell et al  | This work   | This work   |  |
| 7.80           | 7.50   | 1.95   | 2.50  | 0.33  |  |
| 11.96          | 11:92  | 2.99   | <b>3</b> •50  | 0.29  |  |
| 16.12          | 21.10  | 4.03   | 4.36  | 0.20  |  |
| <b>—</b>       | 25.82  | -  | 5.25  | 0.20  |  |
| 31.12          | 31.44  | 7.78   | 6.15  | 0.19  |  |
|                | 4.95   |  | 4.83  | 0.97  |  |
|                | 4.79   |  | 4.33  | 0,90  |  |
|                | 4,75   |  | 3.72  | 0.78  |  |
| ,              | 4.95   |  | 3+69  | 0.74  |  |
|                | Terrell et al<br>7.80<br>11.96<br>16.12<br>31.12 | Terrell et al         This work           7.80         7.50           11.96         11.92           16.12         21.10           -         25.82           31.12         31.44           4.95           4.75           4.95 | Valence and core enhancement factor of metal $E_{\nabla}$ $E_{c}$ Terrell et al       This work       Terrell et al         7.80       7.50       1.95         11.96       11.92       2.99         16.12       21.10       4.03         -       25.82       -         31.12       31.44       7.78         4.95       4.75         4.95       4.95 | $ \begin{array}{c c c c c c c c c c c c c c c c c c c $ |  |

TABLE 1

The obtained  $E_v$  and  $E_c$  values for alkali and transition metals are given in Table I. The corresponding values for alkali metals from the report of Terrell et  $a!^{(11)}$  are also given for the sake of comparison. The two sets are found in fair ugreement. The ratio of  $E_c$  and  $E_v$  is observed to increase with the number of holes in the '3d' shell of transition metals. Furthermore, core annihilation rate for Ha is found to be 3.5 R<sub>o</sub> in good agreement with theoretical estimate 3.6 R<sub>o</sub><sup>(12)</sup>



Fig. 1.

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#### DISCUSSION:

- V.G. Kulkarni : The experimental data on angular correlation shows that the distinction between core electrons and valence electrons diminishes as we go away from alkali metals. For transition metals such a distinction is not very meaningful.
  - J.C. Garg : I agree; but rough estimations can be made for the core annihilation contribution in the total annihilation rate as done by TERRELL et al which in turn can explain the bell shaped curve of 2- $\gamma$ -correlation for these metal. In fast, the ratio of  $\frac{Re}{R\gamma}$  increases as we pass from alkali metals to transition metals in accordance with 2-photon angular correlation curves.
  - S.K. Joshi : How far is one justified in applying the free electron gas model to the transition metals considered by you?
    - J.C. Garg : If there are no free electrons in these metals, then one must observe bound positronium atom formation which is to be reflected both in life time and two photom angular correlation experiments. However, what we have calculated is just qualitative.

# POSITRON ANNIHILATION IN MONOMER AND POLYMER PHASES OF TRIOXANE

AND

POSITRON ANNIHILATION IN OXIDES OF ANTIMONY AND ARSENIC

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It is well known<sup>(1,2,3)</sup> that the value  $(\mathcal{T}_2)$  and intensity  $(I_2)$  of the slow component observed in the lifetime studies of positrons annihilating in condensed media, are structure sensitive quantities. In particular,  $\mathcal{T}_2$  is sensitive to the electron density while  $I_2$  is sensitive to the crystalline or amorphous character of the medium. Measurements of  $\mathcal{T}_2$  and  $I_2$  in monomer and polymer forms of trioxane, and in arsenic oxide and antimony oxide are reported in these papers.

 $C_2$  was measured by using the standard slow fast coincidence set up reported earlier. I<sub>2</sub> is defined as the ratio of the area under the slow component to the area under the entire curve<sup>(1)</sup>.

# TRIOXANE (CH, 0)

Trioxane is a molecular ring formed by 3 units of CH<sub>2</sub>O. These molecular rings are packed by weak molecular forces to form a crystalline lattice, and known to posses a very high degree of crystallinity. When such a monomer is subjected to gamma ray irradiation, the individual rings open out to form a highly crystalline linear polymer<sup>(4)</sup>, which is separated from the monomer phase by simply dissolving the monomer portion in methyl alcohol. This leaves the polymer lattice undisturbed during separation. Two points may be noted. (1) The order in the monomer structure directly imposes order and orientation upon the polymer and (2) the process of polymerisation by irradiation isproperty of the solid state, as this process does not occur if the monomer is in a liquid (molten or dissolved) state. The polymer trioxane condsts of long chains of the type  $H - (CH_2O)_n - OH$ , strongly bonded along the C axis. The polymer can also be prepared synthetically from liquid formaldehyde. But the polymer so formed is not highly crystalline, as seen from the X-ray diffraction pictures<sup>(4)</sup>. It is, therefore, interesting to compare the values of  $T_2$  and  $I_2$  in these three phases of trioxane. See Table 3.

It can be seen from the table, that the polymer phase of trioxane obtained by irradiation exhibits a higher value of  $\mathcal{T}_2$  while  $I_2$  shows a significant decrease. This can be understood on the basis of considerations reported earlier<sup>(2,3)</sup>. If v is the average volume of the sites in the medium where positronium atoms are formed and annihilated, then  $\mathcal{T}_2 \otimes v$ , while  $I_2$  which is a measure of the fraction of positrons that form positronium will be proporational to the number of such sites available. It has been shown<sup>(2)</sup> that

$$I_2 \propto \frac{\frac{N_{Positronium}}{N_{Total}} \propto \frac{V}{V}$$

where V is the free volume in the medium. Since the density of irradiated polymer (1.5 gm/cc) is higher than the density of the monomer (1.4 gm/cc), V for the polymer is less than that for the monomer. Also since  $\mathcal{T}_2$  for polymer (2.1 ns) is higher than that for the monomer (1.2 ns) the average site volume in polymer should be higher. As both these factors work in the same direction,  $I_2$  for polymer phase is considerably less. An order of magnitude calculation using these values shows that the value of  $I_2$  in polymer phase should be reduced by a factor of 2.

It has been shown<sup>(2,3)</sup> that correlation between  $T_2$  and  $I_2$  can be represented by distinct curves, each curve representing a class of condensed systems. (see Fig. 1). It is interesting to note that the trioxane points fall very near the curve representing organic single crystals, which is understandable as both these phases are highly crystalline. Preliminary results on chemically synthesised trioxane polymer, show the same trend. Further studies of this phase are in progress.

It is seen from table 3, that the trioxane polymer (irradiated) exhibits, in addition to  $\mathcal{T}_2$  a longer component called  $\mathcal{T}_4$ , (13 ns), of a very small intensity (0.4%). Such a large component is not well understood at present, through presumably it arises out of positronium atoms loding themselves in rather very large sites, such as defects, cracks etc. which would account for a very low intensity, such sites being far less in abundance.

The existence of such very long lifetimes in some oxides has been reported recently<sup>(5)</sup>. Even though these long components are notwell understood at present, a systematic search for these, in oxides or other substances, might reveal some use-ful trends. Investigations on two oxides are recorted below.

#### ANTIMONY OXIDE:

Antimony oxide in dimer form  $\text{Sb}_{40_6}$ , exhibits only one but fairly long component  $T_2 = 3.1$  ns of intensity  $I_2 = 5\%$ . In this phase antimony oxide is very highly crystalline, and it is interesting to note that this point firs the curve for orystals in Fig. 1 quite well.

#### ARSENIC OXIDE:

Arsenic oxide was taken in the arsenolite phase, consisting of 4 tetrahedra of  $As_2O_3$ , joined through the oxygen atoms to form a cage like structure<sup>(6)</sup>. Foly-crystalline powderwas spressed at a pressure of one ton per sq. inch to form pellets.  $T_2$  and  $I_2$  were measured as a function of temperature and the datais given in table 1.

Table 1 shows that  $as_{40}^{0}$  exhibits a very long component of fairly high intensity. It is important to note, that as the temperature increases,  $\mathcal{T}_4$  decreases, and near about 135°C disppears permanently, i.e.  $\mathcal{T}_4$  does not reappear after cooling the sample to room temperature. If one assumes that  $\mathcal{T}_4$  originates in positronium atoms annihilating in some very large sites such as crystal defects, interstices of



Fig. 1. I. -  $\mathcal{T}_2$  correlation curves for liquids, polymers and crystals.

powder grains, cracks, etc., then it appears reasonable to suppose that thermal vibrations at higher temperatures would irreversibly bleach such sites. In that case it should be possible to cause effect by subjecting the specimens to avery high pressure<sup>(7)</sup>. Pellets were therefore prepared under a pressure of 100 tons sq. inch, and the experiment repeated. The data obtained is shown in table 2. It is interesting to note that  $\mathcal{T}_4$  shows a smaller value at room temperature, and follows the same irreversible behaviour with temperature, disappearing at about  $130^{\circ}$ C. It is known<sup>(6)</sup> that  $As_4O_6$  in arsenolite form begins to sublime and undergoes a phase change at this temperature. It is quite likely therefore, that sites are very efficiently bleached at this temperature.

The behaviour of  $\mathcal{T}_2$  and  $I_2$  with temperature is easily understood (see Table 1). Expansion caused by the increase of temperature accounts for the systematic increase in  $\mathcal{T}_2$  accompanied by a decrease in  $I_2$ .  $\mathcal{T}_2$  comes back to normal again after cooling, but  $I_2$  is probably affected by the bleaching of some sites. It can be noted from table 2, that siteshave been squeezed by pressure, so that  $\mathcal{T}_2$  now has a very low value.

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#### TABLE I

| Semple        | Temperature                 | 72<br>Nanoseconds | I2<br>in % | 74<br>Nanoseconds | 1 <sub>4%</sub> |
|---------------|-----------------------------|-------------------|------------|-------------------|-----------------|
|               | Room                        | 1.2               | 25         | 13                | 5               |
| Arsenic oxide | 100 <sup>0</sup> 0          | 1.2               | 9          | . 9               | 16              |
| AS O          | 150 <sup>°</sup> C          | 1.8               | 3          |                   |                 |
| Low pressure  | 200 <sup>0</sup> C          | 1.9               | 3          |                   |                 |
| pellets       |                             |                   |            |                   |                 |
|               | Back to room<br>temperature | 1.2               | 11         |                   |                 |

| · · ·       | TABLE II    |        | . •         |
|-------------|-------------|--------|-------------|
|             |             |        |             |
| Temperature | $\tau_{2}$  | I.2 .4 | $T_4$       |
|             | Nanosēconds | in %   | Nanoseconda |

400.00

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6

8

13

13

I. 4%

5 5

6.5 5

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| TAB | LE | 11 |
|-----|----|----|
|     |    |    |

< 1 < 1

2.3

1.7

1.2

1.0

Room 100<sup>0</sup>C

130<sup>0</sup>0

145<sup>0</sup>0 155<sup>0</sup>0

Back to room Temperature

TABLE 111

|  |             |     | •          |                   |       |           |
|--|-------------|-----|------------|-------------------|-------|-----------|
| Sample .   | Temperature |     | I<br>in 2% | T4<br>Nanoseconds | I 4%  | , <u></u> |
| Trioxane (Monomer)   | Room        | 1.2 | 27         |                   |       |           |
| Trioxane (Polymer)<br>obtained by<br>irradiation               | Room        | 2.1 | 9          | 13                | .0 •4 |           |
| Trioxane (Polymer)<br>chemically prepared<br>from formaldehyde | Room        | 4•7 | 1.6        |                   |       |           |

# DISCUSSION:

Sample

Arsenic oxide

high pressure

AS 406

pellets

| A.P. Patro | 8  | Have you made the temperature changes keeping the sample in vacuum?              |
|------------|----|--|
|            |    | It has been observed that unless degassing is done oxygen quenching              |
|            |    | introduces anomalous results.  |
| R.G. Lagu  | t  | After observing this remarked le variation of $\mathcal{T}_{A}$ with temperature |
|            |    | in $As_4^0_6$ , we now propose to repeat the temperature cycle in vacuum.        |
| A.M. Ghose | :  | Have you tried to separate the polymers according to their chain                 |
|            |    | lengths by high speed ultracentrfuging and repeat your measurements              |
|            |    | to observe continuous variation of the relevant parameters according             |
|            |    | the molecular weight of the sample?  |
| R.O. Lagu  | \$ | We have not done such a separation so far.                                       |
| R. Ramanna | \$ | Does the structure of the radiation polymer not depend on the tem-               |
|            |    | perature at which the sample is irradiated? Did you control the                  |
|            |    | temperature when the irradiation was done?                                       |

The polymer structure is likely to be affected by the irradiation temperature only to a small extend through the temperature-induced disorder in the monomer.

P. Sen : I think if you degas  $Sb_40_6$ ; the lifetime  $\mathcal{T}_2$  will change a lot and shall not fall in the curce plotted between  $I_2$  vs  $\mathcal{T}_2$ .

R.G. Lagu

£

I think that so far as  $C_2$  is concerned, the quenching is due to  $Sb_40_6$  lattice. The occluded gas effect can possibly be connected to  $C_4$  (as in  $As_40_6$ ) which is absence in  $Sb_40_6$ . It is also difficult to see how considerable amount of gas could get occluded in a crystalline solid form at room temperature. I feel that the issue can be settled by taking the  $Sb_40_6$  through the temperature cycle with and with our vacuum and studying the variation of  $C_2$  and  $I_2$ with temperature.

# POSITRON LIFETIMES IN CCL, SICL AND SnCL

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# INTRODUCTION:

It is well known that in most liquids positron annihilates with two lifetimes. Attempts have been made<sup>(1)</sup> earlier to correlate the trends in the values of  $\mathcal{T}_2$  or  $I_2$ , in different chemical compounds. One of the features observed is the quenching effect of  $\mathcal{T}_2$  exhibited in halogen compounds. Most of the liquids studied are carbon compounds and the quenching effect of the halogen is explained on the basis of positron capture process due to the halogen. This quenching increases with halogen i.e., going from Fluorine to Iodine. However, not much experimental data exists for compounds where the carbon itself is replaced. In our earlier measurements we found that silicone compounds exhibit a larger  $I_2$  than carbon compounds. This investigation reports results in CCl<sub>4</sub>, SiCl<sub>4</sub> and SnCl<sub>4</sub>. In all these compounds the halogen part is common.

#### EXPERIMENTAL TECHNIQUES:

The measurements were made using a conventional time-to-amplitude converter and a multichannel analyzer. The lifetime measurements were made using a set up having a resolution (f.w.h.m.) of 0.70 n sec.

#### RESULTS:

 $CCl_4$  and  $SnCl_4$  does not show any long component at least upto three decayeds and are in consistent with that of earlier works<sup>(2,3)</sup>, but  $SiCl_4$  shows a very long component of  $\mathcal{T}_2(3.26 \pm 0.06)$  n sec. with intensity  $I_2 = 47\%$ . Fig. 1 shows the time distribution curve for  $CCl_4$  and  $SiCl_4$ . The results of Germagnoli et al<sup>(4)</sup> on  $SnCl_4$  has been argued that the low  $\mathcal{T}_2$  component is either because of source sample preparation or instrumental.

In the cases of  $CCl_4$  and  $SnCl_4$ , it may be that some form of chemical association can occur to provide the positron a means of fast annihilation or that capture of positrons by halogen might become so probable as to prevent positronium formation completely. This explanation can not explain the large intensity of the long component in SiCl<sub>4</sub>.

As such it is difficult to correlate the results in any general form. Attempts are being made to understand these results in a more general way.



Dotted line is for CCl4.

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OXYGEN QUENCHING OF POSITRON LIFETIMES IN SILICONE FLUIDS

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#### INTRODUCTION:

Recent experiments (1-4) have shown that the oxygen content of a liquid greatly influences the linglived  $(\mathcal{T}_2)$  component for positron annihilation in that liquid. Fast experiments on halogen derivatives of benzene and hexane and on hexane and benzene themselves have all been performed with unknown quantities of oxygen dissolved in the system. Although the idea that molecular structure would affect positron annihilations in organic substances was thought to be highly probable, the measurements made without oxygen removal prohibited the observation of any such structural correlations.<sup>(5)</sup>. Gray et al<sup>(4)</sup> have shown for the first time a correlation between the triplet positronium lifetime and molecular structure. Their results obtained for positrons annihilating in 15 normal aliphatic hydrocarbon liquids show that the lifetime,  $\mathcal{T}_2$ , of the triplet-positronium decreases as the hydrocarbon chain increases in length. They also observe that there is less dependence of the intensity,  $I_2$ , of the triplet-positronium component on molecular structure.

Measurements made on the DC 200 silicone samples which had not been degassed have already been reported  $^{(6)}$ , and no molecular structural correlation was observed there. EXPERIMENTAL TECHNIQUES:

Measurements have been made using a conventional arrangement with time-to-amplitude converter and a multichannel analyser. The source deposited on a thin nickel foil was put in a cylindrical sample container. The details of the experimental set up is given elsewhere (7). A resolution (f.w.h.m) of 0.70 n sec. was used in these studies.

The general trend of the time distribution curve is shown in Fig. 1.  $T_2$  has been estimated by applying Peierls<sup>(8)</sup> method.

Degassing of the samples were done in two ways. One of the methods employed for degassing was the well known vacuum-freeze-thaw technique. In the second method the sample under study was heated to  $100^{\circ}$ C and to  $220^{\circ}$ C for about an hour or so in vacuum and then allowed it to room temperature.

#### RESULTS:

The values of  $\mathcal{T}_2$  and  $I_2$  from the degassed samples obtained by the above two methods were same with in errors. The results obtained for the degassed silicone fluids are shown in Table I. From these results one can see that the lifetime,  $\mathcal{T}_2$ , of the triplet positronium decreases as the length of the chain of the silicone fluids increases, though the charge is quite small.



Fig.1. Time distribution curve obtained with a degassed sample of DC 200 (100 cs at  $25^{\circ}$ C). Dotted line is with  $Co^{60}$  source.

We do not observe any dependence of the intensity,  $I_2$ , of the triplet positronium or molecular structure and is in contrast to the finding of Gray et al<sup>(4)</sup> i.e., lighter hydrocarbons have slightly greater triplet intensities. Another finding is that dissolved oxygen has no effect on the triplet positronium intensity.

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#### DISCUSSION:

N. Nath : I am sure you have kept the energy gates the same in taking the prompt curve as in the main measurement with Na<sup>22</sup>.

P. Sen : Yes.

M.G. Hhide : Can you estimate the effect of dissolved  $0_2$  in your sample on the  $T_2$  component and hence on  $\mathcal{T}$  for quenching of  $T_2$ ?

P. Sen: The effect of dissolved  $O_2$  on  $\mathcal{T}_2$  is quite clear from the results of the degassed samples and the sample which had not been degassed.

The quenching cross-section  $\mathcal{T}$  is quite easy to calculate though we have not made such calculations. The way of calculating  $\mathcal{T}$  can be seen in the paper of Gray et al.

| Samp <b>le</b> | Viscosity<br>(cs at 25°C) | τ <sub>2</sub><br>(x 10 <sup>-9</sup> sec) | Error<br>(x 10 <sup>-9</sup> sec) | (%)  |
|----------------|---------------------------|--|-----------------------------------|------|
| DC 200         | 10                        | 3.84                                       | 0.06                              | . 41 |
| DC 200         | 50                        | 3.80                                       | 0.07                              | 37   |
| DC 200         | 100                       | 3.77                                       | 0.06                              | - 44 |
| DC 200         | 350                       | 3.73                                       | 0.06                              | - 44 |
| DC 200         | 1.000                     | 3.72                                       | 0.06                              | 42   |
| DC 200         | 100.000                   | 3.69                                       | 0.05                              | 41   |
| DC 200         | 1.000.000                 | 3.66                                       | 0.06                              | - 39 |

TABLE I

#### ELECTRONIC MAND STRUCTURE OF InBi INTERMITALLIC COMPOUND

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As reported earlier  $\binom{11}{11}$  the nuclear magnetic resonance (MR) spectrum of  $\frac{115}{1n}$ was recorded at room temperature in an InBi intermetallic compound. From the observed spectrum the isotropic Knight shift (+0.18%), the axial component of the Knight shift (+0.02%) and the guadrupole coupling constant (6.6 Mc/s) at the site of the  $^{115}$ In nucleus have been measured. Further it has been observed<sup>(2, 3)</sup> that the Knight shift in the compound changes appreciably on melting whereas there is little change in the shift on melting in pure metal<sup>(4)</sup>. This interesting observation has prompted us to conduct a detailed NMR study of the compound at various temperatures ranging from 77° to 390°K. The NMR measurements were made at 8 Mc/s on a Varian Wide-Line NMR spectra meter with its temperature accessory. The measured Knight shift and quadrupole coupling constant at the site of <sup>115</sup>In the compound against temperature are plotted in Fig. 1. At lower temperatures the central signal (corresponding to the transition nent of the Knight shift is negligible. At higher temperatures (60°C and above). the axial component of the Knight shift could not be determined as the signal-to-noise ratio was poor.

The salient features of the experiment are the following: The Knight shift increases with increasing temperature more or less smoothly but abruptly gets doubled soon after melting the compound. This is in contrast to the observations made in pure indium metal<sup>(4)</sup> where the Knight shift remains constant throughout. At lower temperatures the quadrupole coupling constant at the site of the <sup>115</sup>In nucleus in the InBi compound decreases with increasing temperature reaching minimum at about  $170^{\circ}$ K and then increases with increasing temperature whereas in pure indium metal the quadrupole coupling constant decreases with increasing temperature such a such about 100°K and then increases with increasing temperature such smoothly.

From the X-ray powder patterns at room temperature and liquid air temperature it has been found that the c/a ratio of the unit cell of the compound increases with decreasing temperature. It is being planned to obtain X-ray powder patterns at intermediate temperatures to correlate the quadrupole coupling constant with the c/a ratio.

In pure indium metal it has been found that the Knight shift is insensitive to the changes in temperature (implicitly to the changes in the c/a ratio). This is understandable as indium is trivalent metal; with 3 valence electrons  $(5s^2 5p^1)$ , we expect one and a half Brillouin Zones to be filled, giving a large area of Fermi surface and with no Brillouin Zone - Fermi surface interaction. Thus the density of states at the Fermi surface with s-character, which mainly determines the amount





of Knight shift, should be independent of temperature and thus of the c/a ratio.

In InBi intermetallic compound there are 3 + 5 valence electrons per molecule and 16 electrons per unit cell (2 molecules per unit cell). In absence of the overlapping of the Brillouin Zones, one should expect the compound to behave like an insulator. But due to overlapping of the zones, there will be a few clusters of electrons in the next zone leaving a few holes in the corners and the edges of the filled zones. The appearance of several sets of de Haas - Van Alphen oscillations in InRi intermetallic compound (5) confirms the presence of Brillouin Zone - Fermi surface interactions in the compound. The prediction of small area of Fermi surface in InBi intermetallic compound is in confirmity with the observed small Knight shift<sup>(1)</sup> and reported high electrical resistivity<sup>(6)</sup>. In such a case one should expect the variation of the Knight shift with respect to temperature if the c/a ratio varies with temperature for it is well-known that the variation of c/a ratio alters the degree of overlapping of the Brillouin Zones. In turn the change in degree of overlapping will affect the relative percentage of s and p conduction electrons at the Fermi surface due to strong admixture of s and p electrons at the Fermi surface (Fig. 2).

InBi has a tetragonal structure of PbO type (7), the space group being p4/nmm. At room temperature c/a = 0.953, and this ratio increases with decreasing temperature. When c/a is less than 1 as at room temperature, the zone is elongated along c-axis and the tendency for overlapping is reduced. When c/a is increased with decreasing temperature, the reciprocal lattice may be squashed down and the overlap in the axial directions is likely. Due to increase in overlapping of the zones at 🔔 lower temperatures, there will be increase in p-electron density and corresponding decrease in s-electron density at the Fermi surface (Fig. 2). This will result in considerable decrease in direct hyperfine interaction and increase in core polarisation by p-electrons. As the core-polarisation gives rise to negative Knight shift, the resultant Knight shift should decrease with decreasing temperature. This is actually what is observed in the Knight shift curve in Fig. 1. At low temperatures the Knight shift due to direct hyperfine interaction is masked by that due to core polarisation. As the axial component of the Knight shift decreases with decreasing temperature one may question the increase in p-electrons at the Fermi surface with decreasing temperature. Since the c/a ratio is tending towards one with decreasing temperature one may not expect much contribution to the axial component of the Knight shift from the p-electrons at Fermi surface.

In conclusion, we expect that the Fermi surface in InEM is dominated by p-electrons and the Brillouin Zones are almost completely full with a few number of electrons spilling to the higher zones.

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NUCLEAR MAGNETIC RESONANCE IN SOME TRANSITION METAL DOUBLE FLUORIDES

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# INTRODUCTION:

The nuclear magnetic resonance study of non-magnetic nuclei which are directly bonded to the paramagnetic ion, in paramagnetic materials have been studied extensively in recent years, particularly the transition metal fluorides (1,2). The Hamiltonian of interaction for the kth <sup>19</sup>F nucleus in such a paramagnetic system is given by

$$\mathcal{H} = -r \hbar \vec{I}_{k} \cdot \vec{H}_{0} + \sum_{j} \vec{I}_{k} \cdot \vec{A}_{jk} \cdot \langle \vec{S}_{j} \rangle + \sum_{i} r \hbar \vec{I}_{k} \beta g \vec{S} \frac{(1-3 \cos^{2} \theta_{ik})}{r_{ik}^{3}}$$
.....(1)

The first term is the ordinary Zeeman energy in a diamagnetic crystal. The second term which is the most important term, represents the hyperfine interaction resulting from the covalent bonding of the  $\mathbf{F}$  ion to a paramagnetic ion. The last term is the magnetic dipole interaction of the nuclear moment with the paramagnetic ion moment. The nuclear resonance position is largely shifted due to these fields and the fractional shift  $\boldsymbol{i}$  is defined by the equation

 $h z = g_{\rm H} \, \mathcal{A}_{\rm H} \, H_{\rm o} \, (1 + \alpha)$  .....(2)

In these compounds where there is an appreciable overlap of the wavefunctions of the nominally non-magnetic atom and the paramagnetic ion, the shift in the NMR is much larger than due to the dipolar field, and is explained in terms of the transfered hyperfine interaction at the <sup>19</sup>F site due to the covalent bonding between the paramagnetic ion and the fluorine. The shift produced by these fields has an isotropic and anisotropic component. By a careful study of the angular dependence of the shifts in a single crystal, it is in general possible to estimate the strength of hyperfine interaction, both isotropic A<sub>g</sub> (due to the s-electrons) and A<sub>p</sub>, the anisotropic part (due to p-electrons). In polycrystalline samples, the anisotropic shift is determined by the centroid of the absorption line. The A<sub>g</sub> is then calculate using the formula

 $= \frac{\operatorname{Ngg}_{\mathbb{N}}\partial \partial_{\mathbb{N}} \alpha_{B}}{n \chi_{\mathbb{M}}} \qquad \dots \dots \dots (3)$ 

where N, the avagadro number, n, the number of nearest paramagnetic atoms, and m' the molecular susceptibility. The factional unpaired s-electron spin density at the fluoride orbital can be estimated as

where  $A_{29}$  is the atomic hyperfine interaction of the s-electrons of the fluorine. In this paper we report the field and temperature dependence of the <sup>19</sup>F nuclear magnetic resonance in KFeF<sub>3</sub>, RbFeF<sub>3</sub> and K<sub>2</sub>NiF<sub>4</sub> and results correlated with their magnetic susceptibility data and discussed in terms of the hyperfine interactions.

#### EXPERIMENTAL:

All spectra were recorded using a varian wide line NMR spectrometer with their temperature accessory. The Fluorine shift was taken with reference to teflon (the diamagnetic shift in teflon is negligibly small compared to the large paramagnetic shift in these compounds) and the Rubidium shift with respect to the Rb resonance in  $Rb_{0}Co_{3}$  solution.

The samples KFeF<sub>3</sub> were obtained through the courtesy of Bell Telephone Laboratories and pure  $K_2NiF_4$  from K & K Laboratories, New York. KFeF<sub>3</sub> and RbFeF<sub>3</sub> are isomorphous having cubic perovskite structure with the Fe ion at the body center, the K, Rb at the corners, and F at face centers. The K, Rb ionsare located at sites with cubic point symmetry while the point symmetry of F sites is tetragonal. In the structure of  $K_2NiF_4^{(3)}$ , there are Ni-F-Ni bonds (exactly like in perovskite KMiF<sub>3</sub>) in the (OO1) planes, whereas in the (OO1) direction NiF<sub>2</sub> planes are separated by two KF planes. Ni<sup>2+</sup> cation in both cases are surrounded by an octahedron of fluoride. It has been reported <sup>(4,5)</sup> that  $K_2NiF_4$  is the first example of a system to exhibit a genuine two-dimensional antiferromagnetically ordered state. Though layer structures are not rare, what makes  $K_2NiF_4$  of particular interest is that unlike in other layer structured compounds (where the intraplane interaction is ferromagnetic and interplane is ferro or antiferromagnetically ordered), the interplane interaction is antiferromagne tic, and there is negligible interaction in the 3rd dimension.

Table I gives some general properties of these three compounds.

#### RESULTS AND DISCUSSION:

Figs. 1 and 2 shows the field and temperature dependence respectively of the <sup>19</sup>F resonance in KFeF<sub>3</sub>, RbFeF<sub>3</sub> and  $K_2NiF_4$  and <sup>85,87</sup>Rb resonance in RbFeF<sub>3</sub>. The flucrine NMR was shifted towards lower field in all the three compounds. The room temperature shift was 1.71%, 1.6% and 0.6% in KFeF<sub>3</sub>, RbFeF<sub>3</sub> and  $K_2NiF_4$  respectively. Whereas the isotropic shift of the fluorine resonance is towards lower field at


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constant frequency, the shift of the 85,87Rb resonance is to higher field. Though the Rubidium shift is small, of the order of 0.15% at room temperature, the interest is due to its negative character. We shall discuss this point later.

The <sup>19</sup>F nuclear magnetic resonance shift and its temperature dependence is nearly the same in both KFeF3, but in K, NiF, there is very little dependence of the shift on the temperature. This is rather evident from the fact that the  $1/\chi$  vs temperature in KFeF, and RbFeF, is similar and obeys Curie-Weiss law at high temperature; whereas in  $K_{\rm N}$  NiF<sub>4</sub> the susceptibility varies by less than 10% between 100 - 400°K with a weak maximum at  $\sim 250^{\circ}$  K <sup>(6)</sup>. The lines were very asymmetric and exceptionally broad close to Neel temperature; and disappeared completely below T. . In the case of K.NiF., the signal was asymmetric, but when recorded at high fields, it appeared as though the asymmetry is partly due to the overlap of two lines, one sharp and the other broad having nearly the same shift. Unfortunately we could not resolve them and hence results for K\_NiFA are corresponding to the main line. As seen in Fig. 2 the <sup>19</sup>F shift in K\_NiF\_ shows only a small temperature dependence and disappears below 228°K. We have confirmed this by taking measurements accurately every 2° close to 228°K. Hence, we feel that the long range ordering sets in this compound much earlier than the  $T_N \approx 180^{\circ}$ K reported by the magnetic susceptibility measurements <sup>(6)</sup> and confirmed by Neutron diffraction measurements (5,7).

Figs. 3 and 4 are the plot of <sup>19</sup>F nuclear magnetic resonance shift against the molar susceptibility in RbFeF<sub>3</sub> and K<sub>2</sub>NiF<sub>4</sub> respectively. As can be seen from the figure the shift follows the susceptibility in a linear way in the high temperature region. The slope of the straight line gives us an estimate of the isotropic part of the hyperfine interaction constant, A<sub>8</sub>. These results along with the calculated s-electron spin density at the fluoride orbital, fs, are given in Table II. In the case of K<sub>2</sub>NiF<sub>4</sub>, the curve of shift vs  $\mathcal{X}_m$  intersects at the positive side of  $\mathcal{X}$  axis, giving a temperature -independent contribution to the susceptibility,  $\mathcal{X}_{temperature}$  -independent = 2.5 x 10<sup>-4</sup> emu/mole, which is of the same order of the calculated value(4).

The  $^{85,87}$ Rb resonance lines were symmetric due to the cubic point symmetry at the Rb site, and gave a small negative shift and is appreciably temperature dependent (Room temperature shift = -  $0_{\sigma}$ 146% and - 0.195% at 123°K). The fact that we get a negative shift implies that the net spin density at the Rb<sup>+</sup> is of opposite direction to the Fe<sup>2+</sup> spin. If the Fe<sup>2+</sup> orbital extend far enough toward a Rb<sup>+</sup> ion, an electron in one of the Rb<sup>+</sup>S orbital can be transfered into the empty Fe<sup>2+</sup> (4s) orbital. The value of the isotropic hyperfine interaction constant  $A_g$  for  $^{85}$ Rb and  $^{87}$ Rb and the corresponding negative spin densities at the Rb site are calculated from the experimentally obtained shofts and are given in Table II.

#### ACKNOWLEDGEMENTS

The author is thankful to Dr. R. Vijayaraghavan for his interest in the work.



# TABLE I

Some Properties of KFeP3, RbFeF3 and K2NiF4

| Property              | KFeF.                                   | RbFeF3  | K2N1P4     |
|-----------------------|---|---|------------|
| T <sub>N</sub> °K     | ~ 115                                   | ~ 102   | ~ 180      |
| Structure             | Oubic Perovskite                        | Cubic Perovskite                              | Tetragonal |
| at 298 <sup>0</sup> K | a = 4.121 <sup>0</sup> A                | a = 4.173 <sup>o</sup> A                      | a = 4.006  |
|                       | . :                                     | · · ·   | c = 13.076 |
| Below T <sub>N</sub>  | Rhombohedral                            | 102-87°K Tetragonal                           |            |
|                       | a = 4.108 A                             | c/a = 1.0012                                  |            |
|                       | $= 89^{\circ} 51^{\circ} \pm 1^{\circ}$ | 87 <sup>0</sup> -45 <sup>°</sup> K Orthorhomb | te -       |
|                       |   | ferromagnetic                                 |            |
|                       |   | below 45 <sup>°</sup> K - Monool:             | inic       |
| $\chi_{m} = mu/mole$  |   | 8.95 x 10 <sup>-3</sup>                       | 21.43 x 10 |

# TABLE II

NMR in KFeF3, RbFeF3 and K2NiF4

| Property at 298°K     | KF0F3           | RbFeF3           | K2N1F4  |  |
|-----------------------|-----------------|------------------|---|--|
| 19 F Resonance        |                 |                  |   |  |
| line                  | Asymmetric      | Asymmetric       | Asymmetric - Overlap of<br>two <sup>19</sup> F lines having<br>nearly the same shift. |  |
| Shift (0()%           | 1.71 + 0.02     | 1.60 ± 0.02      | 0.60 ± 0.02   |  |
| A_ C=1                | 15.22           | -                | 23.40   |  |
| f <sub>s</sub> (%)    | 0.405           | -                | 0.32  |  |
| 85,87 Rb in RbFeF, Pr | operty at 298°K | 85 <sub>Rb</sub> | 87 <sub>Rb</sub>  |  |
| · J                   | Shift (%)       | - 0.146 + .00    | 02 - 0.146 + .002   |  |
|                       | A_ Cm-1         | - 0.31 x 10      | -6 - 10.25 x 10-6   |  |
|                       | f (%)           | 0.036            | 0.036   |  |

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DISCUSSION:

- C.M. Srivastava : Which is the dominant interaction in  $K_2 NiF_4$ , the 90° or the 180° c-a-c superexchange? It is important to know this since in  $d^8-d^8$  interaction the signs of the two interactions are opposite?
- K.R.K. Easwaran: The dominent interaction in  $K_2 \operatorname{NiF}_4$  is the 180° cation-anion-cation superexchange. In the Ni<sup>2+</sup>-F-Ni<sup>2+</sup>, the resulting superexchange is dependent on the  $\sigma$  bonding of the fluorine  $P_{\sigma}$  orbital with the nickel  $d_{\overline{\gamma}}$  orbitals, the former simultaneously  $\mathcal{K}$ -bonds with the p orbitals of neighbouring K cations.

N.S. Satya Murthy:

1. The large difference in the Neel temperatures found from neutron diffraction measurements and your measurements appears surprising. I do not expect much residual order above the Neel temperature in these compounds. May be we should take a look at your samples with neutrons and follow the temperature dependence of the antiferromagnetic peaks.

2. What are the exchange integrals like in these fluorides?

K.R.K. Easwaran :

1. I should think so.

2. The values of J reported in the literature for these compounds are:

| KFeF3                           | 5.38 <sup>0</sup> K. |  |  |
|---------------------------------|----------------------|--|--|
| RbFe <sub>3</sub>               | (not reported).      |  |  |
| K <sub>2</sub> NiF <sub>4</sub> | 118 <sup>0</sup> K.  |  |  |

The value of J for  $K_2 \operatorname{NiF}_4$  is surprisingly large; approximately 40% larger than  $\operatorname{KNiF}_3$  in spite of their seemingly identical crystallographic surroundings and the bonding in the two salts.

## NUCLEAR MAGNETIC RESONANCE IN ANTIFERROMAGNETIC Rb\_MnCl\_.2H\_O and Cs\_MnCl\_.2H\_O

V. Negarajan, Tata Institute of Fundamental Research, Bombay-5.

#### and

R.D. Spence and J.A. Casey, Michigan State University, East Lansing, Michigan, U.S.A.

### INTRODUCTION:

Jensen<sup>(1)</sup> has studied the X-ray crystal structure of the isostructural salts  $Rb_2MnCl_4.2H_2O$  and  $Cs_2MnCl_4.2H_2O$ . He finds then to be triolinic with space group P1, the only symmetry elements being inversion centres at each corner of the unit cell, at the face centres and at the body centres of the cell. From studies of Rb,Cl, Proton nuclear magnetic resonance we find that  $Rb_2MnCl_4.2H_2O$  is antiferromagnetically ordered below 2.21°K. Similar studies of Cs, Cl and Proton resonance in  $Cs_2MbCl_42H_2O$ show that it is antiferromagnetically ordered below 1.86°K.

### EXPERIMENTAL RESULTS AND DISCUSSION:

In zero applied field at  $1.1^{\circ}$ K we have observed two Proton resonances at 18.96 Mo/s and 18.30 Mc/s. From observation of proton resonance in a small applied field of 80 cersteds we find that the magnetic space group contains only elements which charge a given field into an oppositely directed field. This information coupled with the fact that the sites of magnetic ions in the lattice cannot be anti-inversion centres led us to conclude that  $P_g$   $\bar{1}$  is the only possible magnetic space group from among the triolinic groups.

In the paramagnetic state we have observed two weak  $^{35}$ Cl pure quadrupole resonance at 3.85 Mc/s and 5.33 Mc/s. In the antiferromagnetic state a total of twelve chlorine resonance were observed. Six of these resonances were strong and six rather weak corresponding to  $^{35}$ Cl and  $^{37}$ Cl respectively. At 1.1°K the six  $^{35}$ Cl resonance occur at 10.72, 10.48, 9.63, 8.56, 7.72 and 6.25 Mc/s. Of these six lines three must be associated with each of the inequivalent chlorines in the unit cell. The proper selections were made based on the fact, that when extrapolated into the paramgnetic state the second moment<sup>(2)</sup> equals the square of the pure quadrupole frequency.

In the paramagnetic state three pure quadrupole resonances were observed due to the isotopes of Ruhidium. The  $^{85}$ Rb resonance occur at 2.67, 3.22 Mc/s and the  $^{87}$ Rb at 3.12 Mc/s.

In the antiferromagnetic state the  $^{87}$ Rb resonance spectrum consists of six lines at 1.22, 3.89, 4.18, 5.12, 5.41 and 9.26 Mc/s at  $1.1^{\circ}$ K. These represent all possible transitions among the four energy levels for I = 3/2.

The  $^{65}$ Rb spectrum consists of four lines at 2.38, 2.78, 3.20 and 3.79 Mc/s at 1.1 $^{\circ}$ K.

The  $^{133}$ Cs (I = 7/2) spectrum in Cs<sub>2</sub>MnCl<sub>4</sub>.2H<sub>2</sub>O consists of seven lines around 1 Mc/c and arises due to the small quadrupole interaction acting as a perturbation on the internal field at Cs site.

For the protons the internal fields at their sites are directly obtained from zero field frequencies. The fields at the two proton sites in  $Rb_2MnCl_4.2H_2O$  are 4439, 4296 oersteds at 1.1°K. In the case of chloric and Rubidium, Cesium the calculations of the internal fields are not so straight forward since one has to take into consideration the quadrupole interaction. The fields at these nuclear sites could however, be calculated from the observed frequencies in the ordered state using a procedure similar to the one we have used elsewhere<sup>(3)</sup>. We find that the internal fields at the two 'Cl' sites in the Rubidium salt are 19490, 21630 oersteds at 1.1°K respectively. The internal field at the 'Rb' site at 1.1°K is 1879 oersteds.

The internal fields at the proton, chlorine, cesium sites in the Cs salt are comparable to those at the proton, chlorine and Rubidium sites in the Rb salt.

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### DISCUSSION:

P. Singh: How do you make sure that throughout the investigation the salts remain in the antiferromagnetically ordered state?

V. Nagarajan:

With the lines in the ordered state under observation if the temperature of the helium bath is raised it can be seen that the lines drift in frequency, get weaker in intensity and ultimately disappear at the transition temperature.

A.K. Saha, S. Sengupta and R. Roy, Saha Institute of Nuclear Physics, Calcutta-9.

### INTRODUCTION:

A new method for the determination of the parameters of a single crystal used for NQR studies was suggested by Saha<sup>(1)</sup> in which the Zeeman split pattern corresponding to rotations of the crystal about the R.F. axis and an axis perpendicular to the R.F. and the Zeeman field axes - need to be analysed. In cases where the value of the asymmetry parameter  $\gamma_i$  is known a priori, the split pattern for rotation about the R.F. axis alone can yield all the orientation parameters for the crystal<sup>(2)</sup>. In this paper the results of an analysis of the split spectra obtained from a single crystal of MaClO<sub>3</sub> are reported.

### THEORY:

Cohen's (3) expression for Zeeman splitting of the Nuclear Quadrupole energy levels can be written as

| Е <sub>р</sub> ±∆р | where | $\Delta \mathbf{p} = \omega_{\mathbf{Z}} \left[ \mathbf{A}_{\mathbf{p}} \cos^2 \theta_{\mathbf{Z}} + \sin^2 \theta_{\mathbf{Z}} (\mathbf{B}_{\mathbf{p}} + \mathbf{C}_{\mathbf{p}} \cos^2 \phi_{\mathbf{Z}}) \right]$ | • |
|--------------------|-------|---|---|
| and                |       | ,<br>,  |   |
| E <sub>n</sub> +∆q | where | $\Delta q = \omega_{\pi} \int A \cos^2 \theta_{\pi} + \sin^2 \theta_{\pi} (B + C \cos^2 \phi_{\pi})^{\frac{1}{2}}$  | t |

where  $\omega_z = \frac{\gamma_{H_z}}{2} = \frac{\gamma_{H_z}}{2} = \frac{\gamma_{H_z}}{2} = \frac{\gamma_{H_z}}{2} = \frac{\gamma_{H_z}}{2}$  and the asymmetry parameter  $\gamma$ , and  $\theta_z$ ,  $\phi_z$  are the polar angles of the Zeeman field direction (2) in the principle axes frame  $\sum_{p}$ .

With the application of Zeeman field the pure NQR line splits up into a quadruplet the frequencies of which are given by

$$\mathcal{V}_{pq}^{[\alpha]} = \mathcal{W}_{pq} - g_{pq} \qquad \mathcal{V}_{pq}^{[\alpha]} = \mathcal{W}_{pq} - f_{pq}$$

$$\mathcal{V}_{pq}^{[\alpha]} = \mathcal{W}_{pq} + g_{pq} \qquad \mathcal{V}_{pq}^{[\alpha]} = \mathcal{W}_{pq} - f_{pq}$$
where  $g_{pq} = |\Delta p - \Delta q|$  and  $f_{pq} = |\Delta p + \Delta q|$ 

It may be noted that  $2g_{pq}$  measures the separation between the inner pair  $(\alpha', \alpha'')$ and  $2f_{pq}$  stands for the separation between the outer pair  $(\beta, \beta')$  of the split pattern.

We may now define a splitting function

$$\mathbf{K} = \frac{1}{\omega_{\mathbf{Z}}^2} \cdot \frac{1}{2} \left( \mathbf{f}_{\mathbf{pq}}^2 + \mathbf{g}_{\mathbf{pq}}^2 \right) = \mathbf{a} \cos^2 \theta_{\mathbf{Z}}^2 + \sin^2 \theta_{\mathbf{Z}}^2 \left( \mathbf{b} + \mathbf{0} \cos^2 \phi_{\mathbf{Z}} \right) \quad \dots \dots (1)$$

where

$$\mathbf{a} = \mathbf{A}_{\mathbf{p}} + \mathbf{A}_{\mathbf{q}}, \mathbf{b} = \mathbf{B}_{\mathbf{p}} + \mathbf{B}_{\mathbf{q}}, \mathbf{0} = \mathbf{O}_{\mathbf{p}} + \mathbf{O}_{\mathbf{q}}$$

### X-ROTATION:

Let the initial position (Position 0) of the crystal be denoted by the suffix O; then  $Q'_{\mathbf{X}}$  measures the rotation around the X-axis from the X meridian (XZ great circle);  $\Theta_{\mathbf{X}0}$ ,  $\Theta_{\mathbf{X}0}$  denote the polar angles of the R.F. field with respect to frame  $\sum_{\mathbf{P}}$ for initial position of the crystal.

Then from the transformation matrix  $\Sigma_p \rightarrow \Sigma_L$  (the Laboratory frame of axes), - for X-rotation, the splitting function can be shown to be given by

$$K(\alpha'_{x}) = a \cos^{2} \Theta_{\tilde{z}} + \sin^{2} \Theta_{\tilde{z}} (b + c \cdot \cos^{2} \phi_{z})$$
  
=  $p_{x} + q_{x} \cos^{2} \alpha' x + r_{x} \sin^{2} \alpha' x$  .....(2)

where,

p<sub>x</sub>, q<sub>x</sub> and r<sub>x</sub> are given by

$$p_{x} = b + \frac{\sin^{2} \theta_{x0}}{2} (a - b - c \cos 2 \phi_{x0})$$

$$q_{x} = \frac{\sin^{2} \theta_{x0}}{2} (a - b - c \cos^{2} \phi_{x0}) + c \cos^{2} \phi_{x0} (a - b - c \cos^{2} \phi_{x0}) + c$$

.....(4)

Substituting,  $\cos 2 \Theta = \frac{q_x}{\Lambda_x}$ ,  $\sin 2 \Theta = \frac{r_x}{\Lambda_x}$ 

where, 
$$\Lambda_x^2 = q_x^2 + r_x^2$$
,

Equation (2) can be written as

Then, p<sub>x</sub> can be determined from

and  $\Lambda_{\mathbf{x}}$  is obtained from

Utilizing the relations (3) and (4) , we obtain the following expressions

$$c \cos 2\phi_{x0} = \frac{(a-b) \left[ \Lambda_{x}^{2} - (p_{x}-b)^{2} - c^{2} \right] + 2c^{2}(p_{x}-b)}{\left[ \Lambda_{x}^{2} - (p_{x}-b)^{2} - c^{2} \right] + 2(p_{x}-b)(a-b)} \qquad \dots \dots \dots (6)$$
  

$$sin^{2} \theta_{x0} = \frac{\left[ \Lambda_{x}^{2} (p_{x}-b)^{2} \right] - 2(p_{x}-b)(a-b)}{(a-b)^{2} - c^{2}} \qquad \dots \dots \dots (9)$$

Thus the experimental study of the rotation pattern gives us the values of  $p_x$  and  $\Lambda_x$ , since a, b, c are known a priori, for the case in which  $\eta$  is known.

### EXPERIMENTAL:

The NQR spectrometer utilized in the present investigation consists of an externally quenched super-regenerate oscillator-detector similar to that of Dean<sup>(4)</sup>, quenched by square waves at 60,000 p.p.s. frequency modulation of the super-regenerative oscillator is achieved by introducing a small 200 cps signal from a temperaturestabilized Wein-Bridge Oscillator on a varicap HC-7001 connected across the tank circuit of the oscillator. The detected NQR signal after amplification in a Twin-Tee amplifier tuned to 400 cps, passes through a lock-in amplifier stage operated by square wave-gate signals at 400 pps, for ultimate display as second derivative signals on a Varian G-11A pen recorder.

The uniform static magnetic field at the site of the sample within the r.f.coil was provided by a pair of Helmholtz coils excited by a stabilised current supply from a Radart Type 808A unit. The magnetic field produced by this Heimholtz coil assembly has been found to be 185/amp.

The determination of the crystal parameters by this method needs a special goniometer assembly (Fig. 1) with the help of which the single crystal can be rotated around the three mutually perpendicular axes, X-axis (R/F axis), Z axis (Zeemanfield axis) and the Y-exis. Typical spectral patterns from the crystal of NaClO<sub>3</sub> mounted initially for Zeeman field perpendicular to 100 plane of the unit cell, shows for rotation around the R/F axis, that the pure NQR line splits up even upto 8 spectral components for particular orientation of the principal axes of the crystal with respect to the laboratory frame.

It may be noted that the unit cell of NaClO<sub>3</sub> contains four differently oriented field gradients<sup>(5)</sup>, parallel to the four body diagonals. In the initial position, the Zeeman field makes the same angle of  $54^{\circ}44^{\circ}$  with all the aforesaid four directions, and the standard three line spectrum is obtained. With rotation about the R.F. axis, however, field gradients in pairs (1 & 4) and (2 & 3) become effective for producing splitting upto 8 components.



Fig. 2

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The curve (Fig. 2) obtained for variation of  $K(Q'_x)$  with the angle  $Q'_x$  gives the measure of the average value  $p_x$ ; from the maximum value of  $K(Q'_x)$ , one obtains also the magnitude of  $\Lambda_x$ .

For spin 3/2 cases, where the value of  $\eta$  is known, the parameters a, b and c are given by

$$a = \frac{15 + \eta^2}{2(3 + \eta^2)}, \quad b = \frac{3 + 2\eta^2}{3 + \eta^2} \quad and \quad c = \frac{-3\eta}{3 + \eta^2}$$
  
$$= \frac{12 + 5}{2^{\frac{4}{7}}} \quad \frac{25 - 3}{5} \quad \frac{-3\eta}{5}$$

where,  $5 = 3 + \eta^2$ .

Substituting these values of a, b, c,  $p_x$  and  $\Lambda_x$  in equations 8, 9 and 10 we readily obtain the value of the angles  $\Phi_{xo}$ ,  $\mu_{xo}$  and  $\Theta_{x}$ .

The initial position of the crystal  $\alpha'_{xo}$ , is found by determining the angle  $\phi_x$  through which the crystal must be rotated to arrive at the position where  $\mathfrak{K}(\alpha'_x) - \varphi_x$  is a maximum. Then  $\alpha'_{xo}$  is given by the relation:  $\alpha'_{xo} = (\phi_x - \Theta_x)$ .

Hence, the direction cosines of the principal axes  $X_p$ ,  $Y_p$  and  $Z_p$  in the laboratory frame, follows from the - transformation matrix, - where all the angles  $\theta_{xo}$ ,  $\phi_{xo}$  and  $\gamma_{xo}$  are obtained experimentally.

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SOME REMARKS CONCERNING THE POWDER METHOD FOR THE DETERMINATION OF ASYMMETRY PARAMETERS FOR I = 3/2 NUCLEI FROM N.Q.R. ZEEMAN SPECTRA

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Department of Chemistry, Indian Institute of Technology, Kanpur.

### INTRODUCTION:

On account of the fact that for a nucleus with spin I = 3/2 there is only one pure nuclear quadrupole resonance (N.Q.R.) transition frequency<sup>(1)</sup> in the absence of a magnetic field it is possible to determine the three principal components,  $V_{ii}$ , of the electric field gradient at the site of such a nucleus only be Zeeman measurements. The theoretical treatment of transition frequencies and intensities of the N.Q.R. Zeeman spectra in single crystals for I = 3/2 cases has been subject of study by Berschn<sup>(2)</sup>, Dean<sup>(3)</sup> and Toyama<sup>(4)</sup>. It is thus possible, in principle, from such single crystal Zeeman studies to obtain the asymmetry parameter  $\gamma = (v_{xx} - v_{yy})/v_{zz}$ for the electric field gradient. However, the number of such  $\gamma$  determinations is rather small in comparison to the vast amount of data available on the N.Q.R. transition frequencies for I = 3/2 nuclei. The requirement that the sample under study be a single crystal is rather difficult to be met in practice and it is apparently due to this reason that the  $\gamma$  values are not available in many cases.

Morino and Toyama<sup>(5)</sup> have outlined a method for the determination of  $\gamma$  for I = 3/2 nuclei using powder specimen. The essence of this method consists in applying the Zeeman field along the axis of the radio frequency coil inducing the N.Q.R. transitions in the powder specimen kept inside this r.f. coil. These authors successfully applied their method to obtain the  $\gamma$  values for  $^{35}$ Cl in paradichlorobenzene and cyanuryl chloride. Later, Adrian<sup>(6)</sup> employed this method to obtain an upper estimate ( $\leq 0.03$ ) for  $\gamma$  in solid chloride obtained by freezing at 77°K. The powder method presented considerable difficulties in solid chlorine due to its low  $\gamma$  value. The method has been successfully employed by Dinesh and Narasimhan for  $^{35}$ Cl resonances in powder specimen of  $H_g Cl_2^{(7)}$ , frozen samples of chlorobenzene  $^{(8)}$  and other chloroaltained due to their very low melting point and the powder method offers perhaps one of the best approaches for the determination of the asymmetry parameters in such cases.

In spite of its attractive possibilities the powder method has not been extensively employed so far. There are three major problems involved in the method. These are: (1) signal-to-noise ratio in the Zeeman spectra of powder specimen or frozen samples (2) location of peaks due to the field gradient asymmetry and (3) the need for extrapolation of data to infinite field strength due to line width. It is the purpose of the present paper to discuss these problems and suggest procedures which will help improve the accuracy of the  $\gamma$  values obtained by the powder method.

### SIGNAL-TO-NOISE RATIO IN N.Q.R. ZEEMAN SPECTRA OF FOWDERS:

The thoretical treatment due to Toyama<sup>(4)</sup> and Morino and Toyama<sup>(5)</sup> shows that in the N.Q.R. Zeeman spectrum for I = 3/2 spins with  $\eta \neq o$  in the powder case the intensity of the transition corresponding to the "zero field" case is distributed over the region -2  $\mathcal{V}_{H}$  to +2  $\mathcal{V}_{H}$  when the field is applied. Here  $\mathcal{V}_{H} = |\mathcal{N}| H/(2\pi)$ ,  $\mathcal N$  being the gyromagnetic ratio of the nucleus and H the magnetic field intensity. Relatively intense peaks appear at  $\mathcal{V} = -(1 \pm \eta) \mathcal{V}_{H}$  and  $\mathcal{V} = +(1 \pm \eta) \mathcal{V}_{H}$ under favourable conditions. These are governed by the line width (  $\Delta \mathcal{V}$  ) and  $\eta$ values. It has been pointed out by Morino and Toyama<sup>(5)</sup> that in order to get -split lines the magnetic field H should satisfy the condition  $H > 2 \pi \Delta \nu / (\eta | \nu |)$ . For \* given value the required fields are large for low  $\eta$  values. The application of the Beeman field along the r.f. coil axis reduces the intensity of the lines and the  $\gamma$ -split lines have an intensity which is only  $(\eta/4)$  of the criginal line intensity in the zero-field case. One easy way of increasing the S/N isto increase the effective esuple volume and use fairly large Helmholtz coil assembly to provide the Zeeman field. It is passumed here that the usual narrow band (phase) detection scheme is used to record the spectra. Superregenerative spectrumeters can be employed in this type of work since only frequency measurements are to be made. However, it is worthwhile to obtain the data also from a regenerative spectrometer wherever possible and thus confirm the essential features of the Zeeman spectrum. Computer averaging techniques can be also profitably employed. However, it is necessary to have a very stable cacillatordetector system in order to be able to scan the Zeeman spectrum repeatedly over the desired range and obtain significant data free from spectrometer instabilities which might distort the information. A spectrometer system employing feedback control<sup>(10)</sup> would be satisfactory for this purpose.

#### LOCAL OF $\eta$ -SPLIT LINES:

Due to the problems arising from S/N the location of the  $\gamma$ -split lines or "kinks" in the Zeeman spectra of powder specimens is often difficult. The situation is considerably improved by nothing the fact that these lines are to be found in the region around  $\pm \gamma_{\rm H}$  and  $\pm 2 \gamma_{\rm H}$  and the value of H being known we can look for such lines at these places in the Zeeman spectrum. However, if the main line width ( $\Delta \gamma$ ) is large these ' $\gamma$  peaks' may not be easily located. In order to improve resolution it may be pointed out here that apart from the usual first derivative presentation it would be hopeful to record the second derivative spectra as well. This can be done by narrow band detection at the barmonic of the modulation frequency. However, it is possible to use an anlog method for the presentation of higher derivatives. This method has been successfully employed<sup>(11)</sup> in the study of electron spin resonance spectra of free radicals in solution. Thrid and even higher derivatives can be obtained and the resolution can be thus enhanced.

#### EXTRAPOLATION TO INFINITE FIELD:

Under favourable conditions the  $\gamma$  peaks around  $\pm \gamma_{\rm H}$  can be recorded in the first derivative (of the absorption) presentation. The general feature of the line is shown in Fig. 1a. The peak-to-peak separation,  $\delta_1$ , corresponds only approximately to  $2\gamma_{\rm H}^{2}$  due to the intrinsic line width. Morino and Toyama<sup>(5)</sup> suggested an extrapolation method employing the line width data  $\delta_1$ ,  $\delta_2$  and  $\delta_3$  (see Fig. 1). In fact the plots of  $\delta_1/(2\gamma_{\rm H})$ ,  $\delta_2/(2\gamma_{\rm H})$  and  $\delta_3/(2\gamma_{\rm H})$  vs 1/H are employed to obtain  $\gamma$ . While it is perhaps not difficult to measure  $\delta_1$  from the first derivative powder Zeeman spectra  $\delta_2$  and  $\delta_3$  are somewhat difficult to obtain. On the other hand, the second derivative presentation can elearly yield  $\delta_2$  values as shown in Fig. 1b. The determination of  $\delta_3$ , in practice, involves a correction for the background absorption. The measurement of all the three  $\delta$  values may not be possible in many cases. It may be pointed out here that the  $\gamma$  value is obtained from the intercept of the curve  $\delta/(2\gamma_{\rm H})$  vs 1/H on the  $\delta/(2\gamma_{\rm H})$  axis. The question then arises as to whether it is possible to obtain fairly accurate values of  $\gamma$  from measurements on, say,  $\delta_1$  slone.

In the weak field case the curve  $\delta_1/(2\gamma_H) \frac{vs}{H}$  1/H can be described by  $\delta_1/(2\gamma_H)$  $\approx \Delta \mathcal{V}/(2 \mathcal{V}_{H})$  while in the strong field case it is described by  $\delta_{1}/(2 \mathcal{V}_{H}) \approx (\eta - \frac{\Delta \mathcal{V}}{2 \mathcal{V}_{H}})$ . There is hence an intermediate region at which  $\gamma \gamma_{\rm H} \approx \Delta \gamma$  and the curve must show a 'turning up' here (see Fig. 2). The curve is symmetric about this point (P) and this fact may be used in obtaining the correct  $\eta$  value. Using the definition of  $\mathcal{P}_{\mu}$  we see that the magnetic field corresponding to this turning point is  $H\approx 2\pi\Delta \mathcal{V}/(\eta|\gamma|)$ . Therefore, this point will be seen at fairly high fields for small 7) values and the S/N considerations may not permit one to reach such a situation experimentally. In these cases the following procedure may be adopted. First, extend the  $\partial_1/(2\gamma_{\rm H})$  vs 1/H curve to the origin 0. Next, from a precise determination of the  $\Delta \mathcal{V}$  value ( in the absence of the external field) draw the horizontal line corresponding to  $\Delta V/(2 \mathcal{V}_{\mu})$  . This line intersects at point P. The vertical line AB passing through P represents the value of H for this turning point. Now we reflect the  $\delta_1/(2v_H)$  ve 1/H curve along the AB line and by the above considerations the reflected line intersects the  $\delta_{1}/(2\mathcal{V}_{H})$  axis at  $\eta$  . It must be pointed out here that the behaviour of the curve at the high field side is symmetric at this point and hence the reflection.

It is clear that the correction term  $\Delta \mathcal{V}/(2\mathcal{V}_{H})$  would be very small if the line width  $\Delta \mathcal{V}$  is small. In such cases  $\delta_{1}/(2\mathcal{V}_{H}) \approx \mathcal{V}$  and the asymmetry parameter can be obtained from  $\delta_{1}$  measurements without recourse to the graphical method.



Fig. 1: a) The  $\eta$  peak (first derivative), b)  $\delta_2$  in the second derivative form.



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Fig. 2: Graphical method for obtaining  $\eta$  from  $\delta_1$  values. The solid line for  $\delta_1/(2\mu_{\rm H})$  represents the experimental region.

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ESR OF TRANSITION METAL ION IMPURITIES IN FERROELECTRIC CRYSTALS

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### INTRODUCTION

As part of a general programme of study of doped and irradiated ferroelectric crystals using electron spin resonance, we have been studying vanadium doped KDP (potassium dihydrogen phosphate) and copper doped Rochelle salt and some preliminary results are presented in this report.

Aqueous solution of KDP containing traces of vanadium pentoxide yields good single crystals on slow evaporation. At room temperature KDP is tetragonal with cell dimensions a = b = 7.543 Å and c = 6.959 Å. The space group is I42d and there are four molecules in the unit cell (1).

Crystals of copper doped Rochelle salt were grown (2) from an aqueous solution containing Rochelle salt and  $CuCO_3Cu(OH)_2$  in 100 : 1 molar ratio. At room temperature the crystal is orthorhombic with cell dimensions a = 11.93 Å, b = 14.30 Å and c = 6.17 Å. The unit cell contains 4 units and the space group is  $P2_12_2^3$ .

An X-band reflection type ESR spectrometer with 100 Kc/s magnetic field modulation was used for the measurements. A  $H_{011}$  rectangular brass cavity was used. The spectrum was displayed on a double beam oscilloscope and a proton resonance probe was used for field measurements. The frequency of the proton resonance oscillator was measured with BC-221 frequency meter. DPPH placed at the sample site was used as a g-marker.

#### VANADIUM DOPED KDP

The ESR spectrum from single crystal of vanadium doped KDP for a general orientation of the crystal in the magnetic field consisted of a large number of narrow lines and was very complex. However, when the magnetic field is parallel to the c axis (Fig.1), the ESR spectrum is very much simplified consisting mainly of eight equispaced lines, very well resolved and of equal intensity. In addition to these eight lines, the spectrum consisted of many weaker lines and an equally intense line very close to the DFPH line. This may be due to the presence of a free radical or a colour centre formed in the crystal in addition to the vanadium ion impurities. The eight line spectrum is the characteristic hyperfine spectrum from the vanadium nucleus  ${}^{51}\nabla$  (I = 7/2). The absence of the additional sets of eight lines characteristic of zero field splitting indicates that the spectrum is from either  $v^{4+}$  or  $(v_0)^{2+}$  having one unpaired electron in d shell. The spectra along a and b axes are also a simplified one similar to that along c-axis. Measurements have therefore been made along these three directions and the g values are shown in Table I.



TABLE I

| No. | Magnetic field<br>direction |          | g-value | Hyperfine<br>yalue<br>in cm |  |
|-----|-----------------------------|----------|---------|-----------------------------|--|
| 1.  | Para<br>c-az                | allel to | 1.93    | 171.51 x 10 <sup>-4</sup>   |  |
| 2.  |                             | b-axis   | 1.99    | 86 x 10 <sup>-4</sup>       |  |
| 3.  | **                          | a-axis   | 1.99    | $87 \times 10^{-4}$         |  |

 $\boldsymbol{g}$  and hyperfine values of vanadium ion in KDP

When the magnetic field is moved away from the c-axis, each of these eight lines undergo splitting into further components of equal intensity, indicating the presence of inequivalent ions. The nature of the splitting indicates the presence of either four or eight inequivalent ions in the unit cell. The stdy of the angular variation of the spectrum to locate the symmetry axis for the vanadium ion and to determine the principal g and hyperfine tensors are in progress.

However, these preliminary ESR study clearly shows that vanadium goes into the KDP lattice in the quadrivalent state (either  $v^{4+}$  or  $(v_0)^{2+}$ ) and occupies predominantly one particular type of site in unit cell with preferred orientations. Many weak lines observed may be due to other types of impurity sites and we have not made any attempt to look into these lines at present.

#### COPPER DOPED ROCHELLE SALT

Copper doped Rochelle salt gave a complex spectrum consisting of a large number of lines for a general orientation of the crystal which reduce, when the magnetic field is along the crystallographic a, b,'c directions, to a simplified spectrum consisting of four well resolved broad lines of almost equal intensity characteristic of Cu<sup>++</sup> together with a number of much weaker lines. The g-values and the hyperfine values along the three crystallographic directions are given in Table II.

## TABLE II

# g and hyperfine values for Cu<sup>2+</sup> ion in copper doped Rochelle salt single crystal

| No. | Magneti<br>direc | c field<br>ction | y value | Hyperfine<br>value in Cm <sup>-1</sup> |  |
|-----|------------------|------------------|---------|--|--|
| 1.  | Parallel         | to c-axis        | 2.223   | 106.53 x 10-4                          |  |
| 2.  |                  | b-axis           | 2.155   | 68.66 x 10-4                           |  |
| 3.  |                  | a-axis           | 2.093   | 63.71 x 10                             |  |

The characteristic four line spectrum indicates the presence of only one type of Cu<sup>++</sup> ion impurity with the axes of distortion oriented in different direction as indicated by the splitting of the four line spectrum, when the field direction is different from the crystallographic directions. The angular variation of the spectrum is being studied for fixing the g-tensor and hyperfine parameters.

### A CKNOWLEDGEMENTS

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#### DISCUSSION:

| B.V.R. Chowdari | 1. The ESR studies of $VO^{2+}$ in $KH_2PO_4$ made by us show that there<br>is a proton interaction i.e., super hyperfine interaction due to |
|-----------------|--|
|                 | proton nucleus. I would like to know whether you have anything   |
|                 | of that type.  |
|                 | 2. What are the additional lines in the spectrum when Hilc-axis?   |
| J. Ramakrishna  | : 1. No, I do not think that we have seen any super hyperfine inter-   |
|                 | action in our spectrum.  |
|                 | 2. We are not yet sure about them. They may be due to additional   |
|                 | impurities. But they are not due to super hyperfine interaction.   |
| K.R.K. Easwaran | : Has any temperature variation studies of ESR been made in these  |
|                 | compounds?   |
| J. Ramakrishna  | We studied the Rochelle salt in its ferroelectric phase but we   |
|                 | did not fine any change. This is probably because the change   |

in the crystal structure is too small to be detected.

RELAXATION EFFECTS IN THE DOUBLE RESONANCE SPECTRUM OF A SYMMETRICAL THREE SPIN SYSTEM (AB.)

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Nuclear magnetic double resonance experiments consist of irradiation by a strong radio frequency field, at one of the lines of an NMR spectrum, and simultaneous observation of the rest of the spectrum by another weak rf field. The irradiation affects the spectra in the following manner<sup>(1)</sup>: (1) the rf perturbation mixes some of the spin states giving rise to new transitions and shifts in the energies of the existing ones, (ii) the population distribution in the spin energy levels is disturbed resulting in intensity changes, these intensity changes depend on the strength of irradiation and the coupling between various levels due to relaxation (generalised Overhauser effect), (iii) the lifetimes of some of the states is eltered causing linewidth changes. These features reflect the mechanism of relaxation for the spins in the molecule for a given strength and frequency irradiation, and a study of these features is thus capable of giving information about these mechanisms.

In the present work frequency sweep double resonance experiments were performed on a symmetrical three spin system  $(AB_2)$  formed by the ring protons of 2,6 dibromoanaline (20% solution by weight in Carbon Tetrachloride). The single resonance spectrum of this molecule, consisting of two groups of four lines each, has been analysed and the values of the chemical shift  $(\nu'_A - \nu'_B)$  and the coupling constant  $J_{AA}$  were determined to be 89.9 cps and 7.9 cps respectively. The 'B' spectrum consists of two doublets each of separation about 0.3 cps. Irradiation of any one of the lines in the 'B' spectrum by a very small amplitude of the order of 0.1 cps resulted in marked changes in the intensities of those transitions in the 'A' spectrum which have an energy level in common with the transition being irradiated. Double resonance spectra were also obtained for strong irradiation of each of the lines of the single resonance spectrum with several amplitudes ranging from 2.2 cps to 9.2 cps. These latter spectra show all the features of a double resonance spectrum in the form of new transitions, shifts in the line positions, intensity changes and linewidth changes.

The linewidth changes in a double resonance spectrum arises due to, besides relaxation, the inhomogeneity of the magnetic field. The inhomogeneity may not contribute the same width to all the lines in a double resonance spectrum because of the circumstance that the frequency shift produced due to double irradiation augments the effects of inhomogeneity for some transitions and annuls it for some others (2,3).

C.S.I.R. Senior Research Fellow.

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All the abovementioned features of the double resonance spectra have been analysed using Rioch's density matrix formalism<sup>(1,4)</sup>. The equation of motion of the spin density matrix,  $\sigma$ , can be written as<sup>(5)</sup>

$$\frac{d\sigma}{dt} = -i[H,\sigma] = -i[H(t) + H'(t),\sigma]$$

where H(t) is the Hamiltonian for the spin system and contains the Zeeman term, the spin-spin coupling term and the interaction with the two rf fields, and is solved by transforming to a coordinate system rotating with the strong rf field.  $H^{\dagger}(t)$  is the relaxation Hamiltonian, representing the coupling between the spin system and the lattice, about which we wish to derive information. This equation is solved for the steady state condition for various possible relaxation mechanisms and the corresponding  $\sigma$  is obtained in each case. The signal intensity in the double resonance spectrum is then given by the time derivative of the trace of the product  $(I_v \sigma)$ .

The above calculations have been done for two relaxation mechanisms (i) Random isotropic external fields and (ii) Internal dipole-dipole interaction, which are expected to be primary mechanisms  $^{(5)}$ . For both these mechanisms, correlations were explicitly considered; for mechanism (i) the calculations were performed for various degrees of correlation; and for (ii) the correlations were determined from the geometry of the molecule.

The theoretical spectra for large amplitudes of irradiation were obtained using Eloch's approximation<sup>(1,4)</sup>. A satisfactory fit with the experimental data was obtained for mechanism (i) with the ratio of mean square fields at the 'A' and 'B' muclei  $P(A)/f(B_1)$  (=f(A)/f(B\_2)) having a value 2.0, as well as for mechanism (ii). Further the calculated spectra for mechanism (i) were not sufficiently sensitive to the degree of correlation. However, it was possible to distinguish between the two mechanisms for spectra with low amplitudes of irradiation. The reason for this is that the strong irradiation spectra, for which Eloch's approximation is valid<sup>(1)</sup>, are dependent only on the ratio (f(A)/f(B))and are independent of  ${\mathcal T}_{m c}$ , the correlation time for molecular motion, while the weak irradiation spectra, for Bloch's approximation is not fully applicable, depend on the ratio of the f's and the value of  $\mathcal{T}_{c}$ . The theoretical spectra for low irradiation, calculated with partial Bloch approximation<sup>(5)</sup>, gave incorrect intensities for mechanism (ii), and a good agreement with the experiment is obtained of mechanism (i) with (f(A)/f(B) = 2.0 and partial correlation of approximately 0.5 between each pair of spins.

Thus, it is possible to conclude that the proton relaxation in 2,6-dibromoaniline is primarily through random external fields with the means square fields at 'A' nuclei being twice as large as that at 'B' nuclei and with a partial correlation of the order of 0.5 for each pair of spins.

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### DISCUSSION:

P. Singh : What is the advantage of double resonance experiment over the single resonance experiment? What are the orders of relaxation times?

A. Kumar :

The single resonance experiment contains little information about the relaxation mechanism in the molecule and the double resonance provides a very effective tool for looking into the processes of relaxation in the molecule.

# ELECTRONIC ABSORPTION SPECTRUM OF NaMnF2

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The optical spectra of transition metal ions in crystals show a number of interesting features. The bands usually observed and assigned to single ion transitions have been successfully explained with the advancement of crystal field theory<sup>(1)</sup>. However, recent studies show that the transitions involving pair of ions may also be present particularly in magnetically ordered materials<sup>(2-5)</sup>. The exchange interaction between the ions is consistered to be instrumental in inducing this pair absorption. One such possibility is that the single ion transitions may be modified by the exchange interactions in pairs<sup>(3)</sup>. The second possibility is that both the ions may be simultaneously excited by a single photon<sup>(2,6)</sup>. In the present studies of NaMnF<sub>3</sub> we shall be concerned with the crystal field transitions and also the second type of pair absorption involving simultaneous excitation of two ions.

The optical absorption of NaMnF<sub>3</sub> single crystal was measured with a cary -14 spectrometer at room temperature and liquid nitrogen temperature ( $77^{\circ}$ K). The observed band positions at  $77^{\circ}$ K are given in Table I. The six bands observed below 35000 cm<sup>-1</sup> are characteristite of Mn<sup>2+</sup> absorption in flourides <sup>(7,8)</sup> and can be assigned to various cubic field quartet levels arising from <sup>4</sup>G, <sup>4</sup>D and <sup>4</sup>P levels of the free ion as given in Table I. The positions of these six bands are very well fitted in terms of the parameters <sup>(8,9)</sup> B, C, Dq and  $\propto$  and the values of the parameters for the  $77^{\circ}$ K spectrum are found to be 845, 3040, 775 and 76 cm<sup>-1</sup> respectively. The fine structure of these bands has been interpreted by considering the effects of non-cubic crystal field, vibronic coupling and spin-orbit interaction on the cubic field levels and these details will be described elsewhere <sup>(10)</sup>.

The spectrum above 35000 cm<sup>-1</sup> shows four main bands all of which do not seem to correspond to remaining quartet levels  ${}^{4}A_{2g}$ ,  ${}^{4}T_{1g}$  and  ${}^{4}T_{2g}$  arising from  ${}^{4}F$  level of the free ion. Our assignments based on the widths and calculated energies of these bands are given in Table I. The band at 41238 cm<sup>-1</sup> is sharp and hence assigned to  ${}^{4}A_{2g}(F)$  level. Its neighbouring band at 41926 cm<sup>-1</sup> is assigned to  ${}^{4}T_{1g}(F)$ level which is expected to lie very close to it. The last band at 44444 cm<sup>-1</sup> is tentatively assigned to  ${}^{4}T_{2g}(F)$  level. The calculated energies are in good agreement with these assignments. The problem now is about the orign of broad 37807 cm<sup>-1</sup> band where no quartet level of single ion is expected to lie. This band is considered to be due to the simultaneous excitation of two ions to the  ${}^{4}T_{1g}(G)$  level. This is the lowest energy quartet level lying at 18950 cm<sup>-1</sup> and the calculated

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energy for this lowest energy pair absorption  ${}^{4}T_{1g}(G) + {}^{4}T_{1g}(G)$  is 37900 cm<sup>-1</sup> which is very close to the observed band. Similar band has been observed in MnF<sub>2</sub><sup>(7)</sup> and RbMnF<sub>3</sub><sup>(8)</sup> around 39010 cm<sup>-1</sup> in the two cases respectively; where as the observed energies of the  ${}^{4}T_{1g}(G)$  level in these two cases are 19500 and 19150 cm<sup>-1</sup> respectively. The calculated energies of the pair absorption  ${}^{4}T_{1g}(G) + {}^{4}T_{1g}(G)$ in the two cases are then 39000 and 383000 cm<sup>-1</sup> which agree with the observed band energies. Finally a similarly unassigned band has been observed in MnCl<sub>2</sub> at 36500 cm<sup>-1 (11)</sup>. The observed energy of  ${}^{4}T_{1g}(G)$  band in MnCl<sub>2</sub> is 18500 cm<sup>-1</sup> and hence the 36500 cm<sup>-1</sup> band may also be due to this pair absorption. The detailed report of this work is being prepared for publication<sup>(10)</sup>.

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| TABLE I |
|---------|

|          | Obser  | ved                       |                   | Openillator Strength | Trensition                       | Calculated            |
|----------|--------|---------------------------|-------------------|----------------------|----------------------------------|-----------------------|
| Band     | 入(\$)  | $\mathcal{V}(\mathbf{c})$ | m <sup>-1</sup> ) | (X10 <sup>7</sup> )  | s→                               | V (cm <sup>-1</sup> ) |
| A        | 5277   | 18                        | 950               | 2.55                 | <sup>4</sup> T <sub>1g</sub> (G) | 18 919                |
| B        | 4334   | 23                        | 074               | 2.13                 | 4 <sub>T2g</sub> (0)             | 23 137                |
|          | 3978   | 25                        | 138               | 2.73                 |                                  | 25 170                |
|          | 3960   | 25                        | 25 <b>3</b>       |                      |                                  |                       |
| <b>C</b> | 3930   | 25                        | 445               |                      | $4_{A_{1g}}(G),$                 |                       |
|          | 3911   | 25                        | 569               |                      | 4 <sub>E</sub> (G)               |                       |
|          | 3895   | 25                        | 673               |                      | g                                |                       |
|          | 3587   | 27                        | 87 <b>8</b>       | · .                  |                                  | · .                   |
|          | 3565   | 28                        | 050               |                      |                                  |                       |
| D        | - 3524 | 28                        | 377               | 1.10                 | <sup>4</sup> T <sub>g</sub> (D)  | 28 349                |
|          | 3470   | 28                        | 81 <b>8</b>       |                      | -                                |                       |
| E        | 3321   | 30                        | 111               | · 1                  | •                                |                       |
|          | 3282   | 30                        | 469               | 1.99                 | <sup>4</sup> E <sub>g</sub> (D)  | 30 021                |
|          | 3084   | 32                        | 425               |                      | . *                              | •                     |
| P        | 3060   | 32                        | 680               | 2.48                 | <sup>4</sup> T <sub>1g</sub> (P) | 32 68 <b>6</b>        |
|          | 2800   | 35                        | זיז 714 ק         |                      |                                  |                       |
| X        | 2645   | 37                        | 807 J             | 4 <sub>T</sub> 1     | $g^{(0)+4}T_{1g}(0)$             | 37 836                |
| Ģ        | 2425   | 41                        | 238               | 4 <sub>A2</sub>      | g (F)                            | 40 836                |
| H        | 2385   | 41                        | 926               | 4 <sub>11</sub>      | g <sup>(F)</sup>                 | 41 694                |
| T        | 2306   | 43                        | 369 J             | 4,                   | (P)                              | 44 487                |
| -        | 2250   | 44                        | 444 J             | -2                   | 8,                               | 11 101                |

Experimental Data and Analysis of the Observed Spectrum of NaMnF<sub>3</sub> at 77°K

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### DOUBLE BOND CHARACTER OF C-Br BOND IN MULTIBROMOBENZENES FROM NUCLEAR QUADRUPOLE RESONANCE

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The deviation from the cylendrical symmetry of the electric field gradient at the site of halogen (X) in a C-X bond is due to the partial double bond formation between carbon 2pTC electrons and halogen's pTC electrons. The asymmetry parameter ?? of the field gradient determined from the Nuclear Quadrupole Resonance analysis<sup>(1)</sup> was related to this partial double bond character by Bersohn<sup>(2)</sup> as

$$\gamma = 3 \rho \left( e^2 q \Omega \right)_{\text{stom}} / 4 \gamma \qquad \dots (1)$$

where  $\rho$  is the partial double bond character,  $(e^2qQ)_{atom}$  the quadrupole coupling constant in the atom and  $\mathcal{V}$  the observed frequency in the compound.

Using simple molecular orbital theory  $\operatorname{Bersohn}^{(2)}$  calculated the double bond character of C-Cl bond in a number of compounds in terms of  $\lambda$  which is equal to  $(\beta_{CCl} / \beta_{CC})$  - the ratio of the carbon chlorine resonce integral and the carbon carbon resonance integral. The calculated value of the double bond character for p-dichlorobenzane is  $0.350 \lambda^2$  while the value calculated from the experimental asymmetry parameter,  $0.08 \pm 0.02$  (Dean<sup>(3)</sup> is  $0.04 \pm 0.01$ . From this Bersohn deduced  $\lambda$  to be approximately 1/3. The values calculated for other multibromobenzenes ( $C_{6H_5}$ Cl,  $o-C_{6H_4}$ Cl<sub>2</sub>,  $m-C_{6H_4}$ Cl<sub>2</sub> and  $C_{6Cl_6}$ ) is also  $0.350 \lambda^2$ . This is due to the approximate nature of the method.

The experimental data on multichlorobenzenes show that  $\gamma$  increases as the number of chlorines increase. Thus the value of the double bond character calculated using Eq. 1 increases as the number of chlorines in the ring increase. The values of the frequencies and asymmetry parameters of the multichlorobensenes and multibromobenzenes reported in literature are given in Table I.

Goldstein (11-13) calculated the double bond character in chlorobenzene and bromobenzene using molecular orbital theory with inclusion of overlap. Using Goldstein's method the double bond character in  $m-C_6H_4Br_2$ ,  $o-C_6H_4Br_2$ ,  $1,3,5-O_6H_3Br_3$ and  $C_6Br_6$  is calculated. The method of calculation is same as that of Goldstein (11-13) and the values of the various integrals are same as those used by Goldstein in the case of bromobenzene. The calculations are performed on the CDC 3600 computers of Michigan State University and T.I.F.R. The values of the calculated double characters are given in Table II.

From the table it is seen that the p77 electron deficit is decreasing when there are one or more ortho or para neighbours. Experimentally it is found that there is an increase in the double bond character (calculated from the asymmetry parameter using Bersohn's equation) as the number of substituents is increased in the case of chloro compounds. The same is true for bromo compounds although there is not enough data. The theoretical values for m-dibromobenzene and 1,3,5-tribromobenzene are same as that of bromobenzene. This is justified in Huckel approximation as the bromines cannot influence the charge distribution in inmeta position. This may not be true in a rigorous self consistent field calculation but the differences may be of the second order. The results of o-dibromobenzene and herabromobenzene show a decrease of double bond character compared to bromobenzene.

The discrepancy may be due to the fact that the experimental  $\gamma$ , determined in solid, is not good measure of the double bond character. The asymmetry parameter of the electric field gradient at the site of bromine in a solid multibromobengene is due to

- (1) The bonding of pT electrons of carbon and bromine which accounts for the partial double bond characters
- (2) The internal electric field gradient produced by the surroundings.

From the experiments on electric field effects in NQR<sup>(14)</sup> it is known that the double bond character may not be effected to a considerable extent by intermolecular fields. Thus the experimental values of  $\gamma$  may not yield the true double bond character of the bonds. This point can further be verified when the microwave spectro-scopic data on the molecules is available.

#### ACKNOWLEDGEMENTS

The authors are grateful to Prof. K.R. Rao for his interest and encouragement throughout the calculations. The authors are deeply thankful to Dr. J.A. Ryan of Michigan State University, U.S.A. and Dr. V. Udaya Sankara Rao of T.J.F.R. for their help in the computer calculations. One of the authors (K.K.R.) gratefully acknowledges the financial assistance rendered by C.S.I.R.

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| Compound                           | )<br>in MHz     | γ            | Ref.       |
|------------------------------------|-----------------|--------------|------------|
| Chlorobenzene<br>o-dichlorobenzene | 34.622<br>34.84 | 0.095        | (4)<br>(5) |
|                                    | 35.12           | 0.105        |            |
| p-dichlorobenzeme                  | 34.779          | 0 <b>.08</b> | (3)        |
| 1,3,5-trichlorobenzene             | 35.020          | 0.09         | (6)        |
| • •                                | 35.296          | 0.11         |            |
|                                    | 35 • 545        | 0.13         |            |
| 1,2,4,5-tetrachlorobenzene         | 36.3            | 0.13         | (7)        |
| Hexachlorobenzene                  | 38.07           | 0.15         | (8)        |
|                                    | 38.041          | 0.15         |            |
|                                    | 38,051          | 0.15         | ,          |
| p-dibromobenzene                   | 226.49          | 0.45         | (9)        |
| -                                  | 230.350         | 0.062        | (10)       |
|                                    | 231.695         | 0.084        |            |

TABLE I

| Compound              | Charge | pЛ                                  | Electron Deficit      |
|-----------------------|--------|-------------------------------------|-----------------------|
| Bromobenzene          | 1.9694 | <u>Auto - No fo de anti-ser sin</u> | $3.06 \times 10^{-2}$ |
| o+dibromobenzene      | 1.9708 |                                     | $2.92 \times 10^{-2}$ |
| m-dibromobenzene      | 1.9693 |                                     | 3.07 x 10-2           |
| 1.3.5-tribromobenzene | 1.9693 |                                     | $3.07 \times 10^{-2}$ |
| Hexabromobenzene      | 1.9734 |                                     | 2.66 x $10^{-2}$      |

# DISCUSSION:

| R.Roy | : | Are the exper |
|-------|---|---------------|
|       |   | from NOD atud |

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imental data referred to, obtained 🔅 from NQR studies on single crystals?

K. Kameswara Rao :

All the results are from the NQR Zeeman effect data on single crystals reported in literature.

# OPTICAL ABSORPTION OF Co<sup>2+</sup> DOPED NH<sub>4</sub>C1: PHASE TRANSFORMATION STUDIES

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#### ABSTRACT

The absorption spectrum of  $\operatorname{Co}^{2+}$  doped NH<sub>4</sub>Cl single crystal hasbeen studied in the temperature range 300°K to 78°K. From the temperature dependence of the spectrum it is proposed that at room temperature the  $\operatorname{Co}^{2+}$  exists partly as substitutional having b.c.c. symmetry and partly as interstitial with octahedral symmetry. On reducing the temperature there seems to be a migration of ions from substitutional to interstitial sites resulting in a spectrum corresponding to predominently octahedral symmetry at 78°K. Various models for the interstitial complex are examined and the one in which the metal ion is surrounded by four chlorine ions lying in the plane of octahedron and two water molecules lying along 100 direction at NH<sub>4</sub><sup>+</sup> sites is found to be the most probable. A large blue shift is observed in the  ${}^{4}T_{1}$  (P) band between -30°C and -40°C and is interpreted in termsof the anomalous lattice contraction at the phase transformation (-30°) in NH<sub>4</sub>Cl. The spectrum of interstitial complex is analysed in the octahedral field approximation and the parameters obtained are Dq = 840 cm<sup>-1</sup>, B = 870 cm<sup>-1</sup> and C = 4.4B.

### ANALYSIS OF THE ABSORPTION SPECTRUM OF Mn<sup>2+</sup> IN ZnS

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#### ABSTRACT

The absorption spectrum of  $Mn^{2+}$  in ZnS has been analysed and it is found that in spite of the highly covalent character of ZnS the crystal field theory giv es quite a good description of the experimental results. The crystal field parameters obtained are B = 750, C = 2500, Dq = 355 and  $\alpha = 76$  cm<sup>-1</sup>. In contrast to the octahedral complexes the position of the  ${}^{4}T_{1}$  (P) level in the present tetrahedral coordination is found to be below  ${}^{4}E(D)$  level because of the low Dq value. The reasons for the high ground state splitting observed in paramagnetic resonance experiments are discussed. COLOUR CENTRES IN X-IRRADIATED KC1 DOPED WITH COBALT

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### INTRODUCTION:

The influence of alkaline earth impurities on the properties of colur centres im alkali halides have been extensively studied<sup>(1)</sup>. It is known that such substitutional impurities enhance the x-ray coloration, and also that when subjected to special treatments, give rise to new centres (the Z-centres). However, comparitively little work has been done on the effect of doping transition metal ions in alkali halides. In this paper, we report some preliminery results on the growth and heaching rates of colour centres in  $Ce^{2+}$ :KCl, irradiated with x-rays at room temperature.  $Co^{2+}$  ion has a  $5d^7$  electronic configuration, and from its optical absorption spectrum in KCl, Washimiya<sup>(2)</sup> concludes that the  $Ce^{2+}$  ion goes interestitially, with a tetrahedral site symmetry.

### EXPERIMENTAL

The  $\operatorname{Co}^{2+}$  doped KCl and the pure KCl crystals used for comparitive study have been grown in our laboratory from melt. Freshly cleaved pieces were used in the experiments. General Electric CA-7 type x-ray tubes were used for irradiation. The studieson grown rate have been done using a copper target operating at 40 kv and 19 ma while the irradiations for the bleaching studies were done with a molybdenum target operating at 45 kv and 17.5 ma. The optical absorption measurements were done on a Cary 14 spectrophotometer and the bleaching with F-band light was done using the tungsten lamp of the spectrophotometer.

### RESULTS AND DISCUSSION

Fig. I shows the growth of the F.band in pure and cobalt-doped KCl with increasing time of irradiation. The coloration proceeds in two stages: the first, a rapidly increasing one, and the second, a slowly increasing one. The amount of first stage coloration,  $n_F^0$ , is obtained by extrapolating the linear part of the curve to the ordinate, and then calculating the number of F centres/cm<sup>3</sup> corresponding to this absorption coefficient, with the help of the Smakula-Dexter formula<sup>(1)</sup>. The values os estimated for pure and cobalt-doped specimens are 1.61 x 10<sup>17</sup> and 1.95 x 10<sup>17</sup> per cc., respectively.

Thus, while an enhancement of coloration does exist, it is not as much as one finds in alkali halides doped with alkaline earth impurities (3,4). It is believed that the excess positive ion vacancies present in such doped crystals are converted into negative ion vacancies upon irradiation, which in turn are responsible for the enhancement of F-centre production. Then, one expects an even greater enhancement in Co<sup>2+</sup>: KCl, since an interstitial cobalt ion hasto be compensated by two positive ion vacancies, compared to one required by a substitutional divalent impurity.







An attempt is made to explain this anomoly by suggesting that most of the positive ion vacancies in  $\operatorname{Co}^{2+}$ :KCl are at nearest neighbour sites to the cobalt, forming impurity-vacancy pairs. This view is supported by two studies: (1) to explain the observed oscillator strengths of the optical absorption bands of the  $\operatorname{Co}^{2+}$  ion in KCl, Washimiya<sup>(2)</sup> finds it necessary to assume the presence of vacancies at mearest neighbour sites; (2) Ikeya et al<sup>(3)</sup> have shown that the enhancement of first stage coloration in divalent impurity-doped NaCl is due to the existence of isolated positive ion vacancies rather than impurity-vacancy pairs. Thus the comparitively smaller number of isolated vacancies in  $\operatorname{Co}^{2+}$ :KCl could probably be the reason for the rather small enhancement in coloration.

Figure 2 shows the effect of bleaching the x-irradiated crystals with F-band light. The fractional decrease in the F-centre absorption and the absorption coefficient at the M-hand peak are both plotted against the time of bleaching. It is clear that the F-band bleaches at a much slower rate and the M-band increases at a faster rate in the doped crystal, than in the pure one. The exact process of optical  $F \rightarrow M$  conversion isnot well understood at present<sup>(5)</sup>, and it is difficult to speculate on the exact effect of the impurity on the precess except noting that the interstitial cobalt seems to catalyze the conversion.

Now on the question of a possible new absorption band associated with the cobalt impurity, it is certain that no such band exists in the visible region, even after optical and thermal bleaching of the F-band. However, these seems to be a new absorption in the region of  $210 - 220 \text{ m}\mu$ . Since this region is crowded by the presence of the  $V_2$  and  $V_3$  bands of KCl and the 'charge-transfer' bands of cobalt<sup>(6)</sup>, it is rather difficult to separate out the new band. Cappelleti et al<sup>(7)</sup> in their study on the Co<sup>2+</sup>:NaCl system do not report any band. Further work in the CO<sup>2+</sup>:KCl system isin progress.

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# DISCUSSION:

A.S. Chakravarthy : 1. Have you studied the temperature variation of these absorption bands?

2. Are they electricdipole or are magnetic dipole allowed?

E.V.R. Sastry : 1. No.

2. They are all electricdipole transitions.

# FUNDAMENTAL BAND EDGE ABSORPTION OF NaClo,

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### INTRODUCTION:

The long wave length edge of the fundamental absorption band which is known to be due to transfer of an electron from the negative ion to a neighbouring positive ion in an ionic crystal, has been of considerable interest as regards the shape, fine structure, effect of crystal imperfections and its dependence on temperature. Point defects like impurity atoms, vacancies and interstitials are known to perturb the long wavelength edge. The  $\mathcal{A}$ ,  $\beta$  and  $\gamma$  bands <sup>(1,2,3)</sup> in coloured alkali halides are ascribed to be due to perturbation of the fundamental absorption edge.

It is worthwhile to extend the knowledge obtained from a study of the alkali halides to other crystals. In our efforts to produce and explain the origin of colour centres in sodium chlorate crystals as reported earlier (4-7) a band similar to

band is noticed in the long wavelength edge of the fundamental absorption. This has suggested a study on its modification by imperfections. The crystals are studied at different temperatures above room temperature and a modification of the fundamental absorption by the thermally produced defects is looked for.

#### RESULTS AND DISCUSSION:

The absorption spectrum of a thin crystal (.045 cm thick) of sodium chlorate is shown in Fig. 1 for different temperatures in the range  $25^{\circ}C$  to  $220^{\circ}C$ . The measured optical densities are plotted against light energy expressed in electron volts. Data for lightenergies greater than 5.65 eV (220 m/L) are not fully reliable because of stray light problems of the spectrometer in the extreme ultraviolet and thus shown by dotted lines.

For temperatures upto  $140^{\circ}C$  then wave length edge is a smooth curve without any subsidiary peaks. Mott type excitation banks could not be found as an extention of the long wavelength edge. Unlike AgBr and TlBr the dielectric constant of NaClo<sub>3</sub> is 5.2 at room temperature which is not unduly large compared to 4.8 of NaCl to suggest the crowding of exciton peaks. The crystal also is a very clear piece and appeared to be quite perfect. Even at liquid nitrogen temperature the tail did not develop into bends. This clearly indicates that exciton bands are not observed.

At each temperature the long wavelength edge of the absorption can be fitted into an  $Urbach^{(8)}$  type formula

 $D = D_0 e^{-\frac{B}{KT}} (E_0 - E)$ 

.....(1)


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as in the case of CdS crystals reported by  $Dutton^{(9)}$ . The long wave edge of the absorption has shown a progressive shift to longer waves with increase of temperature. Plots of  $\log_{10} D$  vs light energy E electron volts are shown in Fig. 2. They are straight lines over a large range of optical densities.

Fig. 1 also shows the absorption of the crystal at temperatures nearing the melting point. A new peak is developed at 5.5 (225 mµ). This must be one of the  $\beta$ -type greek bands. The difference in absorption at higher temperatures from the room temperature values is plotted in Fig. 3. The presence and the increase in intensity of a band peaked around 5.5 eV or 225 mµ is evident. It is very likely that the band is due to the transition of the electron from the negative ion to the positive ion in the crystal in the vicinity of some point defect, produced by the temperature. A rough estimate of the number of centres N can be made by using a formula due to Mott and Gurney<sup>(10)</sup>

$$N = 1.131 \times K \times \Delta V \times 10^{12}$$
 .....(2)

where  $\Delta v$  is the half width of the band in wave numbers and K is the absorption coefficient in cm<sup>-1</sup>.

Production of Schottky or Frenkel defects involves activation energies and the concentration of the defects increases as exp ( -E/KT) where E is the activation energy. A plot of  $\log_{10}N$  vs  $\frac{1000}{T^0}$  has yielded a straight line (inset Fig. 3) with a slope of 0.15 eV. Unfortunately the activation energies of NaClO<sub>3</sub> for the Schottky and Frenkel defects are not known from theory or other experiments for a comparison with the above. However, the value of 0.15 eV is rather small to be identified with the energies required for the formation of vacancies that may be attached to divalent impurities or a similar other process requiring lower energies. A graphical analysis of the additional absorption due to temperature can be made by resolving it into two bands one at about 5.68 eV (218m/r) and the other at 5.5 eV (225m/r) but the data is not considered to be sufficiently accurate to warrant such an analysis particularly because the shorter wavelength side of the additional absorption due to temperature 18 not sufficiently resolved. The second band may however yield a higher activation energy.

An alternate explanation for the shift of the long wavelength edge of the fundamental absorption with temperature is that it might be due to thermal expansion of the lattice at higher temperatures. A calculation based on Von-Hippel model yielded negligibly small shift of the fundamental absorption edge due to the thermal expansion of the crystal. Effect of lattice vibrations in broadening the absorption band is also estimated and found to be small compared with the observed effect.



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## DISCUSSION:

A.S. Chakravarty : 1. Have you calculated the oscillator strengths of these transitions?

2. Probably if you go down the temperature scale upto liquid helium (if possible) then you might get the line-widths much shorter.

8.B.S. Sastry : 1.

2. Yes. Facilities here are not adequate.

LUMINESCENCE MECHANISM IN Cas(2r) PHOS-PHOR

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Alkaline earth sulphide phosphors are one of earliest known phosphors. The mechanism of luminescence in them is however not yet very clear. Much of the work on these phosphors has been done in  $1920 \cdot s^{(1)}$ . Later on Urbach et al (1964) drew attention to the infrared stimulability of phosphors of this class. Recently Levshin and coworkers<sup>(2)</sup> have investigated the CaS phosphors in the form of thin films. However so far no model isproposed for the CaS phosphors. In the present paper the results and conclusions of the study of the absorption, excitation and fluorescence characteristics of CaS(Zr) powder phosphors are given.

Method of preparation consists in heating an intimate mixture of the sulphate together with the required amount of activator and flux in a reducing atmosphere provided by a reducing agent like carbon. The charge is contrained in a graphite crucible and is heated for two hours at  $900^{\circ}$ C.

Results are summarized in Table I and also shown in the form of curves in figures 1 (absorption) and 2 (Excitation).

| Absorption Peaks in MM<br>(eV) with Possible<br>Assignments | Excitation Peaks<br>in m4 (eV) with<br>possible Assignments.   | Emission Peaks in M/A<br>(eV) with Possible Assignments of the Centre.  |
|---|--|---|
| 229(5.38); Fundamental                                      | बेलाके के भी की स्वीरणनंत के राजित गांव संप्रताद के प्रताद के प्रताद का का किया है। इस्तानक स्वीरण की रही की क<br>अग | nan na karanaka mata metapada darika na dalah (na angka nakara nakarang karang karang karang karang karang kara |
| Lattice.  |  |   |
| 260(4.79): Perturbed  | 260(4.79): Perturbed   | 550(2.26): Absorption   |
| Host Lattice.   | Host Inttice   | in One Centre and<br>Emission in the Other.   |
| 288(4.30): Due to Zr  | 315(3.95): Zirconium   |   |
| lons in aq. Solution  | Levels   | 450(2.77): Absorption<br>in One Centre and  |
| 520(2.39): Perturbed Zr                                     |  | Emission in its Vicinity.   |
| Levels.   |  | , · · · · · · · · · · · · · · · · · · ·   |

TABLE I



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In Fig. 1 curve A is for  $CaSO_A$  (the chemically pure one before heating) and curve B for CaS with all flixes but no activater. With the variation in the concentration of zirconium no change was noted in the band with peak at 229mpc. . The bend with peak at 260m  $\mu$  however, becomes flat at higher concentrations of zirconium. In the visible region one band occures at 520m u only for higher concentrations of zirconium (.48 per cent and above). Aqueous solution of zirconium nitrate showed an absorption band at 288mµ . This band, however, was not exhibited by CaS(Zr) phosphors. It is possible that this being a weak band is suppressed by the strong and broad band at 260mµ. As the rise in the concentration of zirconium does not affect the band at 229m/t , it is possible to associate it with the fundam mental lattice band. This band at 5.58 eV agrees well with the band gap of 5.4 eV as given in literature, 3. The band with peak at 260 m $\mu$  is attributed to the perturbed host lattice, because this occures in the sample with triple fluxes only (curve B) and broadens with the rise in concentration of the activator (curve D). Now the band at 520mfl which is observed for higher concentrations of zirconium only, probably, is associated with perturbed zirconium levels. This perturbation is due to host lattice, as aqueous solution of zirconium did not exhibit this band. It was found that 229m $\mu$  could not contribute much for excitation, however 260 m $\mu$ was an excitation hand for the long wave length emission. The second excitation maximum was found to be at 315m (Fig. 2). This excitation band was found to contribute for blue emission. We observed two fluorescence bands with peaks at 450mpl (blue) and 550mpl (yellow). The blue band is very weak in comparison to the yellow band. However, with higher concentrations of zirconium the yellow band is quenched. For the explanation of quenching we could think of macroscopic distortion of the lattice which reduces the possibility of radiative transitions.

As stated earlier by Seitz<sup>(4)</sup> that most of the phosphors fall in either class i.e., alkali halide type or ZnS type, we thought of establishing a similarity of our phosphor with either class. From structure point of view they are similar to alkali halides as both being of f.c.c. structure. The same criterion is preferred by Levshin<sup>(2)</sup> in concluding his results. But the observation of electroluminescence in CaS Phosphors by Watchel<sup>(5)</sup> and photoconductivity by Bube<sup>(3)</sup> extends a support in favour of similarity with ZnS type phosphors. Many of other similarities observed by us, which shall be dealt in a subsequent publication, lead to believe in terms of a band model for CaS phosphore. However, the perfectly acceptable idea cannot be given unless ionicity of the crystal is known. Looking for the mechanism of energy transfer, we find that instead of resonance transfer, the movement of charge carriers is capable of giving an explanation of energy transfer over relatively larger distances. The phosphors in which optimum efficiency occurs at low concentration of activator, there the distance between neighbouring centres The optimum efficiency in CaS (Zr) is for 8 x 10<sup>-9</sup> gm of zirconium islarge. This gives the estimated distance between neighbouring centres per gm of CaS. approximately. For resonance transfer, the distance should be 250Å to be

of the order of  $35^{\circ}_{A}$  or less<sup>(6)</sup>. On the basis of the spectroscopic considerations and the absence of spin resonance at room temperature, the more probable valency state of zirconium is +4. Fluxes do not provide complete charge compensation for that we assume that Ca<sup>2+</sup> vacancies occur. In particular, we assign vacancy centres with blue emission, because it gets prominence with the introduction of second activator which enters into the lattice in the highly positive state<sup>(7)</sup>. We assume that to compensate this highly positive state more vacancies are created and hence blue bend becomes intense.

#### CONCLUSIONS:

- 1. CaS (Zr) phosphors are similar to ZnS type phosphors.
- 2. The energy transfer is predomently by the movement of charge carriers.
- 3. The solid state defect seems to be of Schottky-Wagner type.

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## PHOTO LUMINESCENCE SPECTRA OF HEAVILY DOPED SINGLE CRYSTALS OF KC1 WITH T1C1

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## INTRODUCT ION:

The luminescence spectrum of thallium activated potassium chloride has received considerable attention both from theoretical and experimental workers. The spectrum of phosphor containing traces of thallium have been explained by Seitz William's Model. Additional emission bands in the visible region and the absorption bands in ultraviolet region are obtained for large concentration of thallium in potassium chloride. The long wavelength emission bands (377, 430 and 520 m $\mu$ ) gain in intensity and the short wavelength emission band with peak at 305 m $\mu$  is gradually suppressed. It has not yet been possible to establish uniquely the nature of centres responsible for all the long wavelength absorption and emission bands of potassium chloride with high thallium content. However, attempts have been made by several authors<sup>(2,3,4)</sup> to explain the luminescence of KC1:T1 phosphor with large thallium concentration in terms of causes like aggregate formation in (T1<sup>+</sup> - T1<sup>+</sup>), complex formation of (T1C1m<sup>-</sup>) type and undissociated T1C1 being present in the lattice. The bands in the peak at 377 and 420 m $\mu$  are due to associated pairs (T1<sup>+</sup> - T1<sup>+</sup>) and complex centre of T1C1m<sup>-</sup>) in potassium chloride.

Most of the experimental data available regarding the KC1:T1 phosphor with large thallium content is on powdered sample because to grow single crystal with large impurities is still a problem due to many reasons for example solubility. Since thallous chloride under proper heat treatment diffuses in potassium chloride very easily and its solubility in potassium chloride is also affected very much . Single crystals of potassium chloride under proper condition has been doped with thallous chloride with a view to study the optical properties of single crystals of KC1:T1 phosphor which is large thallium concentration. So the present measurement of emission spectra of single crystal of KC1 with large T1C1 contents have been undertaken.

### SAMPLES:

Single crystals of potassium chloride have been raised to  $500^{\circ}$ C in the atmosphere of TlCl for 12 hrs and then slowly cooled to room temperature in 48 hours. Some of the doped single crystals have been annealed at  $400^{\circ}$ C for 12 hrs. For recording emission spectra freshly prepared, polished, cleaved and annealed single crystals doped with TlCl of the size 0.5 x 0.5 x 0.1 cm have been used. Polishing has been done by ethyl alcohol.

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# EXPERIMENTAL PROCEDURE:

The emission spectra of the crystals have been studied by exciting them with 265 m<sub> $\mu$ </sub> line of H<sub> $\mu$ </sub>. The source used is a high pressure mercury AH4 lamp with outer glass cover removed. The exciting radiations from the source were monochromatised with Gaertner monochromator. For recording the spectrum another Gaertner monochromator mator with IP28 RCA photomultiplier have been used. The signal is recorded with a sensitive electrometer. The voltages have been kept constant by using a FE voltage stabilizer during the measurements. The annealed crystals have been excited by 253.7 m<sub> $\mu$ </sub> and wave length below it.

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## RESULTS:

The emission spectra of single crystals of KCl with large thallium concentration have been given in Fig. 1, and 2 and the peak positions and the extensions of the various bands obtained in various samples have been given in Table I.

From the emission spectra measurement it is observed that for a freshly prepared sample a band with peak at 520 m M is obtained only and in general it has been found that it is the most intense band in all the samples. For the polished samples, another band with peak at 380 mM is obtained in addition to the band at 520 mM. For the cleaved sample the bands with peaks at 320, 420 and 520 mM have been obtained. For the annealed samples all the four bands with peaks at 310, 380, 420 and 520 mM have been obtained but the intensity of the short wavelength band is very low. When excited with 253.7 mM line of Hg or below it. has been observed that the intensity of long wavelength band with peak at 520 mM is reduced considerably. Comparing <sup>(5)</sup> the emission spectra of single crystals with that KC1:T1 phosphor with large thallium concentration it appears that the spectra seem to be of eingle crystals of potassium chloride with large thallium doped in it. From the results it is also observed that the long wavelength bands are relatively more intense than the short wavelength bands and the intensity of the bands decrease as one examines the spectra from the surface to the interior of the crystals.

CONCLUSIONS:

From all the measurements the following conclusion are made:-

- (1) The band with peak at 320 mµ obtained in this case has been ascertained as due to complex ions of (TlCln) type.
- (2) The band with peaks at 470 m $\mu$  has not been obtained in this case but a new band with peaks at 320 m $\mu$  and 520 m $\mu$  has been obtained which found to shift to 310 and 500 m $\mu$  when annealed. The bands with peaks at 320 and 520 m $\mu$  are also obtained when the bands at 380 m $\mu$  is obtained. Thus the band peaks at 320, 380 and 520 m $\mu$  are due to (T1<sup>+</sup> - T1<sup>+</sup>) centres in the lattice.





FIG. 2

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TABLE I

| Samples |                  | Band Extension in m <sub>H</sub> < | Position of the<br>Peak in m <sub>M</sub> | Remarks      |  |
|---------|------------------|------------------------------------|---|--------------|--|
| 1.      | Freshly prepared | 380 - 640                          | 520                                       | <b>m.</b> 5. |  |
| 2.      | Polished         | 300 - 440                          | 380                                       | 8            |  |
|         |                  | 440 - 640                          | 520                                       | 1.8.         |  |
| 3.      | Cleaved          | 290 - 350                          | 320                                       | 8            |  |
|         |                  | 360 - 500                          | 420                                       | W            |  |
|         |                  | 420 - 640                          | 520                                       | II.•\$•      |  |
| 4.      | Annealed         | 280 - 340                          | 305                                       | ₩            |  |
|         | · · ·            | 340 - 400                          | 380                                       |              |  |
|         |                  | 410 - 600                          | 500                                       | 8            |  |
| 5.      | Mixture of KC1   | 290 - 350                          | 320                                       | 8            |  |
|         | with 10% TICI    | 360 - 460                          | 420                                       | *            |  |
|         |                  | 400 - 600                          | 500                                       |              |  |
|         |                  | · · · ·                            | •   |              |  |

## ON THE RECOMBINATION LIFE-TIME OF AN ELECTRON IN A PHOTO-CONDUCTOR

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### ABSTRACT

Generally in the analysis of thermoluminescence curves and TSC\* identical. techniques are used. In this process it is assumed that the factor  $\mu \tau$ , where  $\mu$  is the mobility and  $\tau$  the recombination life-time of an electron, is assumed to be temperature independent. However, it may not be always true. It is suggested, therefore, that if the simultaneous studies of thermoluminescence and thermally stimulated current are carried out, then a plot of  $\sigma/I$  vs T would give some information about the variation of  $\tau$  with temperature. In the same way useful information can be obtained about  $\tau$  by simultaneous measurements of the decay of phosphorescence and photoconductivity.

Thermally Stimulated Current.

#### RED FLOURESCENCE OF THALLIUM SALTS

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#### ABSTRACT

The near infrared flourescence of the thallium salts TICl, TIBr, TII  $Tl_2SO_4$  and TINO<sub>3</sub>, as excited by the 3650 Å group of mercury lines, is studied with a PbS photoconducting cell as the detector. A spectral analysis of the flourescence after correcting for the spectral response of the detector indicated bands with maxima at 0.7 $\mu$ 1.02 $\mu$ , 1.35 $\mu$ , 1.6 $\mu$ , 2.1 $\mu$  and 2.4 $\mu$  (?) for TII and 0.8 $\mu$ , 1.02 $\mu$  and 2.4 $\mu$  (?) for TIBr. (TII prepared either by precipitation from solution or by evaporation gives the same flourescence). Similar flourescence was observed in the other saltsof thallium also.

Since the strong  $1.02 \,\mu$  band occurs in the same position for the different salts it may be due to a common impurity ion and not due to structural imperfections as suggested by Vishnevskii and Pidzirailo. It has been observed that TII from which some iodine is evaporated also gives the same flourescence, thus indicating that halogen ion vacancy is not responsible. The flourescence, may be due to inner transitions of a rare-earth ion, the 4f electrons of which are shielded from the interaction of the lattice.

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# THERMOLUMINESCENCE OF CaFo: (Ce + Mn) SYSTEM

#### S.C. Sen

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## ABSTRACT

The thermoluminescence of  $\operatorname{CaF}_2$ : (Ce + Mn) system have been reported in this paper. Three glow peaks at 370, 461 and 528°K have been obtained in general whereas the peak at 347°K is obtained for low concentration of cerium fluoride. The spectral nature of thermoluminescence is different in different peaks. The glow peak at 347 and 370°K rich in uv. emission during thermoluminescence are due to metastable states of cerium ion. The peaks at 460 and 528°K are due to the traps provided by the perturbed levels of the lattice defects in the neighbourhood of isolated Ce<sup>3+</sup> at a comparatively large distance of the investigation indicate that the energy is stored in the metastable state of cerium ion and also in the perturbed levels of the lattice caused by cerium activation; increase in the manganese concentration reduces such storage probability.

### NEUTRON DIFFRACTION STUDIES OF ZINC-NICKEL FERRITES

# M.G. Natera<sup>\*</sup>, R.J. Begum, S.I. Youssef<sup>\*\*</sup>, C.S. Somanathan, B.S. Srinivasan and N.S. Satya Murthy, Ehabha Atomic Research Centre, Trombay, Bombay-74.

# INTRODUCTION:

Zinc ferrites exhibits a completely normal spinel structure while nickel ferrite shows an 80% degree of inversion.<sup>(1)</sup>. Below 9°K the Fe<sup>3+</sup> ions in ZnFe<sub>2</sub>O<sub>4</sub> exhibit a complicated antiferromagnetic arrangement which gives rise to superlattice reflections and a zero net moment<sup>(2)</sup>. When Zn<sup>2+</sup> ions are replaced by Ni<sup>2+</sup>, a magnetic moment is developed at the A sites due to the Fe<sup>3+</sup> ions going to these sites. The moments at the B sites are modified by the presence of Ni<sup>2+</sup> ions. We have investigated the systematics of these spin arrangements in the mixed system,  $Zn_xNi_{1-x}Fe_2O_4$  (x = 0.25,0.50 and 0.75).

# RESULTS AND DISCUSSION:

We have taken powder neutron diffraction patterns at various temperatures upto and beyond the Neel temperature of the ferrites. Fig. 1 shows the diffraction pattern of  $2n_{0.75}Ni_{0.25}Fe_2O_4$  which shows some interesting results which will be discussed later. Table I gives a summary of the results.

TABLE I Zn\_Ni\_\_\_Fe204.

| x    | Cation Di  | stribution                                  | a     | u  | TN  | N             | lagne ti | c Momen | ts <b>†</b> |
|------|--|---|-------|--|-----|---------------|----------|---------|-------------|
|      | A-Site   | B-Site                                      | R     | هی غذ اند که این بین ای طالع این از این ای | °ĸ  | A-Site        |          | B-Site  |             |
|      | ·  |   |       |  |     | EXPT          | CALC     | EXPT    | CALC        |
| 0.25 | $2n_{0.25}^{2+}$ Fe $0.75$                             | Ni <sup>2+</sup><br>0.75 <sup>Fe</sup> 1.25 | 8.346 | 0.257  | 695 | 3 <b>•</b> 54 | 3.75     | 3.77    | 3.87        |
| 0.50 | Zn <sup>2+</sup><br>0.50 <sup>Fe</sup> 0.50            | Ni <sup>2+</sup><br>0.50 <sup>Fe</sup> 1.50 | 8.374 | 0.258  | 540 | 2.44          | 2.50     | 3.57    | 4.25        |
| 0.75 | <sup>2n</sup> <sup>2+</sup><br>0.75 <sup>Fe</sup> 0.25 | N1 <sup>2+</sup><br>0.25 <sup>Fe</sup> 1.75 | 8.400 | 0.259  | 300 | 1.20          | 1.25     | 1,44    | 4.63        |

Values were extrapolated to UVK

CALC Values were calculated using spin-only values.

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The data were analysed in the first instance on the basis of a simple Neel model. The A site moments were evaluated from the (220) intensities which depend only on the scattering amplitudes at these sites. The B site moments were evaluated from the (11) intensities which depends only on the B sites are too small to extract the moments accurately. We find that the A site moments closely agree with the spin-only values, while the B site moments show a large departure from the calculated spin-only values. The experimental values for the B site moments exhibit a maximum in the x = 0.40 region, indicating a departure from the Neel Model.

Yafet and Kittel (3) have shown that if the AA and BB interactions are comparable to the AB interaction, then the Neel type (4) is not the ground state but that a triangular arrangement of spins will be more stable. Kaplan et al (5) have shown rigorously that the ground state of normal cubic spinels is not of the Yafet-Kittel type but of the more complicated multi-spin configuration or spiral structure. They did not, however, treat the case of inverted spinels or of mixed ferrites. A recent neutron diffraction work by Boucher et al (6) on NiMn<sub>2</sub>O<sub>4</sub> shows conclusively that for this example, which is an inverted cubic spinel the ground state configuration is of the Y-K type. That the Neel model is not followed by the entire Zn-Ni ferrite system can also be seen in Fig.2 from the curve of saturation magnetization versus concentration (7). If the system is of the Neel type, there should be a linear increase of the saturation moments with concentration. On this basis we have investigated the possibility of a Y-K typeof ordering on the B sublattice. Assuming that the A site moments are due to the spin-only value of the  $Fe^{2^+}$  ions on these sites as suggested by the neutron diffraction results, we can find what would be the angles between moments at the  $B_{I}$  and  $B_{II}$  sublattices required to yeild the resultant B site moments. These are shown in Fig. 3. It is interesting to note that the Y-K angles follow a straight line for high zinc concentration and extrapolates to  $180^{\circ}$  for  $2nFe_2O_4$ . The region near x = 0.3 shows that  $B_{t}$  and  $B_{tT}$  are collinear and this composition should behave like a Neel ferrimagnet. The effect of a splitting in the B sublattice should give rise to purely magnetic (200) and (420) reflections. For Zn 0.75 Ni 0.25 Fe 204, where the Y-K angle is large, we do find noticeable peaks, as shown in Fig. 1, in the (200) and (420) regions and broad humps under the (111) and (400) regions. (These humps probably arise from short range ordering effects.). These suggest the possibility of the Y-K ordering of spins. As shown in Fig. 3, NiFe<sub>2</sub>O<sub>4</sub> should also exhibit a Y-K ordering.

Recent Mossbauer work by Kedem and Rothem (8) on N<sub>1</sub>Fe<sub>2</sub>O<sub>4</sub> based on the widths of their Mossbauer lines show that NiFe<sub>2</sub>O<sub>4</sub> is of the Y-K type. In the enly neutron diffraction work by Hastings and Corliss (1) on NiFe<sub>2</sub>O<sub>4</sub> a peak was observed in the (200) positron for NiFe<sub>2</sub>O<sub>4</sub>, which was indexed as  $(\frac{-400}{2})$ , i.e., aue to  $(\frac{\lambda_2}{2})$ contamination of their neutron beam. However, no estimate of this contamination was given. On the other hand, for ZnFe<sub>2</sub>O<sub>4</sub>, which has a higher (400) inten-



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sity no corresponding  $(\frac{400}{2})$  reflection was observed. It is possible that the " $(\frac{400}{2})$  " of Hastings and Corliss<sup>(1)</sup> in NiFe<sub>2</sub>O<sub>4</sub> is due indeed to the Y-K angles in the B sublattice.

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#### DISCUSSION:

- C. Srinivasan : What is the basis for the calculation of magnetic moments of A and B sites in  $NiFe_0O_A$ ?
  - M.G. Natera : The theoretical A and B site moments in NiFe<sub>2</sub>O<sub>4</sub> were calculated from the cation distribution at the A and B site and assuming spin-only values of the magnetic moments. The experimental A site moment was expected from the (200) intendity which depends only on the magnetic scattering amplitudes at this site. Knowing this value, the B site moments was determined from the (111) intensity.

K.S. Chandrasekaran :

In applying Debye-Waller temperature factors to the observed intensities to compare them with calculated intensities one has to employ, to start with, an additional term to represent the ordering and this will wary with composition. This will be particularly desirable if the diffraction intensities are found to be applicable at high 20 values.

P. Singh 1

Why are the calculated magnetic moments on site B larger than the experimental ones? Is the ordering between the various magnetic ions predominantly antiferromagnetic? M.G. Natera : The calculated magnetic moments on the B sites are the spin-only values and are assumed to be collinear. The experimental values at the B site are smaller than the calculated values especially for x = 0.50 and 0.75 due to the splitting in the B lattice. The ions on the A sites are antiferromagnetic to those in the B sites. The A sites are all ferromagnetic while the B sites have antiferromagnetic components.

K.R. Rao : I would like to know the physical origin of two results presented in your paper. They are:

> 1. There seems to be a systematic departure of the lattice constants as determined by x-ray diffraction studies of Srinivasan from the same obtained by other methods.

2. The large difference between the theoretical and experimental magnetic moments at the B sites for x value of 0.75.

M.G. Natera :

Our lattice constants agree with the values of Sage and Guilland. We do not know why Srinivasan's results depart from our values. The theoretical magnetic moments at the B sites were calculated using Neel collinear model and spin-only values of the magnetic moments. The observed magnetic moments at the B site for x = 0.75 indicate a noticeable departure from the Neel collinear model.

We have assumed a splitting in the B-sublattice to account for our result.

### SUBLATTICE MAGNETIZATION IN MIXED MAGNESIUM-MANGANESE FERRITES

## R.J. Begum, S.I. Youssef<sup>\*</sup>, M.G. Natera<sup>\*\*</sup>, C.S. Somanathan, B.S. Srinivasan and N.S. Satya Murthy, Bhabha Atomic Research Centre, Trombay, Bombay-74.

This paper reports on a study of the mixed ferrite system  $Mg_X Mn_{1-X} Fe_2 O_4$ (x = 0.25, 0.50 and 0.75) by means of neutron diffraction. All the ferrites in the series were prepared in an identical manner since the cation distribution among the two available lattice sites is known to depend rather sensitively on the firing schedule and the subsequent heat treatment.

Conflicting results exist at present in the laterature regarding the distribution of Mg ions in various ferrites. Nathans et al<sup>(1)</sup> conclude that in Mg-Mn ferrites almost 90% of the Mn ions go into A sites, while Kleinstuck and others<sup>(2)</sup> reported that for  $Mg_{0.52}Mn_{0.51}Fe_{1.97}O_{4.001}$ , only 67% of Mn ions are in the A sites. For the Mn Fe<sub>3</sub>-y<sub>4</sub> system, Yamzin et al<sup>(3)</sup> did not find any Mn ion on A sites upto y = 0.53, but at y = 0.84, 92.8% of the Mn ions on A sites began to fall and reached a value of 59.3% for y = 1.50. Alperin and Pickart<sup>(4)</sup> have studied the same system for x = 0.4 and 0. 6 and got the fraction of Mn ions occupying the A site as 87.5% and 90% respectively.

We have studied the Bragg intensities in all the samples over a wide range of temperature from about 100 <sup>O</sup>K to get the respective Neel temperatures and the individual sublattice magnetizations. Data above the Neel temperature were analysed to get the cation distribution, the oxygen parameter u and the Debye-Waller factor. The results thus obtained are used with the low temperature data to get the magnetic moment values. In the diffraction patterns no evidence was found for the ordered triangular or helical spin structures, so the data were analysed in terms of the Neel model. The results are given in Table I

### TABLE I

#### CATION DISTRIBUTION:

A site -  $(Mg_{\alpha x}^{2+}Mn_{\beta}^{2+}(1-x)^{Fe^{3+}}1 - \beta - (\alpha - \beta)x)$ 

$$B \text{ site } - \left[ Mg^{2+}(1-\alpha)x^{Mn^{3+}}(1-\beta)(1-x)^{Fe^{2+}}(1-\beta)(1-x)^{Fe^{3+}}x(1+\alpha)+2\beta(1-x) \right]$$

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- \* Guest Scientist from the Philippine Atomic Research Center, Manila, The Philippines.

| Parameters                                       | x =0.25            | $\mathbf{x} = 0.50$ | <b>x</b> = 0.75    |
|--|--------------------|---------------------|--------------------|
| T <sub>N</sub>                                   | 610 <sup>0</sup> K | 620 <sup>0</sup> K  | 635 <sup>0</sup> K |
| u  | 0.260              | 0.256               | 0.255              |
| ά  | 0.08               | 0.26                | 0.33               |
| β  | 0.39               | 0.68                | 0.28               |
| b <sub>A</sub>                                   | 0.565              | 0.450               | ) <b>0.760</b>     |
| р <sub>В</sub>                                   | 0.604              | 0.772               | 0.729              |
| μ <sub>A</sub> (100 <sup>0</sup> K)              | 4÷45               | 3.72                | 3.34               |
| μ <sub>A</sub> (calc.,0°K)                       | 4.90               | 4.35                | 3.75               |
| <sup>/</sup> μ <sub>B</sub> (100 <sup>°</sup> κ) | 3.71               | 3.24                | 3.19               |
| $\mu_{B}(calc., 0^{\circ}K)$                     | 3.97               | 3.92                | 3.57               |

The fraction of cations occupying the A sites is plotted in Fig. 1, along with the distribution curves of theprevious authors. The trend of the curve for the Mn ion distribution is similar to that obtained by Yamzin et al. the shift being probably due to the presence of Mg ions. Nathans has asumed that all the Mn ions are in the divalent state, while Kleinstuck considered the B-site Mn ions to be in the trivalent state. The magnetic moment values obtained from the present work are consistent with 'spin only' magnetic moment values having  $Mn^{2+}$  ions on the A sites and  $Mn^{3+}$  ions on the B sites. In fact Goodenough and Loeb (5) have suggested that  $Mn^{2+}$  should show a preference for the A sites as a result of its tendency to form partially covalent tetrahedral bonds, while  $Mn^{3+}$  will prefer B sites because of square bond formation.

Reflections like (220), (422) and (620) have magnetic contributions from the A sites only, while (222) and (622) reflections involve contributions from the B sublattice only. These peaks show distinct temperature dependences. The sublattice magnetizations extracted from these peaks are plotted on a reduced temperature scale in  $F_{ig}$ . 2. The fall-off for (222) is sharper than that for (220) showing that the thermal agitations are less effective in disturbing the A sublattice spin alignments than in the B sublattice. Each A ion has twelve B and four A nearest neighbours whereas each B ion is surrounded by six A and six B neighbours. Since the experimental results show that the molecular field acting on the A sites is stronger than that on the B sites, it can be concluded that in these ferrites the A-B interaction is the dominant one.

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Fig. 2. Temp. dependence of sublattice magnetization in Mg 0.25 0.75 2 4°

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#### DISCUSSION:

A.S. Chakravarthy :

I suppose it is possible to calculate the value of the exchange integral from your neutron diffraction measurements. Have you calculated it? If so, it would be interesting to compare it with those calculated from theoretical stand-point.

R.J. Begum : Yes, the exchange integrals,  $J_{AA}$ ,  $J_{PB}$  and  $J_{AB}$  can be evaluated from the temperature dependence of the magnetic Bragg peaks. Reflections like (220) and (222) have contributions respectively from the A sublattice and B sublattice only while (111) is a mixed reflection. So the temperature dependence of these peaks will yield the values of  $J_{AA}$ ,  $J_{BB}$  and  $J_{AB}$ .

K.S. Chandrasekaran :

The plot of the integrated intensities versus temperature seems to indicate that for some reflections, the intensity is practically independent of temperature over a quite a large range of temperature. Does this fit in with the explanation in terms of the magnetic sites?

R.J. Begum :

The integral intensities of all the three peaks (111), (220) and (222) are plotted on the same scale. Since the intensity of (111) is much higher than that of others, in the intiial temperature range, the decrease in the intensities of (220), and (222) is not very obvious. In fact the Brillouin function does not change much from O<sup>O</sup>K to room temperature as the transition temperature is quite high, around 600 K for all the cases.

#### MEASUREMENT OF EXCHANGE INTEGRAL IN CrF<sub>2</sub> BY PARAMAGNETIC NEUTRON SCATTERING

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### INTRODUCTION :

During the last few years paramagnetic neutron scattering from simple salts of the 3d system has been studied  $\binom{(1)}{}$ , principally to determine the strength of the exchange interation that exists between the magnetic ions. This technique, which forms a useful complement to other techniques such as spin wave dispersion measurements and opin-wave resonance, is particularly suited to those magnetic systems characterised by one dominant exchange interaction describable by the Heisenberg Hamiltonian in a realistic fashion.

Chromium difluoride is an ionic antiferromagnet  $(T_N = 53^{\circ}K)$  and has the distorted rutile structure (Space Group  $P2_1/c$ ). The chromium ion at the body centre is oppositely aligned to the chromium ions at the cube corners : the magnetic unit cell is identical with the chemical unit cell, in size (2). The dominant interaction is of the  $\sigma$  type between the cations at the body centre and cube corner via the intervening anion. The cation is surrounded by a tetragonally distorted octahedron of the fluorine ions (Jahn-Teller distortion) which removes completely the orbital degeneracy of the cation. The magnetic moment is therefore carried by only the spin of the chromium ion.

## PRINCIPLE

The double differential cross-section of neutrons scattered from an exchange coupled system of paramagnetic ions at sufficiently large scattering angles or momentum transfers was shown by de Gennes  $\binom{3}{}$  to be essentially Gaussian. The second moment  $\int_{1}^{2} \langle \omega^{2} \rangle$  of this distribution is given by

$$\frac{1}{\hbar^{2}}\langle\omega^{2}\rangle = \frac{2}{3}\frac{S(S+1)}{\hbar}\sum_{k}\frac{Z_{k}(2J_{k})^{2}}{\hbar}$$

Where  $Z_{j}$  is the number of magnetic neighbours in the i<sup>th</sup> shell and Ji the corresponding exchange integral. The experiment consists essentially in determining the second moment  $\frac{1}{2}\langle \omega^2 \rangle$ .

#### EXPERIMENT

The experiment was performed on the rotating crystal spectrometer at the CIRUS reactor, Trombay. Spectroscopically pure, anhydrous CrF<sub>2</sub> was pressed in the form of a disc. Time-of-flight spectra were measured at room temperature for two scattering angles of 40° and 50°. The inset to Fig. 1 shows the time of flight spectrum taken at scattering angle of 40°. The strong elastic peak is due to nuclear incoherent scattering. The time of flight spectra were converted to energy spectra making corrections for variation of the magnetic form factor, absorption, air scattering and efficiency of the detector.

## RESULTS AND DISCUSSION

The logarithm of the intensity of the spectra was plotted against the square of the energy transfer. Fig. 1 shows this plot for the spectrum at 40°. The straight line shows that the energy distribution is essentially Gaussian. The slope of this line yields the second moment  $\frac{1}{2}\langle\omega^2\rangle$  of the distribution. Assuming one dominant interaction, the exchange integral J os extracted. The follow-ing table shows the values obtained from our experiment as also the theoretical values predicted by the molecular field approximation, BFW model <sup>(4)</sup> and the Green's function technique<sup>(5)</sup>.

TABLE

Paramagnetic Scattering

 $2.0^{\circ} \pm 0.2^{\circ} K (\phi = 40^{\circ})$  $1.9^{\circ} \pm 0.2^{\circ} K (\phi = 50^{\circ})$  Theoretical Models( from T<br/>m)M.F.EPWG.F.1.67°K1.95°K2.31°K

Good agreement is observed with the value predicted by the HPW method. It is seen, however, that the molecular field approximation predicts a rather low value for J while the value predicted by the Green's function technique is slightly high. Unfortunately, no other experimental results such as susceptibility at  $T_N$ , specific heat etc., are available which would make a comparison with our results upre mean-ingful.

#### REFERENCES :

- L. Madhav Rao, N.S. Satya Murthy, G. Venkataraman and P.K. Iyengar, Phys. Letters <u>26A</u>, 108 (1968). and other references listed therein.
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- 3. P.G. de Gennes, J. Phys. Chem. Solids. 4, 223 (1958).
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DISCUSSION:

- P. Singh : I think that recently calculations of exchange integral have been made by Marshall and surprisingly the values come out to be extremely small.
- L. Madhaw Rao : Collins and Marshall (Proc. Phys. Soc. <u>92</u>, 390 (1967)) have given an expression for the scattering function which consists of a Gaussian plus a higher order term. The higher order term is extremely small compared to the Gaussian term and in order to see its influence on the exchange integral, the experimental accuracy has to be better than 2%.
- R. Fatehally : Can this method of estimation of J be used when the orbital angular momentum is not completely quenched?
- L. Madhav Rad : Yes, where the incomplete quenching of the orbital angular momentum give rise to an uniaxial anisotropy, for instance. The experiment however has to be performed over wide momentum transfer range.
- B.A. Desennacharya : I would like you to mention how the exchange integrals derived from paramagnetic measurements compare with those derived from dispersion relation measurements and what their accuracies are.

L. Madhav Rao :

They compare favourably well with the case of  $\operatorname{RbMn} \mathbb{F}_3$ ,  $\operatorname{Mn} \mathbb{P}_2$ 

ELECTRON PARAMAGNETIC RESONANCE OF Cu<sup>2</sup> ION IN RbSO<sub>A</sub> SINGLE CRYSTAL

S.K. Banerjee, B.V.R. Chowdari and Putcha Venkateswarlu Departmenf of Physics, Indian Institute of Technology Kanpur, India.

#### INTRODUCTION:

Chowdari and Venkateswarlu<sup>(1)</sup> have recently studied the EPR spectrum of  $Mn^{2+}$ ion doped in  $Rb_2SO_4$  single crystal and as such it was felt that it would be interesting to study the EPR spectrum of other paramagnetic ions doped in  $Rb_2SO_4$ . It is with this idea that EPR studies of  $Cu^{2+}$  ion in  $Rb_2SO_4$  single crystal have been taken up.

# CRYSTAL STRUCTURE:

The arrangement of positive and negative ions in  $\text{Rb}_2\text{SO}_4$  is similar to that of  $\text{K}_2\text{SO}_4$  and is described elsewhere<sup>(2)</sup>. The dimensions of unit cell at room temperature are a = 5.948 Å, b = 10.311 Å. The crystal contains two different sets of rubidium ions being called  $\propto$  and  $\beta$ , the oxygen environment of the rubidium ions being different for two sets in the structure. The crystal has orthorhombic symmetry at room temperature.

#### EXPERIMENTAL RESULT AND DISCUSSION:

Rubidium Sulphate crystals doped with Cu<sup>2+</sup> ion are grown from aqueous solution by evaporation technique EPR spectra were recorded on V-4502 X band EPR spectrometer.

The EPR spectrum of free Cu<sup>2+</sup> ion which has an electronic configuration  $3d^9$ and a ground state  ${}^{2}D_{5/2}$  in orthorhombic fields is expected to show single absorption line (S = 1/2) split into four hyperfine components. Both copper isotopes  ${}^{63}$ Cu and  ${}^{65}$ Cu have nuclear spin quantum number I = 3/2 and as such the copper ion is expected to have four hyperfine lines due to each isotope. In the present experiments however the individual hyperfine spectrum from each isotope is not resolved probably because of larger line widths of the order of 30 gauss.

A well resolved spectrum (Fig. 1) corresponding to a maximum g value and maximum A value is obtained when H makes an angle of  $42^{\circ}$  from the C axis in the bc plane (z axis) while the g minimum and A minimum occur exactly at an angle of  $90^{\circ}$  from the z axis in the same plane. The origin of this spectrum is same as due to  $Mn^{2+}$  in RbSO<sub>A</sub> single crystal<sup>(1)</sup>.

The study of angular variation of the spectrum when H isparallel to the ab plane suggests that there is another complex in the crystal whose symmetry axis is at an angle.

The study of angular variation of the spectrum when H is parallel to the ab plane suggests that there is mother complex in the crystal whose symmetry axis at an angle of  $35^{\circ}$  from the b axis in the ab plane. In fact, when H makes an angle of



EPR spectrum of  $Cu^{2+}$  ion in  $Rb_2SO_4$  single crystal when H makes an angle of  $42^{\circ}$  with the crystallographic c-axis in bc-plane. The four lines marked I are due to complex I with its z-axis parallel to H.





EPR spectrum of  $Cu^{2+}$  ion in  $Rb_2SO_4$  single crystal when H makes an angle of  $35^{\circ}$  with the b-axis in the ab-plane. The four lines marked II in the region 2650-2950 are due to complex II with its z-axis parallel to H.

Fig. 2

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35° with b axis in the ab plane (z axis) a well resolved spectrum (Fig. 2) corresponding to a maximum hyperfine separation and maximum g value is observed. This vacancy complex is interpreted as one in which  $Cu^{2+}$  substitutes a  $\beta$ -Rb<sup>+</sup> site and gets associated with a nearly  $\beta$ -Rb<sup>+</sup> site vacancy in the ab plane. There are equivalent complexes in the ab plane.

The spectra corresponding to both the vacancy complex have been analysed using the usual spin Hamiltonian corresponding to rhombic symmetry.

Spectra have been recorded in the temperature range  $+30^{\circ}$ C to  $-120^{\circ}$ C. There is no apparent change in the nature of spectrum or in the spin-Hamiltonian parameters.

|             |                        |                                | · · · · · · · · · · · · · · · · · · · |
|-------------|------------------------|--------------------------------|---------------------------------------|
| Designation | g                      | $A(X10^{-4} \text{ cms}^{-1})$ |                                       |
| Spectrum I  | g <sub>z</sub> = 2.276 | A <sub>z</sub> = 85.59         |                                       |
| (Fig. 1)    | $g_{y} = 2.168$        | $A_{y} = 24.7$                 |                                       |
|             | $g_{x} = 2.228$        | $A_{x} = 79.30$                |                                       |
| Spectrum II | $g_{z} = 2.398$        | $A_{z} = 91.64$                |                                       |
| (Fig. 2)    | $g_{x} = 2.193$        | $A_{\rm x} = 70.78$            | · .                                   |
| · · · ·     | $g_{y} = 2.0504$       | $A_{y} = 48.83$                | , · ·                                 |

# TABLE I

#### **REFERENCES:**

1. B.V.R. Chowdari, "EPR of Mn<sup>2+</sup> & Fe<sup>3+</sup> in certain single crystals", Ph.D Thesis, Indian Institute of Technology, Kanpur, India (1967).

2. B.V.R. Chowdari and Putcha Venkateswarlu, J. Chem. Phys. <u>48</u>, 49 (1968).

# ELECTRON PARAMAGNETIC RESONANCE OF Mn<sup>2+</sup> IN Rb<sub>2</sub> SO<sub>4</sub> SINGLE CRYSTAL

B.V.R. Chowdari and Putcha Venkateswarlu, Department of Physics, Indian Institute of Technology, Kanpur.

### INTRODUCTION:

In recent years 'Electrin Paramagnetic Resonance' technique has been extensively used in investigating lattice defects and the possible phase transformations in single crystals. It is known from the work of Watkins<sup>(1)</sup> that when an NaCl or KCl crystal is doped with  $Mn^{2+}$  the magnetic ions goes in substitutionally and grts associated with first or second neighbour alkali vacancies, while in magnetic site. It is known from the work of Shrivastava and Venkateswarlu<sup>(2)</sup> than when the NaCl lattice contains oxygen as impurity the magnetic ion gets associated with first neighbour atomic or molecular oxygen. It is also known from the work of 0' Reilly and his collaborators<sup>(3)</sup>, the effect of phase transformations on the features of EPR spectra. In view of investigating the lattice defects and the possible phase transformations the EPR studies of several transition metal ions such as  $Mn^{2+}$ ,  $Cu^{2+}$  has been taken up in single crystals of  $(NH_4)_2SO_4$  and its isomorphic sulphates like K $_2SO_4$  and Rb $_2SO_4$ . In this paper we report a detailed study of the EPR of  $Mn^{2+}$  in Rb $_2SO_4$  single crystal.

## CRYSTAL STRUCTURE:

The arrangement of positive and negative ions in  $\text{Rb}_2\text{SO}_4$  is similar to that of  $\text{K}_2\text{SO}_4$  which was described elsewhere<sup>(4)</sup>. The dimensions of the cell at room temperature are a = 5.948Ű and b = 10.311Ű and c = 7.780Ű. The structure consists of layers of atoms parallel to (100) with a spacing a/2. The crystal contains two different sets of rubidium ions called  $\propto$  and  $\beta$ ; the oxygen encironment of the rubidium ions of  $\chi$  -type and four of  $\beta$ -type. The symmetry of the crystal is orthorhombic at room temperature.

# EXPERIMENT, RESULTS AND DISCUSSION:

 $Rb_2SO_4$  crystals doped with  $Mn^{2+}$  are grown by slow evaporation of the saturated solution. EPR spectra were recorded on varian V-4502 X - band EPR spectrometer.

Since the ground state configuration of  $Mn^{2+}$  is  ${}^{6}S_{5/2}$ , in orthorhombic fields it is expected to show in EPR five fine structure transitions each of which will have six hyperfine components. The spectra are taken in all the three crystallogtaphic planes. The spectrum is found to be very much angular dependent. It is found to be due to  $Mn^{2+}$  ion substituting one of the rubidium sites and gets associated with another type of rubidium site vacancy such that the site symmetry axis (2-axis) is at an angle of  $42^{\circ}$  with C-axis in bc plane. Fig. 1 shows the spectrum taken at



FIG. 1. EPR spectrum of Mn<sup>2+</sup> in Rb<sub>2</sub> SO<sub>4</sub> single crystals at room temperature; the direction of magnetic field making an angle of 42° with the crystallographic c-axis in bc-plane i.e. H||Z-axis.

room temperature with H//Z-axis. The spectrum taken with H making  $42^{\circ}$  with the C-axis on the left is the same as the one that one gets with H making equal angle on the other side of the C-axis. In the present experimentsonly four fine structure transitions associated with hyperfine structure are observed (marked in Fig. 1) instead of the expected five. From the analysis of the spectra the relative separations of the doublets are estimated to be 0.3647 cm<sup>-1</sup> ( + 5/2 to  $\pm 3/2$ ) and 0.183 cm<sup>-1</sup> (  $\pm 3/2$  to  $\pm 1/2$ ). The zero field separation between the levels  $\pm 5/2$  and  $\pm 3/2$  is 0.3647 cm<sup>-1</sup> which ismore than 0.3 cm<sup>-1</sup>, the microwave energy used in the X-band spectrometer explaining the reason why one of the two transitions  $\pm 5/2 \rightleftharpoons \pm 3/2$  isnot observed in the present experiments. The y-axis of the spectrum is found to be at an angle of 90° from the Z-axis in the bc plane while the X-axis coincides with the crystal ographic a-axis.

The spectra taken at room temperature when H is parallel to different crystallographic axes are analysed using the spin-Hamiltonian corresponding to rhombic symmetry.

H =  $g\beta$  H.S.+D  $\left[ s_z^2 - \frac{1}{3} S(S+1) \right]$  +  $E\left[ s_x^2 - s_y^2 \right]$  + S.A.I. where the different terms have the usual meaning. The spin-Hamiltonian parameters obtained are  $g_z = 1.973$ ,  $g_x = 2.012$ ,  $g_y = 2.015$ ,  $A_z = 93.0$  gauss  $A_x = 88.7$ gauss,  $A_y = 88.4$  gauss, D = 990.0 gauss and E = 18.0 gauss. Spectra are recorded at different temperatures in the range of +30°C to -160°C keeping H parallel to Z axis. There is no change in the nature of the spectra obtained indicating that there is probably no phase transformation in the range of temperature studied.

#### REFERENCES:

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|----|---|
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| 1. | B.V.R. Chowdari and Putcha Venkateswariu, J. Chem. Phys. 48, 49 (1968                   |

#### DISCUSSION:

| .S. Chandrasekaran | : | 1. Is Rb <sub>2</sub> SO <sub>4</sub> ferroelectric?                                   |
|--------------------|---|--|
|                    |   | 2. The concentration of $Cu^{2+}$ ions in the $Rb_2SO_4$ , I guess,                    |
|                    |   | is quite high. Is this right and can you give some quanti-                             |
| •                  |   | tative information on this?  |
| B.V.R. Chowdari    | I | <ol> <li>Yes</li> <li>Cu<sup>2+</sup> ion is occupying two different sites.</li> </ol> |
| R. Roy             | : | For determination of the angle $42^{\circ}$ referred to with the c-axis,               |

did you need a rotation of the sample in situ inside the cavity, besides rotation of the magnet in the bc- plane?

- .

B.V.R. Chowdari

A.N. Garg

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· ±

B.V.R. Chowdari

rotate the crustal in vertical plane also. May I know how you measured the angle of 42° which Cu<sup>2+</sup> makes along the C - axis in the bc plane? We have a magnet which can be rotated in a horizonatl plane. one can directly know what angle the Z-axis makes with

The crystal was mounted in a holder with which on e can

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crystallographic axis.

ELECTRON PARAMAGNETIC RESONANCE STUDIES OF Mn<sup>2+</sup> IN NH. Br

M. Duttatreya Sastry and Putcha Venkateswarlu Department of Physics, Indian Institute of Technology, Kanpur.

#### ABSTRACT

The electron paramagnetic resonance studies of  $Mn^{2+}$  in  $NH_4Br$  single crystal have been carried out in the b.c.c. and tetragonal phases of the crystal. Room temperature studies indicate that a part of the  $Mn^{2+}$  ions entering the lattice go substitutionally at cation sites, the change compensation site being quite remote from the magnetic ion. This is manifested in the presence of a single sexet at  $g \sim 2$  with  $A = (87.22 \times 10^{-4} cm^{-1})$ . Further the existence of  $Mn^{2+}$  clusters is indicated by the presence of a broad line. As the crystal transforms from b.c.c. to tetragonal phase  $Mn^{2+}$  ions remain at lattice sites symmetry and confirming that  $Mn^{2+}$  ions are at lattice sites. Spectra are analysed using the spin hamiltonian method.

# ELECTRON PARAMAGNETIC RESONANCE STUDIESOF VO<sup>2+</sup> ION DOPED IN POTASH ALUM SINGLE CRYSTALS

K.V.S. Rao and Putcha Venkateswarlu Physics Department, Indian Institute of Technology, Kanpur.

#### ABSTRACT

The electron paramagnetic resonance studies of  $VO^{2^+}$  ion doped in potash alum single crystals have been investigated over a wide temperature range. Spectra have been recorded with  $\langle 100 \rangle$  and  $\langle 110 \rangle$  axes parallel to the magnetic field. From the angular variation of the spectra it was observed that the vanadyl molecular ions substitutes for  $Al^{3^+}$  ion. It was also found that when the  $VO^{2^+}$  ions substitutes for the  $Al^{3^+}$  ion, one of the water molecules in the octahedron surrounding the  $Al^{3^+}$  ion, is missing and the V-O bond direction is along the direction of the missing molecule. Potash alum since it belongs to the O(-type) of alums, the cubic axes of the water octahedron is rotated with reference to the cubic axes of the unit cell along the  $\langle 111 \rangle$  direction. But it was found that the substitution of vanadyl ion for the  $Al^{3^+}$  ion affects the lattice in such a way that the cubic axes of the octahedron coincides with the cubic axes of the unit cell.

All the spectra analysed by using the usual spin-Hamiltonian method.
ELECTRON-RESONANCE STUDIES OF VO<sup>2+</sup> IN ALKALI CHIORIDES

A.V. Jagannadham, Indian Institute of Technology, Kanpur.

#### ABSTRACT

Electron spin resonance spectra of  $VO^{2+}$  are studied in alkali chloride hosts in a temperature range +60°C to - 190°C. These studies indicate that there is a fast readjustment of  $VO^{2+}$  molecular ion in the crystal giving rise to an isotropic spectrum. As the temperature is decreased, the motion of  $VO^{2+}$  molecular ions is hindered and gives rise to an anisotropic spectrum. A systematic study is made and the temperature below which anisotropy in A and g is observed in all the crystals is determined.

Spin-Hamiltonian constants are calculated from isotropic and anisotropic spectra recorded in each case. The variation of line widths with temperature has also been studied. The  $m_I$  dependence of line width is explained in terms of Kivelson's theory for liquids and its validity in the present single crystal study is discussed.

THE EFFECT OF AN EXTERNAL UNIFORM FIELD ON A SINGLE (FERROMAGNETIC) CONTAINING 180° DOMAINS

V.B. Kelkar, Physics Department, Institute of Science, Bombay-1.

# ABSTRACT

The energy of a single crystal of ferromagnetic material with  $180^{\circ}$  domains is calculated when it is kept in a uniform external field. It is assumed that the width of each domain aligned with the field is constant and =  $D_1$ . Also each domain magnetized against the field has a smaller width  $D_2$ . Minimization of energy gives the law that  $D(1 - \phi)$  is constant where  $D = D_1 + D_2$  and  $\phi = (D_1 - D_2)/(D_1 + D_2)$ . EXCHANGE CONSTANTS IN NICKEL - ZINC FERRITE SYSTEM

## C.M. Srivastava, Department of Physics, Indian Institute of Technology, Bombay.

lastered a sull'-e t 355 558: 68 hAD RAS 355 68 hAD RAS 355 168 7/68 7/68 Nickel-zinc system has been extensively studied by several workers. Thus, magnetic moment, Curie temperature, resistivity, anisotropy field, g-factor, magnetic and dielectric spectra, lattice constant have been studied (1) on the system for various Zn contents. The spin configuration in NiFe204 and Ni0.5Fe204 have been determined by neutron diffraction by Hastings and Corliss(2) and Wilson and Kasper (3) respectively. Recently neutron diffraction studies of a number of the members of Ni-Zn system have been undertaken at Bhabha Atomic Research Centre, Bombay. In all these studies, magnetic order has been found mostly to be that of Neel model. However, an attempt by Neel et al (4) to obtain the exchange constants on this model from the study of paramagnetic susceptibility with temperature gave results in contradiction to the qualitative predictions of super-exchange theory. The present work is motivated by a desire to see if it is possible to obtain a set of exchange constants which explains broadly the experimental results and is consistent with the semi-qualitative deductions of super-exchange theory.

> In an inverse spinel consisting of two type of ions on octahedral sites, the Hamiltonian is

$$H = -2J_{AA} \qquad \sum_{(ij)} \underline{\underline{s}}_{i}^{A} \cdot \underline{\underline{s}}_{j}^{A} - 2J_{AB_{1}} \qquad \sum_{(ik)} \underline{\underline{s}}_{i}^{A} \cdot \underline{\underline{s}}_{k}^{B_{1}}$$
$$-2J_{AB_{2}} \qquad \sum_{(i\ell)} \underline{\underline{s}}_{i}^{A} \cdot \underline{\underline{s}}_{\ell}^{B_{2}} - 2J_{B_{1}B_{2}} \qquad \sum_{(k\ell)} \underline{\underline{s}}_{k}^{A} \cdot \underline{\underline{s}}_{\ell}^{B_{2}}$$
$$-2J_{B_{1}B_{1}} \qquad \sum_{(km)} \underline{\underline{s}}_{k}^{B_{1}} \cdot \underline{\underline{s}}_{m}^{B_{1}} - 2J_{B_{2}B_{2}} (\underline{\underline{\ell}}_{n}) \underline{\underline{s}}_{\ell}^{B_{2}} \cdot \underline{\underline{s}}_{n}^{B_{2}}$$

 $\underline{S}_{\underline{i}}^{A}$  is the spin operator for a tetrahedral ion,  $\underline{S}_{\underline{k}}^{B}$  and  $\underline{S}_{\underline{m}}^{B}$  are spin operators of species B(1) and  $\underline{S}_{\underline{\ell}}^{2}$  and  $\underline{S}_{\underline{n}}^{2}$  are spin operators of species B(2) on octahedral sites. Only nearest neighbour interaction has been taken in (1). For this Hamiltonian the Weiss molecular field can be given by a three sublattice model :

$$\begin{pmatrix} \mathbf{H}_{\mathbf{A}} \\ \mathbf{H}_{\mathbf{B}_{1}} \\ \mathbf{H}_{\mathbf{B}_{2}} \end{pmatrix} = \begin{pmatrix} \lambda_{\mathbf{A}\mathbf{A}} & \lambda_{\mathbf{A}\mathbf{B}_{1}} & \lambda_{\mathbf{A}\mathbf{B}_{2}} \\ \lambda_{\mathbf{A}\mathbf{B}_{1}} & \lambda_{\mathbf{B}_{1}\mathbf{B}_{2}} & \lambda_{\mathbf{B}_{1}\mathbf{B}_{2}} \\ \lambda_{\mathbf{A}\mathbf{B}_{2}} & \lambda_{\mathbf{B}_{1}\mathbf{B}_{2}} & \lambda_{\mathbf{B}_{2}\mathbf{B}_{2}} \end{pmatrix} \begin{pmatrix} \mathbf{M}_{\mathbf{A}} \\ \mathbf{M}_{\mathbf{B}_{1}} \\ \mathbf{M}_{\mathbf{B}_{2}} \end{pmatrix}$$

For collinear spin arrangement the paramagnetic susceptibility is given by (5)

$$\frac{1}{\mathcal{F}_{m}} = \frac{T}{2} + \frac{1}{\mathcal{F}_{0}} - \frac{k_{1}}{T - \theta_{1}} + \frac{k_{2}}{T - \theta_{2}}$$

Here  $\frac{1}{2}$ ,  $k_1$ ,  $k_2$ ,  $\theta_1$ ,  $\theta_2$  are functions of the constants  $\lambda_{1j}$ . Thus from Ngel's measurements of the paramagnetic susceptibility of the NiZn series, the exchange constants can be calculated. The results thus obtained for NiZn system are given in table I. A and B<sub>1</sub> sublattices contain Fe<sup>3+</sup> ions, and B<sub>2</sub> sublattice contains Ni<sup>2+</sup> ions.

It is obvious that the two sublattices model in which the interactions of the two different ions, Fe<sup>3+</sup> and Ni<sup>2+</sup> on the B sublattice are averaged over gives values of exchange constants which are contrary to the expectations of the current ideas of the exchange interactions in oxides. On the other hand, the three sublattice model gives results which are fairly consistent with the predictions of superexchange interactions.

| ТA | BPE | I |
|----|-----|---|
|    |     |   |

|  | Three Sublattice ( <sup>0</sup> K) |                   |       |                    | Two Sublattice (Neel)<br>(°K) |                    |                 |                 |                 |
|--|------------------------------------|-------------------|-------|--------------------|-------------------------------|--------------------|-----------------|-----------------|-----------------|
| ,  | JAA                                | J <sub>AB</sub> 1 | JAR   | J <sub>B1</sub> B1 | J <sub>B1</sub> B2            | J <sub>B2</sub> B2 | J <sub>AA</sub> | J <sub>AB</sub> | J <sub>BB</sub> |
| NiFe204  | -9.4                               | -22.2             | -45.0 | -13.7              | -47.3                         | -91.3              | -9•4            | -30.0           | -8.4            |
| Ni0.8 <sup>Zn</sup> 0.2 <sup>Fe</sup> 2 <sup>0</sup> 4 | -9.4                               | -24.7             | -45.0 | -13.7              | -47.5                         | 91.3               | -20.9           | -29•4           | -9.5            |
| Ni0.4 <sup>Zn</sup> 0.6 <sup>Fe</sup> 2 <sup>0</sup> 4 | -5.6                               | -28.7             | -45.0 | -10.0              | -47.5                         | 91.3               | -61.8           | -35.5           | -10.6           |

In spinels the major contribution to the superexchange comes from correlation and dislocation effects.(6). Considering only correlation superexchange, and 180° and cation-anion-cation interactions, the anticipated (6) sign of various interactions is as shown in Table II.

| TAB  | LE | II |
|--|----|----|
| Construction of the local division of the lo | _  | -  |

|  | Angle Distance<br>A |      | 180°c-a-c S           | uperexchance | 90 <sup>°</sup> c-a-c \$ | N                    |                    |
|--|---------------------|------|-----------------------|--------------|--------------------------|----------------------|--------------------|
| بر بی کو کی کر             |                     |      | Correlation Delocali- |              | Correlation Delocali-    |                      | t e                |
| <sup>J</sup> AA<br>(d <sup>5</sup> -d <sup>5</sup> )           | 79 <b>°-</b> 351    | 5.26 |                       |              | ↑↓ -                     | ↑↓                   | 11                 |
| $\frac{J_{AB_1}}{(d^5-d^5)}$                                   | 125°-9'             | 3.89 | 1↓                    | ↑↓           | ∕↓                       | ∕↑↓                  | 11                 |
| J <sub>AB2</sub><br>(d <sup>5</sup> -d <sup>8</sup> )          | 125 <b>°-</b> 9     | 3.69 | <b>↑</b> ↓            | ↑↓           | 1                        | 1↓                   | 1↓                 |
| $J_{B_1B_1}^{J_{B_1}B_1}$<br>(d <sup>5</sup> -d <sup>5</sup> ) | 90 <sup>°</sup>     | 4.17 | ·                     | -<br>-<br>-  | $\uparrow\downarrow$     | ↑↓                   | ↑↓                 |
| $J_{B_1B_2}$<br>(d <sup>5</sup> -d <sup>8</sup> )              | 90 <sup>0</sup>     | 4.17 | <br>·                 |              | î ↑↓                     | $\uparrow\downarrow$ | ↑↓                 |
| J <sub>B2</sub> B2<br>(d <sup>8</sup> -d <sup>8</sup> )        | 90 <b>°</b>         | 4.17 | ·                     |              | $\uparrow\uparrow$       | $\uparrow\uparrow$   | $\uparrow\uparrow$ |

From Tables I and II it can be seen that the calculated exchange constants have the expected sign. Regarding the magnitudes of  $J_{ij}$ , it is fairly well established (7) that the tetrahedral-octrahedral interaction for Fe<sup>3+</sup> ions in spinels and garnets is about 25° which agrees with our calculated value of  $J_{AB1}$ . The order of magnitude of  $J_{AB_2}$  is not unreasonable considering that in NiO,  $J_1$ , the first neighbour exchange interaction, is -150°K (7). The sign of this interaction is the same as in NiTiO<sub>3</sub> (6) and is opposite of NiO since the dominant antiferromagnetic 180° next neighbour interaction of NiO is absent in nickel ferrite and NiTiO<sub>3</sub>.  $J_{AB_2}$  and  $J_{B_1B_2}$  interactions which involve Ni<sup>2+</sup> ions are expected. The magnitude of  $J_{B_1B_1}$  is seen to decrease with increasing Zn content which is expected since ZnFe<sub>2</sub>O<sub>4</sub> has an exchange constant of approximately -2°K. The magnitude of  $J_{AA}$  is small compared to other  $J_{ij}$  though it appears to be little too large since in CoAl<sub>2</sub>O<sub>4</sub> where only  $J_{AB_1}$  with increase in Zn content has not been possible to explain.

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#### DISCUSSION:

N.S. Satya Murthy :

It appears that we can measure exchange integrals like  $J_{B_1B_1}$  by neutron scattering since the larger exchange integrals would not be picked up in the observed scattered neutron spectrum. We would start with  $2nFe_2O_4$  perhaps and go on through the series.

C.M. Srivastava :

I shall be happy if some direct experimental conformation of some of these exchange constants could be made.

# MAGNETIZATION OF FERRO- AND FERRI-MAGNETIC SUBSTANCES NEAR THE CURIE TEMPERATURE

C. Srinivasan,

Department of Physics, Indian Institute of Technology, Bombay-76.

Recently great attention has been paid to the study of magnetic transition. The magnetization of a ferromagnetic substance near its critical point is believed to be described by the following relation ships:-

a. below T<sub>c</sub>, the Curie Temperature:

$$\frac{\sigma_{\rm B}}{\sigma_{\rm o}} = D(1 - \frac{T}{T_{\rm c}})^{\rm f} , \qquad \dots \dots (1)$$

where  $\sigma_{\overline{B}}$  = specific spontaneous magnetization at temperature  $T^{\circ}K_{s}$  $\sigma_{\overline{B}}$  = specific magnetization at  $O^{\circ}K_{s}$ 

b. at  $T = T_c$ ;  $\sigma_i = CH$ ,

.....(2)

....(3)

where  $\sigma_i = magnetization of the paraprocess at T = T_c;$ 

c. above T,

$$X^{-1} = A(T - T_c)^{V}$$

where  $\chi_{o}$  = initial susceptibility,

D, C, A, f,  $\delta$  and  $\gamma$  are critical parameters.

According to the molecular field theory and the Landau theory of second-order phase transition<sup>(1)</sup> in which only long-range order is taken into consideration, the critical phase f,  $\delta$  and  $\gamma$  have values  $\frac{1}{2}$ ,  $\frac{1}{3}$  and 1 respectively. These may be compared with the values of  $\gamma = 4/3$  for the Heisenberg model,  $\gamma = 5/4$ ,  $f \approx 1/3$  and  $\delta = 1/5$  for the Ising model, given by the recent theoretical investigations (2-4). The difference in the values of the critical indices thus stimulated experimental work on their determination. It may be mentioned that in almost all the experimental investigations reported so far<sup>(5,6)</sup>, only one or two of the indices have been determined.

The aim of the present investigation was to determine all the critical indices not only for ferromagnetic but also for ferrimagnetic substances. The results of measurements carried out<sup>#</sup> on nickel, nickel-copper alloys (95% and 92% Ni) invar

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(36% Ni) are reported. As ferrimagnetic specimens were chosen the simple ferrites - Nickel, Magnesium and Magnetite prepared by the usual ceramic process and single crystal of manganese ferrite grown by the Verneuil method. The specimens were of such shape and size that the demagnetizing field in the specimens was very small, particularly near the Curie temperature.

Measurements of magnetization of all specimens were carried out by the ballistic method in fields upto 2000 Oe and of nickel in fields from 3.5 to 14 KOe. by the method of Domenicalli(7).

For all specimens, the behaviour of magnetization at any given temperature near the Curie temperature is very well described by  $\frac{H}{d} = \chi + \beta \sigma^2$ , where  $\chi$  and  $\beta$ are constants. From the graph of  $\chi$  vs T, the Curie temperature T<sub>c</sub> (the temperature at which  $\chi = 0$ ) is determined <sup>(5,8)</sup>.  $\sigma_s$ , the spontaneous magnetization, is determined by extrapolating the straight part of the curve  $\frac{H}{d}$  vs  $\sigma^2$  to the  $\sigma^2$  axis. Above the Curie temperature, the value of  $\chi$  determined by the extrapolation of the straight part of the curve to the H/ $\sigma$  axis, gives  $\chi_o^{-1}$ . All the critical parameters are determined by constructing the corresponding logarithmic graphs.

From the results given in Table I, it is observed that the critical index f is nearer 1/2 (the classical result) than 1/3. The value of f in the region close to the Curie temperature is greater than in the temperature region further away. This result is in accordance with the theoretical result of Callen and Callen<sup>(9)</sup> for ferro-magnetics.

A study of the field variation of magnetisation at the Curie temperature, shows that the index  $\delta = \frac{1}{3}$  for all specimens in fields upto 2 KOe. This result is in agreement with the molecular field theory result. However, measurement of magnetization of nickel in fields from 3.5 to 14 KOe shows that  $\delta$  decreases to a value 0.27. This may be compared with the value of 0.237 obtained by Kouvel and Fisher<sup>(5)</sup> for nickel. This is different from the value  $\frac{1}{5}$  predicted for the three-dimensional Ising model<sup>(10)</sup>.

The value obtained for the index  $\gamma$  for nickel and the simple ferrites agrees with the value given by the recent calculations for the three-dimensional Heisenberg model. For the alloys  $\gamma \approx \frac{5}{4}$ , the value given for the Ising model.

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# TABLE I

Experimental Values of the Critical Indices  $\gamma$ ,  $\delta$  and f.

| Specimen             | <u> </u>           | 8                              | f  | Temperature region   |
|----------------------|--------------------|--------------------------------|--|--|
| M1                   | 1.30 + 0.03        | B.0.32 ± 0.02<br>b.0.27 ± 0.01 | 0.41 ± 0.02<br>0.38 ± 0.01               | $\begin{array}{c ccccccccccccccccccccccccccccccccccc$  |
| 95% Ni<br>5% Cu      | 1.25 + 0.04        | 0.32 + 0.03                    | 0.53 + 0.02<br>0.38 <u>+</u> 0.01        | $\begin{array}{c} 0.979 & \leq & T/T_{c} \leq 0.997 \\ 0.835 & \leq & T/T_{c} \leq 0.979 \end{array}$    |
| 92% Ni.<br>8% Cu     | 1.18 + 0.03        | 0.32 ± 0.02                    | 0.56 ± 0.03<br>0.42 ± 0.02               | $\begin{array}{rrrr} 0.977 & \leq & T/T_{c} \leq 0.999 \\ 0.938 & \leq & T/T_{c} \leq 0.977 \end{array}$ |
| Invar                | 1.20 <u>+</u> 0.04 | 0.33 ± 0.02                    | 0.55 <u>+</u> 0.03<br>0.44 <u>+</u> 0.01 | 0.961 $\leq$ T/T $\leq$ 0.998<br>0.827 $\leq$ T/T $\leq$ 0.961   |
| NiFe204              | 1.32 + 0.04        | 0.32 + 0.03                    | 0.53 <u>+</u> 0.04<br>0.42 <u>+</u> 0.01 | $\begin{array}{rrrr} 0.990 & \leq & T/T_{c} \leq 0.997 \\ 0.895 & \leq & T/T_{c} \leq 0.990 \end{array}$ |
| Fe304                | 1.34 + 0.03        | 0.34 + 0.03                    | 0.58 <u>+</u> 0.03<br>0.50 <u>+</u> 0.01 | $\begin{array}{cccc} 0.980 & \leq & T/T_{c} \leq 0.998 \\ 0.930 & \leq & T/T_{c} \leq 0.980 \end{array}$ |
| MgFe <sub>2</sub> 04 | 1.32 <u>+</u> 0.04 | 0.33 + 0.02                    | 0.71 <u>+</u> 0.03<br>0.53 <u>+</u> 0.01 | $\begin{array}{rrrr} 0.967 & \leq T/T_{c} \leq 0.995 \\ 0.883 & \leq T/T_{c} \leq 0.967 \end{array}$     |
| MnFe204              | 1.35 + 0.02        | 0.33 +                         | 1.00 <u>+</u> 0.02<br>0.44 <u>+</u> 0.01 | $\begin{array}{rrrr} 0.975 & \leq & T/T_{c} \leq 0.995 \\ 0.834 & \leq & T/T_{c} \leq 0.975 \end{array}$ |

a. in fields upto 2 KOe.b. in fields from 3.5 to 14 KOe.

#### DISCUSSION

| E.G. Remachandran : | What quantities of the material are used for determination of |
|---------------------|---|
|                     | the Curie Points?   |
| C. Srinivasan :     | 1.5 - 2.0 gm of all substances for measurements in fields up- |
|                     | to 2 KOe. About 0.4 gm for measurements in higher fields.     |

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## SPIN-ORDERING IN DILUTE MAGNETIC ALLOYS

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# INTRODUCTION:

For many years it has been recognized that the paramagnetic properties of Cu-Ni. alloys are not easily explained on the basis of the band model of Mott<sup>(1)</sup>, Wohlfarth<sup>(2)</sup>. Recent studies<sup>(3)</sup> on this alloy have revealed that non-compliance of the band model arises from the fact that this system is not a perfect solid solution but forms localized clusters rich in Nickel. Furthermore, it, has been shown by Kheller<sup>(4)</sup> that in the absence of magnetic interaction between neighbouring clusters (which is realised only in dilute alloys) the initial susceptibility  $\mathcal{X}_{o}$ is given by

.....(1)

 $\chi = c_{\beta}$ where  $\beta = 1/T$  and C is given by  $NM_2^2 V^2/3k$  and M and V are the volume and the spontancous magnetization of each cluster and N is the number of such clusters per cm<sup>2</sup>. However, this simple relationship is unable to account for the observed anomalous temperature dependence of  $\chi$  (3). A possibility of explaining this is to improve the above relationship by introducing the effect of magnetic interaction between the neighbouring clusters; but for all the alloys below 40 per cent Nickel concentration Curie temperature is zero, hence, the direct exchange interaction is small. An indirect exchange mechanism based on Rudermann-Kittel interaction has been proposed by Marshall<sup>(5)</sup>, for dilute magnetic alloys. We have introduced this long rang indirect magnetic interaction in redriving equation (1) and assuming the angular distribution of the clusters to be antiferromagnetic, the initial susceptibility is written as:

where 01 and 02 are constants which arise from long range exchange.

An attempt to interpret the preliminary susceptibility observations on 2.37 at % Ni alloy over a temperature range of 100°K to 800°K shows a qualitative agreement with equation (2). This has led to the present investigation in which the magnetic susceptibilities of six-Cu-Ni alloys have been examined and the results interpretes on the basis of the above model.

 $\chi_{o} = c_{o}\beta - c_{1}\beta^{3} - c_{2}\beta^{3/2}$  .....(2)

## EXPERIMENTAL:

The magnetic measurements were carried out in a susceptibility balance which was described by one of the present authors in an earlier communication<sup>(b)</sup>.

The spectrographically pure Cu and Cu-Ni alloys were procured from Johnson and Matthey. After susceptibility measurements were completed at all temperatures on the unannealed samples, the specimens were annealed in a vacuum furnace at  $800^{\circ}$ C for 48 hours. Chemical analysis made on pieces taken from the top and bottom of each sample indicated a nickel content of 0.54, 1.73, 2.37, 10.73, 21.29 and 31.68 atomic per cent for the specimens.

#### RESULTS AND DISCUSSION:

In Fig. 1 the mass susceptibility data of 10.73% and 31.66% Ni-alloys are reproduced as a function of temperature. The results of 10.73% and 31.66% Ni alloys are shown together with the effect of plastic deformation and heat treatment. It should be noted that a puzzling phenomena arises for unannealed samples in which  $\chi$  vs T curve passes through a maximum. This maximum disappears only on prolonged heating. The present data on annealed samples in the low temperature region agree with the data of Ryan et al<sup>(3)</sup> but at high temperatures considerable departure has been observed with the only available data of Kaufmann and Starr<sup>(7)</sup>. But since practically there is no field dependence of susceptibility for our samples, we infer that Kaufmann and Starr's data, which also showed disagreement in the low temperature region with the data of Ryan et al<sup>(3)</sup>, was contaminated with foreign impurity.

In Fig. 1 atomic susceptibility vs T has been plotted for annealed alloys with 1.73, 2.37 and 21.29 at % Ni alloys. It is significant that the nature of temperature variation of susceptibility isalike upto 10.73 at % Ni concentration; from 120°K to 350°K the variation is only 5% whereas between 350°K to 800°K  $\times$  decreases more rapidly. For 21.29% and 31.68% Ni alloy X decreases continuously from 120°K to 800°K by about twenty per cent. It is to be noted that the temperature variation upto 10.73% alloys can be fitted with equation (2) mentioned in an earlier section. This eqation is derived by the present authors (unpublished) from the elementary theory of superparamagntism where the spins of the superparamagnetic particles interact via the long range oscillatory Rudermann - Kittel interaction. This formal treatment explores the idea of Marshall (5) on the effective field distribution in dilute superparamagnetic alloys and makes a self-consistent postulate in analogy with Weiss molecular field theory. In the present work we have analysed in detail the data on 2.37 at % Ni alloy and interpreted them on the bais of equation (2) and the constants  $C_0 = 8.4 \times 10^{-3}$ ,  $C_1 = 22.65$  and  $C_2 =$ 5.60 x 10<sup>-2</sup>. C is the usual Curie constant from which magnetic moment/Nickel atom is found to be 1.65 Bohr magnetons. This is very close to the magnitude of the magnetic moment of pure Ni in the paramagnetic region which was observed to be 1.61 Bohr magnetons<sup>(7)</sup>. The  $T^{3/2}$  term in equation (2) is comparatively large showing that the magnetic interaction consistered here is quite significant. It is important to note that the method of analysis pursued above, is able to explain E variation for all the alloys up to 10.73% Ni concentration. X

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#### DISCUSSION:

M.F. Merriam : Do you know that your specimens had the solute homogeneously distributed in the solvent?

S.K. Dutta Roy :

The point you mention was clarified first by preparing different samples by induction melting and then annealing for 96 hours at  $800^{\circ}$ C. These samples were checked again by x-ray diffraction analysis. This procedure was repeated for all the samples before they were work-hardened.

Also another variety of samples procured from M/s Johnson & Mathey was subjected to the above analysis.

# ELECTRON SPIN RESONANCE IN IRRADIATED L1, SO, H,O

N. Hariharan and J. Sobhanadri, Department of Physics, Indian Institute of Technology, Madras.

#### INTRODUCTION :

Since the first experimental observation of paramagnetic resonance in irradiated crystals by Hutchinson<sup>(1)</sup> Electron Spin Resonance has become an important tool for identifying the paramagnetic defects produced in irradiated crystals. The present paper presents the results obtained from e.s.r. studies of irradiated Lithium Sulphate monohydrate.

# EXPERIMENTAL:

Single crystals of  $\text{Li}_2\text{SO}_4$ . $\text{H}_2\text{O}$  grown from aqueous solutions were exposed to X-radiation for several hours. E.S.R. spectra of these irradiated crystals were taken at room temperature on a Varian-X-band spectrometer (Varian type V-4500). For the monoclinic  $\text{Li}_2\text{SO}_4$ . $\text{H}_2\text{O}$  the two crystals axes 'a', 'b' and a third axis of were taken as the three orthogonal axes.

# RESULTS:

The spectra consisted of a strong isotropic line with 'g' near the free spin value and some anisotropic lineson both sides of this central line. The spectral distribution for rotation about 'a' axis is not bery much different from that about 'b' axis. If Fig. 1 few typical e.s.r. spectra are shown for certain specified orientation. Fig. 2 shows the angular dependence of the resonance lines for rotation about the  $\int 010^{-3}$  axis, the two fold axis of the monoclinic crystal.

An examination of Fig. 2 indicates that there are two anisotropic lines with identical 'g' variation on either side of the free spin line. Other than these lines, two more anisotropic lines are present whose angular variation indicate that there are two possible sites per unit cell for the paramagnetic defect responsible for this spectrum.

A comparison of these spectra with those obtained by Wigen and  $Cowen^{(2)}$  and Aseltine and  $Kim^{(3)}$  on electron irradiated  $Li_2SO_4$ .H<sub>2</sub>O studied at liquid air and liquid nitrogen temperatures present an interesting reading. In the present investigation both irradiation and expérimental studies are carried out at room temperature. The two spectra are common in that they have an isotropic line occuring at the free spin value which might be attributed to an electron trapped at a vacancy or lattice defect in the irradiated crystal. The loop like pair of lines has not been observed in the spectra of the electron irradiated crystal.





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The other two anisotropic lines which might be associated with a centre exhibiting hyperfine structure from a single nucleus of spin 1/2 arealso differently oriented in the X-irradiated crystal. For the electron irradiated crystal the two lines are mostly on the lower field side of the free spin line except for a few orientations whereas for the X-irradiated crystal the two lines are entirely on either side of the free spin line.

The 'g' tensor and 'A' tensor are calculated by the usual methods.

#### DISCUSSION:

Apart from an electron or hole trapped at a vacancy or lattice defect, certain radical ions also might have been produced in the irradiated crystals. The paramagnetic radicals that can be formed in irradiated  $\text{Li}_2\text{SO}_4$ .H<sub>2</sub>O are  $\text{SO}_2^-$ ,  $\text{SO}_3^-$  or  $\text{SO}_4^-$  all of which may not show any hyperfine interaction (<sup>33</sup>S with spin 3/2 is only 0.8% abundant). Though Lithium has a spin 3/2, Aseltin and Kim have shown that Lithium hyperfine interaction isnot needed to derive the observed anisotorpy. This leaves proton hyperfine structure to be the only possibility and the configuration of the defect responsible f or the anisotropic spectra of Group B must contain H. The radicals containing one hydrogenatom that are most likely to be formed during irradiation are H, OH, and O<sub>2</sub>H.

The two line group having principal 'g' values of 2.0320, 2.0116 and 2.0078 does not seem to exhibit any proton hyperfine structure and probably the defect responsible for this spectrum might be a sulphur oxy-radical. From a comparison with the spectra of other sulphate, it can be concluded that this spectrum might be due to  $SO_4^-$  radical ion.

The paramagnetic centre exhibiting hyperfine structure from a single nucleus of spin 1/2 can be compared with the anisotropic lines obtained in the electron irradiated crystals. Commenting on the conclusion of Wigen and Cowen that the doublets in their spectra werearising from the interaction of 'hole' with a single proton; Ovenhall<sup>(4)</sup> suggested that the paramagnetic center might be a hydroxyl radical hydrogen bonded to the sulphite group. The conclusion of Aseltine and Kim also was that the defect of axial symmetry responsible for this spectra is probably an OH radical with insignificant bonding to its neighbour. In these investigations carried out at low temperatures, the twp 'g' values are wide apart,  $g_{\perp} = 2.002$  and  $g_{\parallel} = 2.040$ . Other data encenring OH radical<sup>(5)</sup> also indicate that for OH radical one value is near 2.005 and the other heigher around 2.06.

In the present investigation, though the 'g' tensor and 'A' tensor for the defect responsible for this spectra are nearly symmetric,  $g_{\parallel} = 2.0133$ ,  $g_{\perp} = 2.0065$  the actual values are not agreeing with those obtained at low temperatures. The suggestion of Syons<sup>(6)</sup> that the anisotropic spectra may be attributed to  $0_2$ H radical is also worth mentioning.  $0_2$ H is found to have  $g_{\perp} = 2.004$  and  $g_{\parallel} = 2.024$ .

An analysis of the spectra obtained at liquid nitrogen temperature for ultra violet irradiated crystal at room temperature, which are in progress, may yield confirming evidence for the identification of the radicals.

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#### DISCUSSION:

A.V. Patankar :

r : In view of the formation of OH and OH2 radicals, it is possible that H2 gas would evolve.

N. Hariharan :

It is possible that molecular hydrogen may be evelved in the process of irradiation. H.f.s. due to H atom reveal a doublet with a separation of 100 gauss. But we have observed a doublet with a separation of about 30 gauss. So we feel that h.f. interaction might be due to OH or  $O_2$ H which are the other possible radicals that can be formed with one hydrogen atom.

V. Subrahmanya Murty :

N. Hariharan :

Did you observe the hyperfine splitting due to Li?

No. But the experiments done on crystals doped with Li<sup>b</sup> and Li<sup>7</sup> isotopes separately by Aseltine and Kim revealed that only the width of the doublet changes, thus exhibiting that the h.f. interaction of the electron spin with the Lithium nucleus is not appreciable.

M.V. Rao : Do you find any difference in the E.S.R. spectra obtained from the crystals grown at different temperatures?

N. Hariharan:

Yes. E.S.R. spectra of crystals grown at different temperatures are slightly different. High temperature crystal reveals more lines, showing the presence of more paramagnetic centres. We are doing a systematic study of  $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$  grown at 30°C.

# EPR SPECTRA OF CARBON TETRACHIORIDE PRODUCED BY 1 -MeV ELECTRONS AT $77^{\circ}$ K - EVIDENCE FOR TRAPPED CHIORIDE ATOM

P.S. Rao Radiation Laboratory, CSMCRI, Bhavnagar.

## ABSTRACT

The electron paramagnetic resonance spectrum of pure carbon tetrachloride taken at  $77^{\circ}$ K after irradiation with 1 -MeV Vande Graaff electrons showed an anomalous hyperfine splitting. The observed hyperfine spectrum is a quartet with unequal intensities (1,4,4,2), the field for free electron resonance lying at about 3.5 G. away from and between the stronger lines with the weaker lines 13.5 G. farther, with linewidths of 2.5 G. This hyperfine structure is attributed to a trapped chlorine atom, hitherto undetected. It is assumed that the electrons move mostly round the outer chlorine nucled leading to hyperfine structure mainly from the abundant <sup>35</sup>Cl isotope (75.4%) with spin I = 3/2 resulting in four lines (the smaller structure from  $3^{7}$ Cl(24.6%) contributing to the observed unequal intensities. This work is carried out at Michigan state University, East Lansing. ELECTRON MICROSCOPY OF RADIATION DAMAGE IN PDI, AT LOW TEMPERATURE

A.V. Pathankar, E.E. Schneider\* and J. Congleton\*\*, Tata Institute of Fundamental Research, Bombay - 5.

## INTRODUCTION:

Lead Iodide is a divalent ionic compound and its crystal has planar sandwich structure. It consists of a plane of lead ions sandwiched between two layers of hexagonally packed iodine ions.

Patankar and Schneider<sup>(1)</sup> have studied the irradiation centres produced in single crystals after  $\Upsilon$  -irradiation at liquid nitrogen temperature and have shown that the centres are formed in regions of very high distortion. This was c concluded from the powder-like line shapes of the electron spin resonance singuls. In addition, the energy required to produce a colour centre is about 3 ev. which is very low compared to those observed in the alkali halides. They have also studied the optical properties of the centres in the infra-red region<sup>(2)</sup>. The most interesting feature of the absorption lines is their unusual breadth which again suggests that the centres are subjected to local strains.

Our work is concerned mainly with the identification of the defects which are produced by  $\Upsilon$  -irradiation and electron bombardment at liquid nitrogen temprature.

## EXPERIMENTAL:

We have used a JEOL electron microsope for observing irradiation effects in PbI<sub>2</sub>. A cooling state was employed to cool the smaples to liqued nitrogen temperature. The crystals were prepared by slow cooling of supersaturated acqueous solution of lead iodide (Analar). To obtain high resolution 100 keV electrons were used for observing the specimen with the smallest available apertures to avoid decomposition by the energetic electrons. The samples were examined before irradiation at a magnification of 50000 diameters. The defects produced by  $\gamma$  -irradiation were observed at liquid nitrogen temperature in crystals which were warmed up to the room temperature from liquid nitrogen temperature after irradiation with a 500 Ci Co<sup>60</sup> source. The electron irradiation of the crystal was achieved by using the electron beam of the microscope to irradiate the specimen in the cooling stage held at liquid nitrogen temperature.

In an electron micrograph the bend contrours, particularly their edges, are the regions of high contrast and are, therefore, sensitive to changes in orientation of

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atoms resulting from any distortion in the lattice (3). The unirradiated specimens have always shown very sharp contrast at the edges of the bend contours even at magnification of 30,000.

The irradiated samples show a 'mottled' appearance at the bend contours. As the bend contour moves around due to flexing of the crystals, the bright region in the erystal appear as a 'mottling', which indicates that the defects are formed uniformly in the lattice in the process of electron and gamma irradiation and after thermal annealing of the samples (plate 1). The presence of distortion is also shown by the electron diffraction patterns of such a mottled region which show ring pattern superimposed on the diffraction pattern due to unaffected regions (plate 2). A close examination of the mottled region shows that the most significant contrast consists of two lobes (black and white) about a line of no contrast (plate 2 contrasts A and B).

# DISCUSSION:

The diffraction contrast from spherical inclusions or vacancy clusters has been treated by Ashby and Brown<sup>(4)</sup>. In general, the contrast appears as a pair of lobes symmetrically placed about a line which there is no contrast, when the incident electrons are diffracted strongly by one set of lattice planes. For spherical strains the line of no contrast is normal to the particular operating reflections as observed by Philips and Livingstong<sup>(5)</sup> and Ashby and Brown<sup>(4)</sup>. They further showed that the intensity change in the contrast due to strins at various depths may depend on depth.

The contrast with two lobes, which is observed in the case of irradiated  $PbI_2$  crystal, therefore, comes from those strain coherencies which are close to the surfaces of theorystal. The mottling appears to be an aggregate contrast of large number of such strain sphere which are not near the surface but embedded in the crystal foil. The strin, therefore, appears to be due to vacancy clusters and interstitial precipitates, and provides the necessary distorted regions in which the radiation centres are likely to be lodgd as expected from the electron spin resonance studies of Patankar and Schneider<sup>(1)</sup>. Ashby and Brown have estimated that the cluster of size less than 50 Å diameter are not visible. Assuming that vacancy clusters of this minimum size are responsible for the mottling, the number of vacancies produced by irradiation is about 10<sup>19</sup> per cc, a figure of the same order as the concentration of colour centres observed before<sup>(1)</sup>.

The electrons which are conventionally used for electron microscopy ( $\sim 100 \text{ keV}$ ) are not energetic enough to produce permanent displacement of atoms. However, there are other ways by which electrons can produce point defects and make them mobile. The point defects could have been produced by a mechanism similar to that of Varley<sup>(6)</sup> in which multiple ionization of Pb and I ions produce vacancies. The production of anion vacancy via excitanic state as suggested by Pooley<sup>(7)</sup> cannot be excluded at this stage. The clustering of these defects at liquid nitrogen temperature, however,



**F 1** 



Pig. 2

can take place through the migration stimulated by the radiation itself, as suggested by Nelson<sup>(8)</sup>. This would be equally true in the case of  $\gamma$  -irradiated samples since the  $\delta$ -rays produced in the process of primary ionization in the crystal should behave similar to the energetic electron beam of the microscope.

# CONCLUSION:

We have shown that in the crystals of lead iodide which are irradiated by electrons or gamma rays at liquid nitrogen temperature, point defects are produced. Under the influence of the radiation they migrate and form clusters which are responsible for extensive strains observed in the crystal after irradiation.

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## DISCUSSION:

A.R. Patel : 1. Is the contrast not produced by the microstructures on the orystal surface?

2. How do you avoid the effect of irradiation during the examination?

A.V. Patankar : 1. The contrast we are referring to is that produced by structures of the size of a few hundred angstrom units, in depth and spread. It is always possible to see microstructure like steps on the surface by this method.

2. This is answered in the script.

## ION INDUCED DAMAGES IN A SILVER MONOCRYSTAL

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#### INTRODUCTION:

In the present work, we shall report the experimental arrangements for studying the sputtered atoms, some resultson the experiments with ions of Kr, Zn and Cd in the energy range 5 - 10 KeV on a silver monocrystal having its 110 plane parallel to its surface with a discussion on the dynamic damages in a crystal induced by fast ions.

## EXPERIMENTAL RESULTS:

The experimental arrangement consists of a magnetic oscillation type ionsource, a collision chamber evacuated to better than  $10^{-5}$  mm. Hg with a diffusion pump and a liquid exygen trap. The target assembly consisting of the silver monocrystal and a hemispherical cup for collecting the deposition of silver atoms are shown in Fig. 1. The target can be rotated at an angle with a wilson seal and the angle of rotation can be measured from the graduated scale. The sputtering yield S, for silver is given by

$$S = 0.873 \text{ x} \frac{\text{Pmgm}}{\text{Q}_{\text{cow}}}$$

where S is the yield of silver atoms per each incident ion, Pmgm is the increase in weight, in mgm, of the collector, Q is the quantity of charge in coulomb on the silver target. Q was directly measured with a current integrator. The increase in weight of the collector in mgm, was measured with a semi-microbalance and tracer method. The silver monocrystal was irradiated in the Harwell reactor to produce Ag-110 isotope. The radioactive sputtered atoms were counted with a scintillation counter and the loss in weight was weighed in a semi-microbalance. At 5 KeV the value of P in mgm was calibrated for the amount of radioactivity. P in different cases was determined by the amount of radioactivity of deposited atoms standardised with the increase of weight of the collector due to sputtered atoms at 5 KeV ionenergy measured by a semi-microbalance.

### RESULTS AND DISCUSSIONS:

The results show that the value of S in Ag (110) for a certain E is less than that in a silver polycrystal and there are definite minima at different axial directions (Fig. 3). These results suggested that there is the influence of channeling in the transparent directions of the lattice, which gives minimum sputtering yield and in polycrystals, no influence of channeling is responsible for higher value of S. It is not unlikely that certain single crystal face with less transparency may produce the yield S higher than the polycrystal, depending upon the randomness







of the orientation of the latter. In Fig. 4, the theoretical arve is plotted in a model which assumes that the incident beam is devided into two parts, one aligned with an open channel of the crystal without sputtering and another part causes sputtering equivalent to sputtering in apolycrystal. According to Onderlinden<sup>(4)</sup> we may write  $S_{jkl}(E) = \epsilon_{nkl}$ .  $f_{nkl} \cdot S_{poly}(E)$ , where E is the energy of the incident ions, poly (E) is the probability<sup>(6)</sup> that the incident ion enters the beam, responsible for sputtering and  $\epsilon_{nkl}$  is the efficiency factor. Average  $\epsilon_{110}$  for Ag (110) Kr was taken equal to 1.08  $f_{nkl}^{(7)}$ is calculated from Lindhard's theory<sup>(3)</sup>:

$$f_{hkl}(E) = n \pi a_0 (9 \pi \frac{2}{128})^{\frac{1}{2}} \left[ \frac{3Z_1 Z_2 e^2 d^2}{(Z_1^{2/3} + Z_2^{2/3})E} \right]^{\frac{1}{2}}$$

where  $Z_1$  and  $Z_2$  are the atomic numbers of the ions and the lattice atoms,  $a_0$ ; the Bohr radius, e, electronic charge, n, number density of target atoms, d is the interatomic spacing in the parallel rows to the channel.  $S_{110}(E)$  is compared with the experimental resultsof Kr on Ag (110). The agreement is fair to support the focussed collision sequences<sup>(1,2)</sup> and channelling<sup>(3)</sup> of f ast ions in a single crystal. The autoradiograph shows the prominence of the spots other than 10 due to assisted focussing<sup>(5)</sup> of ions by the neighbouring axes at increased energy.

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## RADIATION DAMAGE IN CALCITE SINGLE CRYSTALS

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#### INTRODUCTION :

Several investigators have studied the effect of neutron bombardment on various single crystals. Chief amongst them are  $Chang^{(1)}$  on semiconductors, Gilman and Johnston<sup>(2)</sup> on LiF, and Berzina and Berman<sup>(3)</sup> on ionic crystals. The present paper describes the work undertaken with a view to investigate the nature of defects due to the effect of neutron bombardment in calcite crystals.

#### EXPERIMENTAL AND OBSERVATIONS :

Several matched pairs of natural calcite crystals were obtained by cleaving them and one part of each of them were irradiated with neutrons in swimming pool Apsara Reactor at Trombay, with doses of  $1.5 \times 10^9$ .,  $4.3 \times 10^{10}$ .,  $4.2 \times 10^{11}$ .,  $3.8 \times 10^{12}$  and  $3.8 \times 10^{13}$  n/cm<sup>2</sup>. The etching behaviour of the irradiated and nonirradiated counterparts was compared by simultaneously etching them in 20% NH Cl solution at room temperature for five minutes. This process was repeated with all the matched pairs, irradiated with diffent doses. Thus, Figs. 1(a) and 1(b) (X 100) show the typical etch patterns produced on the non-irradiated and irradiated cleavage faces respectively, irradiated with a neutron dose of  $3.6 \times 10^{13}$  n/cm<sup>2</sup>. It is observed that (1) The shape and orientation of the etch pits produced on both the cleavages are the same. (ii) Some pits which are shallower compared to the rest of them on the irradiated face have no corresponding pit on its counterpart. (iii) Clusters and pairs of the etch pits are also observed on the irradiated cleavages. (iv) The density of the etch pits on the irradiated cleavages is comparatively larger.

The matched pairs were etched simultaneously and successively for 2 min., 4 min., and 6 min. The sizes and the depths of the pits in all the three stages of etch were measured and their rates both in extension and in depth were measured as shown in Table I. It is clearly seen from the table that (i) the etch rate both in extension and in depth is more on irradiated cleavages than that on the non-irradiated counterpart. (ii) The rate of growth of pits in extension as well as in depth increases with increase with increase in the intensity of the neutron dose, to which they are exposed. (iii) The increase in the rate is greater along extension than along the depth.

The irradiated crystals were cleaved into five thinner flakes and their thickness were measured. These plates were simultaneously etched successively for three different periods and the etch rates on them, both in extension and in depth were obtained. The observations made on etch rates are shown graphically in Figs. 2 and

× 100 DESAL az C t Cb) PATEL BE 2 17 x 100 ø (H Fix. 1 cas D ø 同 U B J Ũ R C 00 D D n O

PLATE : I

-403-



3. It is seen from Figs. 2 and 3 that the etch rate both in extension and in depth increases as one moves within the body of the crystal, becomes maximum at the centre and then again decreases. The rate of increase in the sizes and depths of the pits increases with increase in the dose of neutrons.

# MEASUREMENTS OF MICROHARDNESS :

The Vicker's hardness mimetals of the irradiated and the non-irradiated clease vages were measured by using Vicker's microhardness indentor and are shown in Table I. It is seen that the hardness increases with increase in the irradiation dose. DISCUSSION :

It is conjectured that some imperfections are introduced due to irradiation. They may be irradiation induced defect clusters or dislocation lines. These imperfections will produce strain in the crystal lattice and consequently will be preferentially etched. These effects will give rise to isolated pits which would not have any correlation of the matched faces, as observed. The strain produced in the crystal lattice may be responsible for fast rate of irradiation.

During irradiation, the crystals might have been heated and when the neutron bombardments are stopped, they are suddenly cooled. Cooling will start from the outer surface and will proceed inward. This might create more strain in the inner surfaces than on the outer ones. This will give rise to faster rate of etching on the inner faces compared to outer ones as observed. The increase in the microhardness of the irradiated crystal may be due to the strain produced in the lattice which will hinder the motion of dislocations and this will give rise to more hardness.

| Obs .<br>No | Particulars                         | Stch<br>rate of<br>size in<br>(M/min. | Rate of<br>Depth in<br>///mm | Vicker's<br>Hardness<br>Numerals in<br>Kg/mm <sup>2</sup> . |
|-------------|-------------------------------------|---------------------------------------|------------------------------|---|
| 1.          | Non-Irradiated Crystal              | 0.62                                  | 0.20                         | 48.54   |
| 2.          | Irradiated Crystal                  |                                       | • • •                        |   |
| н<br>23     | $1.5 \times 10^9 \text{ n/cm}^2$    | 1.40                                  | 0.50                         | 80.69   |
| 3.          | $4.3 \times 10^{10} \text{ n/cm}^2$ | 1.70                                  | / <b>0.81</b>                | 143.12  |
| 4.          | $4.2 \times 10^{11} \text{ m/cm}^2$ | 2.06                                  | 1.12                         | 256.14  |
| 5.          | $3.8 \times 10^{12} \text{ n/cm}^2$ | 2.30                                  | 1.31                         | 270.08  |
| б.          | $3.6 \times 10^{13} \text{ n/cm}^2$ | 2.82                                  | 1.43                         | 310 <b>.3</b> 0   |

TABLE I

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# DISCUSSION:

S. Keerti :

: 1. Is there any variation in the density of dislocation etch pits after irradiating the crystals?

2. If there is any increase in micro hardness of the crystals then what effect will it have on the density of etch pits?

A.R. Patel :

1. There is an increase in the density of etch pits on the irradiated cleavages.

2. The increase in the hardness may be due to the lattice distortion produced in the crystal lattice.

# "COOLED ELECTRONS" IN SEMICONDUCTORS

#### P. Singh

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. Recently Paranjape et al (1,2) have suggested that in semiconductors (polar) the electron temperature may decrease below the lattice temperature by the application of electric field, i.e., the situation leading to  $T \langle T_0$  are the electron temperatures with field (small) and with the zero field. More recently Elotekjaer<sup>(3)</sup> has extended their theory to arbitrarily large field strength. These quthors have neglected the effect of impurity (ionic) scattering. Firstly the electron concentration will be decided by the impurities in the crystal and secondly the impurities offer an additional relaxation mechanism through the process of electron-scattering by them. Therefore the effect of impurity scattering should also be taken into consideration. This present communication consideres this effect of impurity scattering on electron temperature.

In the presence of electric field and for sufficiently large electron density  $\mathcal{N}$ , the momentum distribution of electrons in semiconductors is given by<sup>(4)</sup>

$$f(\underline{p}) = a \exp \left\{ -\frac{(\underline{p} - \underline{p}_0)^2}{2mkT} \right\}$$

$$\left\{ f(\underline{p}) d^3 \underline{p} = n \right\}$$

where the symbols have their usual meaning. The electron momentum distribution f(p) is assumed to satisfy the Boltzmann Transport Eq.

$$\frac{df(\underline{p})}{dt} = \left(\frac{\partial f}{\partial t}\right)_{\mathbf{F}} + \left(\frac{\partial f}{\partial t}\right)_{\mathbf{1}} + \left(\frac{\partial f}{\partial t}\right)_{\mathbf{e},\mathbf{e}} + \left(\frac{\partial f}{\partial t}\right)_{\mathbf{i}} \dots (2)$$

•(1)

where the terms on the right of Eq.(2) denote the rates of change of f(p) due to electric field F. lattice scattering, electron-electron interaction and impurity scattering respectively.

Following<sup>(4)</sup> and remembering that electron-electron interaction conserve both energy and momentum, we can easily write.

$$\frac{eFnP_{o}}{m} = - \left\{ \left[ \left( \frac{\partial f}{\partial t} \right)_{1} + \left( \frac{\partial f}{\partial t} \right)_{1} \right] E(\underline{p}) d^{3}\underline{p} \qquad \dots \dots (3) \\ eFn = - \left\{ \left[ \left( \frac{\partial f}{\partial t} \right)_{1} + \left( \frac{\partial f}{\partial t} \right)_{1} \right] p_{z} d^{3}p \qquad \dots \dots (4) \right\}$$

To calculate  $\left(\begin{array}{c} \partial f \\ \partial t \end{array}\right)_1$  and  $\left(\begin{array}{c} \partial f \\ \partial t \end{array}\right)_1$  a simple method has been followed and the validity of  $p_0^2/2mkT \ll 1$  has been assumed.

# Optical Polar Scattering.

Following Frohlich and Paranjape (4) we write

$$B(\underline{q}) = \frac{2 7 (e^2 \pi^3 \omega(\underline{q}))}{v_q^2} (\frac{1}{\epsilon_{bb}} - \frac{1}{\epsilon_{s}})$$

Where  $\epsilon_{\infty}$  and  $\epsilon_{s}$  are respectively the high frequency and static dielectric constants.  $\star \omega(\underline{q})$  is the energy associated with the phonon with wave vector q.

A simple calculation results in

$$\frac{eFnp_{o}}{m} = 2^{3/2} \sqrt{\pi} \sqrt{\frac{kT_{o}}{m}} \left(\frac{\hbar \omega}{kT_{o}}\right)^{2} J_{o} nq \left(\frac{\Lambda T}{T_{o}} + \frac{p_{o}^{2}}{2mkT_{o}}\right), \dots, (5)$$

$$eFn = \frac{enp_{o}}{m} \left[\frac{1}{\mu_{o}} + \frac{1}{\mu_{1}}\right] \dots, \dots, (6)$$

$$hq = \left[ \exp\left( \frac{h\omega}{kT_{o}} \right) - 1 \right]^{-1}$$

where

$$eF_{o} = \frac{me^{2}\omega}{\hbar} \left(\frac{1}{\epsilon_{\omega}} - \frac{1}{\epsilon_{\beta}}\right)$$

$$J_{o} = \int_{0}^{\infty} \left[ e^{-x} \ln \left\{ \frac{\sqrt{x + \hbar\omega/kT_{o}} + \sqrt{x}}{\sqrt{x + \hbar\omega/kT_{o}} - \sqrt{x}} \right\} \right] dx$$

and

 $\mu_i$  and  $\mu_i$  are respectively the optical polar and impurity mobilities.

$$\mu_{1} = \frac{3}{2\sqrt{2\pi}} \left(\frac{kT_{0}}{n_{1}}\right)^{3/2} m^{-1/2} \epsilon^{2} \frac{e^{-3}}{N_{m}} \dots \dots (7)$$

where the different symbols have their usual meaning.

From (5), (6) and (7) one can obtain for  $\Delta T = T-T_0$  to be negative.

$$\left(\frac{\hbar\omega}{kT_{0}}\right)^{2} \frac{J_{0}}{4I_{e}} > 1 + \frac{\mu_{0}}{\mu I} \qquad (8)$$
Here  $I_{0} = \int_{0}^{\infty} \left\{ e^{-x} + \frac{1}{x} + \frac{1}{2} \sqrt{x + \hbar\omega} \int_{kT_{0}}^{\infty} \right\} dx$ 

In the absence of impurity scattering, (  $\mu_1 = \frac{e^2}{m} \rightarrow \infty$  ) the above condition (8) reduces to

$$\left(\frac{-\hbar\omega}{kT_{o}}\right)^{2}$$
  $\frac{J_{o}}{4I_{o}}$  >

which is exactly the inequality established by the authors of (1,2)

The inequality (8) is an indicative of the fact that the impurity scattering should be small if the condition for electron cooling is to hold.

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TIME DEPENDENCE OF ULTIMATE STRENGTH OF ALKALI HALIDE CRYSTALS UNDER STATIC LOAD

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Present day technological applications are putting everincreasing demand on the strength of materials. Static 'Stress-Strain' curves of most materials under tensile stress exhibt a marked maximum value of stress which the material can sustain; this value of stress is designated as 'Ultimate Tensile Strength' or 'Breaking Strength in Tension'. However, experiments show that materials can break under static stress smaller than the 'U.T.S.', if the load is applied for a finite duration of time. In such a case the 'U.T.S' as defined above loses its significance and assumes a new meaning due to its dependence on the time of endurance of stress by a material. In literature there is evidence of experiments establishing the correlation between the time of endurance and the applied stress for plastic materials  $\binom{(1,2)}{}$ , synthetic fibers  $\binom{(3,4)}{}$ , polycrystalline metals  $\binom{(5,6)}{}$  and polymers  $\binom{(7)}{}$ .

Studies by S.N. Zhurkow<sup>(5)</sup> and co-workers<sup>(6,7)</sup> have shown that for pdycrystalline metals and polymers the endurance time 7 under static tensile stress  $5^{-}$  is given by an equation of the type.

$$T = T_0 \exp\left(\frac{20 - r\sigma}{kT}\right)$$

Where

k = Boltzmann Constant, T = Absolute Temperature, U = Activation Energy, c<sup>-</sup> = Stress, r = Structure Factor, 7 = a constant.

and

The activation energy  $U_0$  calculated by the above relation was found to be of the order of the binding energy of the material. The structure factor r was found to depend on grain-size, heat treatment and previous physical state of the material.

There is no evidence in literature about extending the above study to single orystals. The present investigation has been undertaken to find a correlation between endurance time T and static stress  $\sigma^{-}$  for alkali halide single crystals.

Potassium chloride single crystals were grown from the melt by the Kyropoulos method with different pulling rates and rates of rotation of the seed crystals. The cylindrical single crystals so grown were cleaved into thin circular discs from which specimens of size 2mm x 3mm x 8mm were further cleaved from symmetrical positronshaving identical growth conditions as indicated in Fig. 1., by A, B, C, D and  $A^*$ , B', C', D'. This was done to ensure the same value of "r" for all specimens



under investigation. The dislocation density determined by etch-pit technique was found to be the same for all such specimens; static indentation tests by Vicker's Pyramidal indenter indicated that the specimens were of the same hardness.

A simple apparatus (Fig. 2) was fabricated to study the specimens in tension under constant static load and to record the endurance time automatically. It was possible to study the internal stresses in the specimen by placing it between crossed nicols during the experiment. To avoid unwanted grip-effects <sup>(8)</sup> the specimens were fixed by an adhesive to special holders (Fig. 3) . With the help of specially made jigs the stress direction was kept perpendicular to the (100) faces of the specimens during the investigation.

Table I gives the stress-endurance time for a typical set of specimens and the values of structure factor and activation energy  $U_0$  calculated therefrom. In these investigations the variations of the endurance time is of theorder of 10<sup>6</sup>. Graph 1 shows log  $\Upsilon$  vs  $\sigma$  plotted on semi-logarithmic co-ordinates. All the specimens are found to fracture along (100) cleavages planes. On examination by a Rejchert metallur-gical microscope by reflected light bright field illumination typical crack pattern as in Plate 1 was revealed. The cracks diverge from the focal point P (Plate 1) covering the whole surface. The familiar 'River Pattern<sup>(14)</sup>' is also seen at the point R at some distance from P giving evidence of advancing crack front getting jogged abd creating steps which when coalesced give rise to this pattern. The dislocation content and configuration on such a surface is revaled by etch-pit technique (Plate 2). Dislocation density is maximum at the focal point P but decreases markedly at a little distance from it.

Potassium chloride crystal slips on (110) planes in [110] directions. This makes available a set of mutually perpendicular interesting active slip planes and slip directions. Under observation between crossed nicols the (110) planes are found to be regions of high stress. The point of intersection of such planes is found to have maximum stress concentration similar to that reported for MgO crystals<sup>(9)</sup> having similar slip systems. Straight line graph between log T and  $\sigma$  indicates that in tension under static load Potassium chloride single crystals obey Zhurkov's relation for endurance time and applied stress; this also indicates that all the specimens under investigation have the same value of structure factor "r" which is proportional to the tangent of inclination of the straight line plot.

The cracks originate from a single point and the dislocation density as revealed by etch-pits is maximum in the vicinity of the point. This suggests that plastic deformation results in the multiplication of dislocations at such a point during the course of endurance of stress. This high dislocation density coupled with suitable dislocation configuration can lead to the deformation of a micro-crack as a result of local failure. Models for crack nucleation in (100) planes have been suggested by Cotterell<sup>(10)</sup> and Washburn and Gorum<sup>(11)</sup> (Fig. 4). Experiments by Washburn and Gorum and by Stokes, Li and Johnston<sup>(12)</sup> on magnesium oxide crystals clearly indicate that cracks nucleate at the intersection of slip bands. Washburn and Gorum mecha-


Plate 1



Plate 2

nion which favours the formation of cracks at the external surface indeed appears to hold good for the fractures observed in the present investigation. Once a micro-crack is thus formed it can propagate under Griffith's criterion<sup>(13)</sup> and might lead to fracturesobserved in potassium chloride single crystals.

| TA | BI | E | I | • |
|----|----|---|---|---|
|    |    |   |   |   |

| No. | Stress<br>(Kg/mm <sup>2</sup> ) | Endurance<br>Time (Secs) | Structure<br>Factor (mm <sup>3</sup> ) | Activation<br>Energy (K.Cals)          |
|-----|---------------------------------|--------------------------|--|--|
| 1.  | 0.234                           | 1.0                      |  | یے بیٹ ہے <u>سے میں میں مرکب میں م</u> |
| 2.  | 0.219                           | 4.0                      | •                                      |  |
| 3.  | 0.226                           | 11.0                     | •                                      |  |
| 4.  | 0.210                           | 320.0                    | $1.1 \times 10^{-13}$                  | 70                                     |
| 5.  | 0.200                           | 600.0                    |  |  |
| 6.  | 0.183                           | 80620.0                  |  | •                                      |
| 7.  | 0.164                           | 1114220.0                | 1                                      |  |

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EFFECT OF GROWTH CONDITIONS ON THE DISLOCATION DISTRIBUTION IN ALKALI HALIDE SINGLE CRYSTALS GROWN FROM THE MELT

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Alkali halide single crystals are generally grown from the melt for solid state studies. Though great care is taken to minimize imperfections in them during growth, there is no evidence in literature to suggest any correlation between the conditions of growth and their state of perfection. The present paper reports some of the results of such an investigation.

The Kyropoulos method was chosen because recent investigations<sup>(1)</sup> have shown that alkali halide single crystals grown by this method are better than those grown by other methods. The growth unit used has provision for pulling as well as rotating the growing crystal with various speeds.

Dislocation density  $\rho$  throughout the volume of the crystals was determined by the chemical etch method. Small blocks from different regions of the crystal were obtained by cleaving them and then these blocks were etched to determine the dislocation density in them. The etchant used was that developed by the first named author. The variation of  $\rho$  parallel and perpendicular to the axis of the crystal, was obtained.

The growth conditions reported in this paper are (a) the state of perfection of the seed crystal, (b) the rate of cooling of the seed crystal, (c) the rate of pulling and (d) the rate of rotation of the growing crystal. The grown crystals were cooled in the furnace used for growing them, at slow rate of  $10^{\circ}$ C or less per hour. The results reported herein are for potassium chloride single crystals.

Preliminary investigations revealed that the low and practically constant dislocation density region if KCl crystals was confined to the lower half of the crystal when grown from the melt (Fig.2). Crystals of size 4mm x 4mm x 10mm, were carefully cleaved from such a region of a good crystal. These blocks were annealed at 600 °C for 14 hours and were used as seeds. Table 1 gives the dislocation denaity of these seeds. Crystals grown from these seeds were snapped off the seeds at their planes of contact and dislocation density was determined in these planes. Table 1 shows that this dislocation density increases during growth; further, this increase in  $\beta$  is only slightly affected by the rate of water flow. Increase in  $\beta$  is much less when the seed is not water-cooled and is instead held by copper or iron rods. This increase in  $\beta$  can be attributed to a thermal shock which a

water-cooled seed receives when diped in the melt. Alkali halide crystals being poor conductors develop very large thermal gradients with a temperature of about



F/G. 1



 $800^{\circ}$ C at one end and  $50^{\circ}$ C at the other. These gradients being non-linear (2) give rise to a high density of dislocations (3, 4), which explains the observed increase in f during growth. With copper and iron seed holders, the rate of extraction of heat is much slower than with water cooling and therefore the temperature gradient along the length of the seed is less. This results in a smaller increase of f.

Near the seed end of the crystel  $\rho$  falls as we move from the axis to the perimeter; this decrease of  $\rho$  becomes less rapid with increasing water flow. Radial dislocation density gradient in the cross section near the seed end decreases with increasing rate of water flow as shown in Fig. 1. These results may be explained in the following way: With increasing water-flow the radial thermal gradient increases and so does  $\rho$  along the radius, but below the seed  $\rho$  remains practically the same for all rates of flow (Table I); hence the radial dislocation density gradient decreases. It is also noted that along the axis  $\rho$  falls with distance from the seed; this fall is much more rapid when the seed is cooled (Fig. 2).

To study the effect of pulling rate on crystal imperfection, they were grown with different pulling rates without water-cooling the seeds. Dislocation density measured in the lower regions of these crystals was found to increase with the rate of pulling as shown in Fig. 3. Thos is because with quicker rate of pulling some atoms may not have time to take up correct positions resulting in a distorted lattice. From the point of view pf temperature gradients we notice that the quicker rate of pulling does not permit an immediate removal of the heat of solidification; therefore, the temperature gradient between the central and the peripheral portions of the crystallization front increases giving the front a non-planar shape. This results in plastic deformation thereby increasing dislocation density (5, 6).

| Dislocation De         | Rate of water flo      |            |  |
|------------------------|------------------------|------------|--|
| Before Growth          | After Growth           | (668/ ШП)  |  |
| 0.88 x 10 <sup>4</sup> | 4.12 x 10 <sup>5</sup> | 25         |  |
| $0.84 \times 10^4$     | 4.35 x 10 <sup>5</sup> | 50         |  |
| $0.80 \times 10^4$     | 4.62 x 10 <sup>5</sup> | 100        |  |
| $0.79 \times 10^4$     | 5.70 x 10 <sup>4</sup> | Copper rod |  |
| 0.81 x 10 <sup>4</sup> | 3.21 x 10 <sup>4</sup> | Iron rod   |  |

| TA | RLE | Ι |
|----|-----|---|
|    |     |   |



F1G.4.

To study the effect of rotation, crystals during growth were rotated with different speeds. It was observed that the radial dislocation density gradient in the cross-section near the seed end of the crystal increased non-linearly with the rate of rotation as shown in Fig. 4. This is understandable because faster rate of rotation causes a greater circulation of the melt thus reducing the radial thermal gradient; this in turn, decreases the radial dislocation density. Since  $\rho$  below the seed remains the same for all rotations, the radial dislocation density gradient increases with rotation.

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Spectroscopically pure cadmium has been used in the form of thin cylindrical wire of diameter 0.25 mm. Using the photographicmethod due to Mitra<sup>(1)</sup> the line profiles for 0002, 1010, 1011, 1012 and 1122 reflections only could be obtained with high precision. Backgrounds of these line profiles and determined by the method of Mitra and Misra<sup>(2)</sup>. For geometrical line profiles similar studies are carried out with the same sample annealed in vacuum at 100°C for three hours. Fourier coefficients for pure diffraction profiles are calculated by Stokes' Method<sup>(3)</sup>. Variances for observed and annealed line profiles are determined as a function of different ranges of the spread of theprofiles.

For hexagonal crystals reflections of type hkl with h-k=3t, t an integer, are unaffected by stacking and twinning faults. Table I shows that for cadmium, the particle sizes determined from the fault unaffected reflections 0002 and 1122 are 1100 and 515 A.U. respectively. Hence it may be concluded that there exists a real particle size anisotropy and the technique used by Mitra and Halder<sup>(4)</sup> for cobalt will no longer be applicable here. Hence for cadmium the apparent particle sizes have not been converted for fault broadening effects.

Since higher order reflections could not be obtained with high precision, the single reflection techniques for line shape analysis due to Pines<sup>(5)</sup> and Mitra and Misra<sup>(6)</sup> have been used. For Gaussian strain distribution, according to Pines<sup>(5)</sup>,

where  $A_{L}$  and  $A_{L}^{p}$  are nth order Fourier coefficients for pure and particle size line profiles,  $I_{L}$  = nd with

 $\frac{2d(\sin\theta_1 - \sin\theta_0)}{\lambda} \qquad \frac{2d(\sin\theta_0 - \sin\theta_2)}{2d(\sin\theta_0 - \sin\theta_2)} = \frac{1}{2}, \theta_0 \text{ is the Bragg}$ 

angle,  $2\theta_1$  and  $2\theta_2$  are the angles of diffraction corresponding to positions in the intensity distribution where the tails merge to the background,  $\lambda$  is the wavelength used and p is the particle size along the direction considered. Thus for Gaussian strain distribution the particle sizes are determined from the slopes of the  $A_T$  versus L Curves at L = 0.

It can be easily shown that for Gaussian strain distribution hypothesis,

 where s is the r.m.s. strain and 1 is the order of the reflection considering the reflection to be of the type OOL. If s depends on L, the plot In  $\frac{A_L}{A_L^P}$  against  $L^2$  will be a curve, the slope of which at L = o will determine s. For reflection of the type OOL, the crystallite can be treated as one dimensional with particle size line profile of the type  $\sin^2 N \phi / \sin^2 \phi$ , which can be expanded into a cosine Fourier series having coefficients N - n. If we set  $A_0 = 1$ , as is actually done, then

$$A_n = 1 - \frac{n}{N}$$
 and  $A_n^p = 1 - \frac{L}{p}$  .....(3)

Thus we can determine p and s by the equations (1), (2) and (3) on Gaussian strain distribution hypothesis.

For cauchy stmin hypothesis, the corresponding quantities are determined from the equations (8) and (12) of Mitra<sup>(7)</sup>.

Attributing the entire broadening to particle size and strain effects, W, the variance of a line profile in 2 is given by Wilson<sup>(8)</sup>. This is rearranged according to Mitra<sup>(9)</sup> as

$$\frac{\mathbb{W} \cos \theta}{\lambda \sigma} = \frac{1}{2 \pi^2 p} + \frac{n^2 \lambda}{\sigma \cos \theta} \cdot \frac{\langle e^2 \rangle}{a^2} \cdot \dots \cdot (4)$$

where  $p = \frac{t}{\lambda}$  is the apparent particle size, t, the real particle size, K = 1,  $\frac{d}{n} = \frac{t}{2\sin\theta}$ , the angular range in 20, and  $\langle e^2 \rangle$  the variance of strain. As higher order relations are not available, the equation (6) has been used with n = 1. Particle sizes and strains are determined from intercepts and slopes respectively along different directions from

$$\frac{\mathbb{W} \operatorname{Cos} \Theta}{\sqrt{\sigma}} \quad \text{versus} \quad \frac{\lambda}{\sigma \operatorname{Cos} \Theta} \quad \text{curves}.$$

All the results are shown in Tabl I.

Table I shows that there exists a high particle size and strain anisotropy in cadmium. Particle sizes and strains in different directions determined by the line shape and variance analysis are not the same. This is notquite unexpected since these two methods measure two different quantities. While the line shape analysis gives the average thickness of the coherently diffracting columns of layers in the jkl directions, the variance analysis measures the cube root of the average particle volume. Besides, various assumptions involved in different cases is separating the particle size and strain effects are expected to influence their determination. That these physical quantities determined by the different methods are normally different has been already shown by Mitra and Mistra<sup>(10)</sup> theoretically. Therefore, the differences in the resultsby different methods always be expected , over an above that due to experimental error.

It is a deep pleasure to express gratitude to Prof. G.B. Mitra for suggesting the problem and helpful discussions.

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TABLE I

Particle Size (A<sup>O</sup>)

# Strain $(10^{-3})$

| Lines   | Line Shape Analysis |               | Variance    | Line Shape Analysis |        | Variance |        |
|---------|---------------------|---------------|-------------|---------------------|--------|----------|--------|
|         | Gaussian            | Cauchy        | Metnod      | Gaussian            | Cauchy | Method   | •<br>• |
| <u></u> | ······              | <del></del> . |             |                     |        |          |        |
| 0002    | 1100                | 1243          | 1490        | 10.40               | 11.40  | 3.85     |        |
| 1010    | 525                 | 830           | 478         | 28.10               | 30.70  | 2.50     |        |
| 1011    | 1950                | 2638          | 1677        | 10.50               | 11.50  | 3.61     |        |
| 1012    | 2015                | 3365          | 2447        | 17.20               | 18.80  | 3•57     |        |
| 1122    | 515                 | 635           | . <b></b> , | 22.30               | 24.40  |          |        |
|         |                     |               |             |                     |        |          |        |

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DISCUSSION:

K.S. Chandrasekaran

Do you have any measurements of reflections from the sam plane in different orders?

N.K. Misra

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No. Because in this case line profiles for higher order reflections from the same plane could not be obtained with high precision.

### DISLOCATION ETCH PITS IN SINGLE CRYSTALS OF KCL

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The method of selective chemical etching has been widely used in recent years for revealing the site of emergence of dislocations on the surface of crystals. The present work is confined to the choice of new etchants for the selective etching of potassium chloride single crystals and to the study of factors which influence: the etch pit formation in these crystals.

A number of reagents have been reported (1-4) which reveal dislocations in KCl crystals. Keerti and Dubov<sup>(5)</sup> reported the formation of sharply defined pyramical pits on (100) faces of single crystals by developing three different etchants. Etchant (1) is a saturated solution of PbSO<sub>4</sub> in methanol-butanol (3:1), etchant (2) is prepared by adding to a 3 ml saturated solution of Ba(OH)<sub>2</sub> in methanol-butanol (1:1), 20 drops of ethanol and 5 drops of glacial acetic and etchant (3) is prepared by adding to a 3 ml solution of hydrochloric-glacial acetic acid mixture (1:1), 2 drops of saturated solution of CdCl<sub>2</sub> in conc.HCl. The present investigation has been carried out with these etchants.

### EXPERIMENTS:

KCl crystals grown from the melt were obtained from the Solid State Laboratory, Lovov University, U.S.S.R. .The etching is done by immersing the crystal in the etchant and shaking it vigorously as described by Keerti and Dubov. Iso-butanol is used as a post-etching rinsing agent. This treatment produces pyramidal etch pits. The shape of these pits indicates the existance of screw and edge dislocations, as has been inferred by Gilman, Johnsotn and Sears (6). Fig. 1 (a,b and c) shows the etch pits obtained by etchant (1), (2) and (3). Fig. 2 (a) shows the etch pits obtained by vigorous shaking of the crystals for 10 sec. in etchant (2). All these pits have sharp contours. If etching is done without shaking the crystals, the pits show rounded corners (Fig. 2 b). In etchant (1) increased concentration of PbSO<sub>4</sub> in suspension, results in pits with rounded corners(Fig. 3). Acetic acid in etchant (2) increases the size and shape of the pits and also makes the pits better defined.

Tangential velocity of these etch pits is estimated by measuring the width of the etch pits formed by varying the time of etching. These observations are recorded in Graph (1). It has been noted that etchant (1) is slower to act as compared to etchant (2). Multiple etching is found to increase the size of the pits as shown in Graph (2).

To ascertain the role played by the impurity in the etching mechanism investigations were carried out by taking different impurities. Table I gives the etching behaviour of various impurities in the base-hydrochloric-glacial acetic acid (1/1)







Fig. 3. Etch pits by etchant (1) in 210 sec. 200 x.



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along with their cation radii and Table II gives the same for different alcohol bases.

## DISCUSSION:

Rozhanskii and Stepnova<sup>(7)</sup> found that good etch pits were obtained in NaCl crystals if the cation radii of the impurities had the same order as that of Na<sup>+</sup>. The cation radii of the impurities selected in the present investigations are of the same order as that of K<sup>+</sup> which has an ionic radius of 1.33 A<sup>o</sup>.

As seen from the tables, the cation of the impurity no doubt plays an important role in the formation of etch pits, but it is not found to be the dominant ingredient in the etching solutions as observed by Gilman, Johnston and Sears. Impurities AgBr and AgCl give good etch pits, but  $AgNO_3$  and AgI although have the same cation  $Ag^+$ , fail to give such good etch pits. Similarly etchant with  $Pb(CH_3COO)_2$  gives poor etch pits, where PbO as an impurity gives good etch pits. It is also noticed from the tables that  $Ba(OH)_2$  as an impurity gives good etch pits with alcohols but not with acids as base. CaCl<sub>2</sub> acts as a good impurity when used with acids but not so with alcohols.

It is thus seen from the behaviour of  $Ba(OH)_2$  and  $CdOl_2$  that the role of the cation is not entirely independent but depends on the nature and proportion of the base. These observations indicate that during etching the  $K^+$ , the impurity cation and base of the etchant are involved in a chemical reaction, the nature of which is under further investigation.

#### ACKNOWLEDGEMENTS

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| Impurity    | Cation Radius (8) | Etching Behaviour |  |
|-------------|-------------------|-------------------|--|
| å «Br       | 1.26              | Good              |  |
| ARNO-       | 1.26              | Poor              |  |
| AgC1        | 1.26              | Good              |  |
| AgI         | 1.26              | Foor              |  |
| BaSO.       | 1.29              | Fair              |  |
| Ba POA      | 1.29              | Good              |  |
| Ba B4 Öy    | 1.29              | Poor              |  |
| $Ba(OH)_2$  | 1.29              | Poor              |  |
| Pb(CH+COO)2 | 1.21              | Poor              |  |
| PbO         | 1.21              | Good              |  |
| Pb(NO3)2    | 1.21              | Poor              |  |
| *HgI2       | 1.1               | Fair              |  |
| *CaCl2      | 0+99              | Good              |  |
| *CdCl2      | 0.97              | Good              |  |

(The various impurities, about 1 gm, were added to 2 ml hydrochloric-acetic acid mixture and the supernatant is used for etching)

\* Two drops of its saturated solution in conc. HCL.

| TABLE I | 1 |  |
|---------|---|--|
|---------|---|--|

| 3 ml base<br>methanol:butanol                   | Impurity             | Cation<br>Radius (A) | Etching<br>Behaviour |
|---|----------------------|----------------------|----------------------|
| 1:1   | Bac12                | 1.29                 | Round pits           |
| 1:1 + 40 drops ethanol+<br>5 drops acetic acid  | Bac12                | 1.29                 | Small square pits.   |
| 1 #1  | Ba (OH)              | 1.29                 | No pite.             |
| 1:1 + 20 drops ethanol +<br>5 drops acetic acid | Ba (OH) <sub>2</sub> | 1.29                 | Good square pits.    |
| 1:1 + 20 drops ethanol                          | Ba(OH) <sub>2</sub>  | 1.29                 | Round pits.          |
| . 1:1   | BaBAO7               | 1.29                 | No pits.             |
| Methanol: ethanol<br>1:1                        | BaB407               | 1.29                 | No pits.             |
| 3:1   | PbSOA                | 1.21                 | Good square pits.    |
| methanol alone                                  | cdc12                | 0.99                 | No pits.             |
|   |                      |                      |                      |

ASSOCIATION OF POINT DEFFECTS IN NANO, CRYSTALS

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# ABSTRACT

From a study of ionic conductivity in NaNO<sub>3</sub> crystals, it was previously concluded that the predominant disorder of the system consists of Frenkel defects of positive ions and that the migration of interstitial sodium ions is responsible for electrical conduction. Interstitial defects in the structure-sensitive region are produced as charge compensators for divalent anionic impurities. The defects of added divalent cationic impurities on the electrical conductivity are discussed in terms of the association theorynof Lidiard. By comparing calculated and measured conductivity curves, a value of 0.5 eV is shown to be probable for the association energy of divalent cation impurity-sodium ion vancancy omplex. It is also suggested that the binding energy of the anionic impurity-sodium iominterstitial complex must be comparatively small.

## STUDIES ON THE PREPARATIONS AND PROPERTIES OF THALLOUS SULPHIDE CELLS.

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 $C_{ase}^{(1)}$  in 1917 first discovered the infrared detecting properties of thallous sulphide. During World War II, Cashman<sup>(2)</sup> developed the same as a sensitive infrared detector. So far the method of preparation of thallous sulphide cells was only by vacuum evaporation. We report herein a new method of depositing photoconductive thallous sulphide layers by the chemical method, along with a study of the characteristics of these cells thus prepared.

## EXPERIMENTAL RESULTS :

Aqueous solutions of a thallous salt and thiourea are mixed together in suitable proportions (if required together with dopants) and stirred thoroughly using a magnetic stirrer. A perspex holder to which are attached ground glass substrates of dimensions 1 c.m.  $x \ddagger c.m.$  is immersed in the solution being stirred. Then sodium hydroxide solution is added in suitable quantity from a from above and the stirring continued till a mirrory deposit of thallous sulphide is obtained on the ground glass substrates. Subsequently these plates are removed, washed with distilled water anddried for subsequent processing<sup>(3)</sup>. Good adherent layers of 4-5 thick were obtained.

For studying the photoconductivity spectrum, the Carl-Zeiss SFM Monochromator with a lithium fluoride prism was used. The circuit employed for measuring photoresponse consists of a load resistor of about 1/2 megohm in series with thallous sulphide cell and a voltage of 40 volts is applied across the cell and the resistor. The drop across the load resistor has been measured using a Fhilips GM 6020 VTVM. The sensitivity  $S \neq E \times \Delta V / [V_1 \times (E-V_2)]$ , where E is the applied bias,  $V_1$  is the voltage drop across the load when the cell is in darkness,  $V_2$  is the voltage drop across the same resistor after illumination of the photo cell. V is the actual signal measured in the VTVM. The source of illumination was a 60 watt bulb at a colour temperature of about 2800°K. The response time was measured using a Dumont No. 304-A Oscillograph.

#### RESULTS AND DISCUSSION :

The freshly deposited films of thallous sulphide by our method of chemical deposition are of p-type and they have resistance values around 1.5 megohms (for 2 mm electrode spacing). Silver paste gave good ohmic contacts.

The freshly deposited layers of thallous sulphide has a photoconductivity spectrum which shows that the range of sensitivity is seen to be lying between 0.45 micron and 1.3 microns with a peak at 1.05 microns. These findings agree with a peak at 1.05 microns. These findings agree with the data reported in the literature. The reported value of the ground band gap for vacuum evaporated thallous sulphide cells is 1.2 e.v. and that obtained by us corresponds to 1.e.v.

We tried heat treatment of the deposited layers of thallous sulphide (1) in air at two different pressures, (2) in oxygen and (3) in sulpher vapour at a temperature ranging from 200-250°C. The plates were heated for a time ranging from 10-15 minutes in these atmospheres. The results obtained are presented in Table I. Heating the plates in air at atmospheric pressure increases both the dark resistance as well as the photosensitivity enormously. It is interesting to report that in the air-heated plates, there is a characteristic change of colour to blue-grey, which can be reproduced and highest sensitivity is associated with the appearance of this colour. Cashman (Loc. cit) reports attainment of highest sensitivities keeping the resistance of the plates as low as possible. For this, the pressure at which the heat treatment requires to be done is rather critical and a few experiments done by us indicated beneficial results at a very low pressure of air. Further experiments are being pursued in this direction .

| Atmosphere | Pr.     | Temp.              | Dark<br>Resistance | Sensitivity |
|------------|---------|--------------------|--------------------|-------------|
| Pure Cell  |         |                    | 5                  | 1.5         |
| Air        | Atm     | 500 oc             | 8                  | 2.2         |
| Air        | Atm     | 220°C              | 10                 | 3.0         |
| Air        | Atm     | 250°C,             | 2000               | 270.0       |
| Air        | 20 torr | 250 <sup>0</sup> 0 | 5                  | 2.0         |
| Sulphur    | Atm     | 240 <sup>0</sup> C | 2.5                | 2.0         |
| Oxygen     | Atm     | 250 <sup>0</sup> 0 | 5                  | 1.5         |
|            | · .     |                    |                    |             |

TABLE I

Effect of doping is shown in table II.

### TABLE II

| Dopant                          | Dark Resistance | Photo Sensitivity |
|---------------------------------|-----------------|-------------------|
| Cs <sup>+</sup>                 | 200             | 0.5               |
| Cu <sup>+</sup>                 | 100             | 0.1               |
| C1 <sup>-</sup>                 | 40              | 1.0               |
| 17                              | 200             | 2.0               |
| (P0 <sub>4</sub> ) <sup>3</sup> | 2               | 1.5               |
| Pure Tl <sub>o</sub> S Cell     | 2               | 1.5               |

Effect of Dopents (T12S Cells)

In general in no case any beneficial effect has been observed. Photosensitivity has been obtained for 5000 lux at a colour temperature of about  $2800^{\circ}$ K.

The variation of photocurrent with the light intensity is found to be sublinear.

All thallous sulphide cell is very succeptible to conditions of humidity in the atmosphere. Unprotected cells run down in sensitivity. Hence we have found that with suitable optical plastics applied on top the sensitivity can be maintained for long.

The response time is found to be of the order of 600 microseconds.

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#### THERMOELECTRIC POWER OF THALLIUM SELENIDE

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### INTRODUCTION:

Thallium selenide (TISe) belongs to  $A^{III} B^{VI}$  group of semiconductors. These compounds are of great interest because of their possible photoconductive applications. Some studies of this compound have been reported earlier by several workers (1-4). The results of measurements of thermoelectric power are presented here.

#### EXPERIMENTAL DETAILS:

The compound thallium selenide is prepared by sunthesis of spectroscopically pure thallium and selenium. Crystal growth is achieved by Bridgman technique. Crystals obtained in this way have been found to have resistivity of about 1 ohm-cm at room temperature. High resistivity crystals are obtained by subsequent zone refining. All samples showed p-type conductivity. Thermoelectric e.m.f. is measured in the temperature range between 100°K and 540°K. All e.m.f.'s are measured with a precision potentiometer.

### RESULTS AND DISCUSSION:

The variation of thermoelectric power  $(\mathbf{X})$  with temperature is shown in Fig. 1. All the samples have a positive thermoelectric power in the entire temperature range investigated. Curves 1-4 correspond to samples with room temperature resistivities of about 1.2, 2.7, 6.6 and 53 ohm-cm respectively. Sample corresponding to curve 1 is obtained by Bridgman technique and 2 and 4 are obtained by zone refining of first sample while sample corresponding to curve 3 is obtained by annealing of the first sample at 250°C for 36 hours followed by slow cooling to room temperature. For this particular sample, a hump in the curve is observed at a temperature near about 270°K. In general, thermoelectric power is found to increase with decrease in carrier concentration.

The thermoelectric power data can be used to estimate effective carrier mass, temperature variation of energy gap and carrier mobility ratio. For a simple one carrier model, the thermoelectric power is given by  $\binom{5}{5}$ 

where n is the carrier concentration and  $m^*$  the effective mass of the carrier. The sign of  $\alpha$  depends on the sign of the carrier. The carrier concentration can be determined from the measurement of Hall coefficient R, using the relation

> <u>\_3π</u> 8e<sup>B</sup>

.....(2)



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In the intrinsic range, the thermoelectric power is given by

where  $E_{go}$  is the energy gap at absolute zero,  $\beta$  the temperature coefficient of energy gap and b the electron to hole mobility ratio. Equation (3) predicts that a plot of thermoelectric power as a function of the reciprocal of the temperature, in the intrinsic range, should be a straight line with parameters determined by  $E_{go}$ ,  $\beta$  and b.

Effective mass of holes in the extrinsic range is calculated using the measured values of thermoelectric power, using equations (1) and (2). It is found that effective mass increases with extrinsic carrier concentration and remains nearly constant in the extrinsic range for a given sample. It is interesting to note that dependence of  $m_p^*$  with concentration almost ceases with with concentration less than 10<sup>16</sup> cm<sup>-3</sup> as in the case of samples 3 and 4 for which carrier concentrations are 1.6 x 10<sup>16</sup> and 1.4 x 10<sup>15</sup> cm<sup>-3</sup> respectively. The average effective hole mass calculated for samples 3 and 4 is 0.045m and effective mass of electrons calculated from the recelectric power in the intrinsic range is 0.011m. These values are smaller than those reported by Gaseinov et al<sup>(3)</sup>.

1 The temperature coefficient of energy gap estimated from extrapolation of thermoelectric power in theintrinsic range to 1/T = 0 is  $\beta = -1.09 \times 10^{-4}$  eV/°K. The ratio of electron to hole mobility, obtained from slope of the intrinsic thermoelectric power curve is 0.383 which is in good agreement with that obtained from conductivity plot<sup>(4)</sup>. This shows that  $\mu_p > \mu_n$  which partly accounts for the positive thermoelectric power observed in all samples.

 $\label{eq:Fritzsche} {}^{(6)} \ \text{has suggested that the p-type behaviour observed in crystals like} tellurium results from the production of additional holes produced by thermal lattice defects acting as electron traps. The density N_D of thermal lattice defects is assumed to be given by$ 

 $N_{\rm D} = N_{\rm L} \, a \, \exp \, (-E/2kT)$  .....(4)

where  $N_L$  is the density of lattice sites and a depends on the ratio  $N_D/N_L$  and E is defect activation energy. This shows that at high temperatures  $N_D$  should be dominant source of carriers and the graph of log  $\sigma$  vs T should exhibit a slope proportional to E. Since this is not observed in our samples this theory is untenable. Moreover, our measurement of thermal conductivity<sup>(7)</sup> showed that defects in our crystals are negligible. However, higher hole mobility may be explained on the basis of dual valence band theory.

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#### DISLOCATIONS IN NATURAL DIAMONDS

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## INTRODUCTION :

Number of investigators have reported the etch patterns produced by the conventional method of etching on diamond, i.e., by heating them in an oxidising melt at a required temperature. Chief among them are Omar et al<sup>(1)</sup>, Pandya and Tolansky<sup>(2)</sup>, Patel and Tolansky<sup>(3)</sup>, Omar and Kenawi<sup>(4)</sup> and Patel and Remanathan<sup>(5)</sup>.

We have developed in this laboratory, a new method for etching dislocations in natural diamonds. By this method appreciable amount of etching is produced within a second and the etch patterns are comparatively better for studying the content and nature of dislocations as compared to the conventional method of etching in the melt of  $KNO_x$ .

#### EXPERIMENTAL :

The diamonds to be etched were kept in a hole drilled in the lower electrode of a barbon arc, the surface to be etched facing the other electrode and the arc was struck. The surfaces were thus heated, to any desired temperature and a drop of distilled water or a solution of sodium nitrate in water was dropped on them. This produced etching. The crystal surfaces were then cleaned and optically examined.

#### OBSERVATIONS AND RESULTS :

Thus Fig. 1 (X 350) shows the etch pattern produced on natural (111) face of a diamond etched by the conventional method in the melt of  $KNO_3$  at 540°C while Fig. 2 (X 350) is the etch pattern produced on a similar face of another crystal by the new method within one second. That the patterns in Fig. 2 is decided by better than that shown in Fig. 1 can be easily distinguished.

The density of etch pits indicate the density of dislocations threading through the surface. In order to find how the density of dislocations change within the body of the crystal, the same face was successively etched some seven times thus removing a layer of appreciable thickness every time so that new (111) faces were exposed to the etchant every time. The etch patterns were photographed and were studied critically. Thus Figs. 3(a) and 3(b) (X 350) show the typical etch patterns produced on the face at some two different times. It was noted that :

1. The density of etch pits considerably changed in the beginning and then approximately remained constant.



- 2. The etch pattern at any stage of etching consisted of point bottomed as well as flat bottomed pits of different sizes.
- 3. Point bottomed pits on successive etching changed to flat bottomed pits and ultimately were found to be completely washed out and at each stage of etching some new pits were found to be mucleated.

Now according to the dislocation theory no dislocation can terminate within the body of the crystal. How then (1) the point bottomed pits convert themselves into flat bottomed pits and (ii) new pits nucleate on the new (111) surfaces due to etching? In order to investigate this, the small pits were examined at a high resolution by transmission electron microscopy and it was observed that some of them were actually having two point bottoms thereby suggesting that they were due to on set of etching of dislocational loops. Since the point bottomed pits are not fully resolved in optical microscope the pits appear to be one but in fact, they are double. The conversion of point bottomed pits into flat bottomed pits may be due to etching away of dislocation loops.

The comparison of the etch patterns in Fig. 3(b) with the etch pattern in Fig. 3(a), reveals that the pattern has been completely changed though both of them are on regions one above the other. It is conjectured that:

- 1. The etch pits on diamond surfaces nucleated at dislocation loops.
- 2. The dislocation loops are short and narrow.
- 3. The dislocation loops are randomly oriented.
- 4. The density of dislocations on the natural surface of the crystal is more than that their density within the body of the crystals.

The etch pattern in Fig. 3(b) reveal that morphologically the etch pattern produced by the new method of etch on(111) faces resembles the trigon pattern on natural (111) faces which also consists of point bottomed and flat bottomed trigons. Thus the trigons on natural (111) faces may be etch pits produced by dissolution in nature. If this is true at the point bottomed trigons the dislocations still exist while at the flat bottomed trigons the dislocations have been moved or etched away. To confirm this (111) faces having point bottomed trigons on them were etched and it was observed that they were further etched giving rise to etch pits at their bottoms thus confirming the existence of dislocations at their bottoms. This is shown in figure 4(X 500). In addition some small trigons on natural (111) faces were examined in transmission electron microscopy which showed that they have two bottoms indicating thereby that they were due to etching of dislocation loops.

In order to decide whether the square shaped pits on (100) natural faces of diamond were also due to etching of dislocation, a (100) face having square shaped pits was etched and it was observed that i-



Fig. 4

x 350

- 1. Some of the point bottomed pits were further etched and thus they become more deep.
- 2. Some other pits turned flat bottomed.

Thus these square pits on (100) faces also are due to etching of dislocations.

#### DISCUSSION:

It is now clear that the density of the trigons on (111) faces and square pits on (100) faces give the density of dislocations in diamond. That the laboratory etching produced pits other than the trigons and the square pits suggest that new dislocations in the form of dislocation loops might have been introduced in the body of the crystal at a later stage.

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#### DISCUSSION:

- S.B.S. Sastry : In the etching by carbon arc, is it the temperature or the material of the electrode that is important?
  - A.R. Patel : I do not think it is either because of etching of diamond is known to be due to the oxidation process which has nothing to do with the material or the electrodes.
- S.C. Gujrathi : Why are the etch pits produced with faster rate with the carbon arc?
  - A.R. Patel : It seems that the etchant dissociates forming ions which may be more reactive in producing etching at a rapid rate.
    - P. Singh : Can one infer from the study of dislocations anything about the crystal structure?
  - A.R. Patel : Yes, the symmetry of the etch figures are strictly related to the symmetry of the crystal surface.

#### TEMPERATURE DEPENDENCE OF THE 'FAST' SURFACE STATES OF GERMANIUM

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Although the existence of surface states was postulated by Tamm<sup>(1)</sup> and by Bardeen<sup>(2)</sup> prior to the investigation of the transistor by Brattain and Bardeen<sup>(3)</sup> and Shockle y<sup>(4)</sup> the nature of the states is not yet fully understood. Since the first field-effect experiment of Shockely and Pearson<sup>(5)</sup> many investigators<sup>(6-12)</sup> utilized the same principle to determine the relaxation time, capture cross section, number density and energy of these surface states. Most of the investigators used the pulsed field-effect<sup>(7,8,9,11)</sup> and oscillographic display to determine the relaxation time T of the fast states and its variation with temperature in the case of germanium and silicon. In our present experiment, the dependence of the field effect mobility on frequency, f, is studied over the range 30 c/s to 30 kc/s at various temperatures and the relaxation times are evaluated by fitting 25 to 30 experimental points obtained at each temperatures into an expression  $\mu_{\rm FE} = A - \frac{B}{1+4}\frac{B}{T^2T^2}$ . A symmetric study on the variation of T on temperature is made and the trap depths and their capture cross-sections are evaluated.

The experimental set up and the details of which may be found elsewhere (13). The temperature of the cell was controlled by water bath for higher temperatures and by freezing mixtures for the lower temperatures. Measurements were taken in the range 30 c/s to 30 kc/s after allowing sufficient time for the crystal temperature to become study with the current passing through it. The field-effect signal  $\Delta V$  after preamplification by the differential amplifier is measured both on the wave analyser and the VTVM. The field-effect mobility, pr is given by the equation<sup>(7)</sup>

$$\mu_{\text{FE}} = \frac{(R_{\text{a}} + R_{\text{b}} + R_{\text{T}})}{R_{\text{T}}^{2}(R_{\text{a}} + R_{\text{b}})} \cdot \frac{\Delta \nabla}{I C \nabla_{\text{ac}}}$$

where  $R_a$  and  $R_b$  are the variable resistors in the bridge circuit,  $R_T$  is the resistance of the crystal at the temperature. T, I is the steady d.c. current through the crystal, C, is the total capacitance between the crystal and the field plates,  $V_{ac}$  is the a.c. field voltage.

The variation of field-effect mobility,  $\mu_{FE}$  with frequency at various temperatures is shown in Fig. 1. As the higher frequency regions are more affected by temperature, it is reasonable to assume that the relaxation of 'fast' states is more sensitive to temperatures than that of the slow states, which have their effects at frequencies below 2 Kc/s. From the analysis of the data in the frequency region 3 Kc/s to 30 Kc/s the relaxation times (7) are evaluated. The formula developed by Rupprecht<sup>(8)</sup> i.e.,



Fig. 1



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Fig. 2

$$\frac{1}{\tau} = N_0 \mathbf{v}_t \mathbf{Y} \mathbf{O}_{exp}^{-} \left( \frac{\mathbf{E}_0 - \mathbf{E}_T}{\mathbf{K} \mathbf{T}} \right)$$

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is utilized to obtain the trap depths  $E_T$  from the conduction band. The plot of log  $\frac{1}{T}$  vs  $\frac{1}{T}$  is shown in Fig. 2. The slopes of the two straight line parts correspond to surface states located at 0.45 and 0.10 eV below the connoction band, and the corresponding intercepts give the capture cross sections ( $\gamma \sigma$ ) to be 10.3 x 10<sup>-5</sup> cm<sup>2</sup> and 3.9 x 10<sup>-20</sup> bm<sup>2</sup> respectively.

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TABLE I

Summary of Results Obtained by Different Workers on Germanium. Surface.

| Source               | <b>E<sub>C</sub>-E<sub>T</sub></b><br>in eV | <b>0</b> −in cm <sup>2</sup>                       | <sup>H</sup> T cm <sup>2</sup> | (at room temp.)                            |
|----------------------|---|--|--------------------------------|--|
| Bardeen et al (1963) | •5  |  | $1 - 3 \times 10^{11}$         |  |
| Statz (1957)         | 0.2   |  | 1011                           |  |
| Rupprecht (1958)     | 0.24<br>0.49<br>0.44                        | 4.3 x 10 <sup>-15</sup><br>2.0 x 10 <sup>-13</sup> | 8 x 1010<br>6 x 1010           | $4 \times 10^{-2}$<br>2 x 10 <sup>-4</sup> |
| Many et al (1960)    | 0.04<br>0.56                                | 10-12  | 1011                           |  |
| Green et al (1963)   | 0.11  |  | $5 \ge 10^{14}$                |  |
| Present Work         | 0.45<br>0.10                                | 10.3 x 10-15<br>3.9 x 10-20                        |                                | 14.2                                       |

STUDIES ON THE MISCIBILITY OF SODIUM CHLORATE AND SODIUM BROMATE IN THE SOLID STATE

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#### ABSTRACT

Sodium chlorate and sodium bromate are cubic isomorphous crystals (space group  $P2_13$ ), lacking a centre of symmetry. They display optical activity, both dextro and levo forms crystallise from aqueous solutions with equal facility. The planes of the four halate ions are arranged in a spiral fashion along the body diagonal in the cubic unit cell, the sense of the spiral may be left or right handed. The earlier studies on absolute configuration have established that the same sense of the spiral leads to opposite signs of optical rotation in the two crystals.

It has been reported that the two compounds are continuously miscible in all proportions in the solid state and the properties of the mixed system are in accord with Vegard's empirical law. In this paper, work on single crystals of the mixed system through study of X-ray diffraction, optical behaviour and density is described which indicate that, a while the symmetry of the mixed crystals is the same as that of the components, the overall indication is not that of a random solid solution.