**IAEA-204** 

# NEUTRON SCATTERING IN APPLIED RESEARCH

PROCEEDINGS OF AN ADVISORY GROUP MEETING ON NEUTRON SCATTERING IN APPLIED RESEARCH ORGANIZED BY THE INTERNATIONAL ATOMIC ENERGY AGENCY HELD IN LJUBLJANA, YUGOSLAVIA, 1–4 DECEMBER 1976



A TECHNICAL DOCUMENT ISSUED BY THE INTERNATIONAL ATOMIC ENERGY AGENCY, VIENNA, 1977

NEUTRON SCATTERING IN APPLIED RESEARCH, IAEA, VIENNA, 1977

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#### INTRODUCTION

So far the great majority of work carried out with neutron scattering techniques could be classified under fundamental research. Many laboratories in the Member States are feeling pressure to direct more of their efforts into areas related to the national research priorities. Furthermore, it is realized that as the funding situation for several medium flux facilities has become tighter, the need for specialization and international collaboration with the relatively few high-flux facilities increases. To emphasize this point, a study was recently commissioned by the Argonne National Laboratory to determine possible uses of neutron scattering in industrial research and testing and in areas not influenced by present neutron research. The possibilities for fundamental and applied research offered by new high intensity neutron sources currently being proposed have been reviewed elsewhere<sup>21,3,14</sup>

This publication, which is the result of an Advisory Group Meeting on Neutron Scattering in Applied Research held in Ljubljana, on 1-4 December 1976, with subsequent contributions from the participants, focuses more on the possibilities offered by medium flux facilities. The following areas of materials science, technology and biology were revieweds

- magnetism
- determination of hydrogen selfdiffusion constants and ionic mobility in superionic conductors
- liquid crystals
- molecular solids
- polymers
- surface chemistry and catalysts
- colloids
- biology
- physical metallurgy
- neutron diagnostics.

A paper summarizing, in more detail, established applications and new proposals for research projects in these fields with neutron scattering' techniques will be published in the Atomic Energy Review, Vol. 15, No. 4, 1977, which the reader is advised to consult for further information.

The assistance of the participants of the meeting, in the preparation of this publication, is gratefully acknowledged and it is hoped that an even larger audience in the scientific community and industrial research establishments would benefit from their efforts.

- 3/ Uses of advanced pulsed neutron sources, Report of a workshop at Argonne National Laboratory, 21-24 October 1975, ANL-76-10, Vol. 2.
- 4/ A pulsed neutron facility for condensed matter research, edited by L.C.W. Hobbis et al., RL-77-064/C, June 1977.

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<sup>1/</sup> Applications of high flux neutron sources in technology and biology, Study performed by the MITRE Corporation, to be published by the Argonne National Laboratory.

<sup>2/.</sup> Report of the Linac Review Group, UK Science Research Council, Science Board, Neutron Beam Research Committee, November 1975.

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# NEUTRON DIAGNOSTIC INVESTIGATIONS WITH A RESEARCH REACTOR

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#### Abstract

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Some aspects of the use of neutron transmission analysis in applied research, as persued at McMaster University (Canada), are examined. Examples considered are void measurements in two-phase flow, neutron conversion enhancement in neutron radiography, reconstruction of interior bulk heterrogenities in solids and temperature sensing with neutrons.

## Introduction

For purpose of this report, we find it convenient to make a distinction between microscopic and macroscopic neutron diagnostics: the former is based on the use of scattered monoenergetic neutrons and provides information on the atomic scale of a material specimen while the latter is characterized by the use of a spectrum of incident neutrons and the subsequent analysis of the uncollided neutron beam leading to information on the bulk or gross material features under both static and dynamic conditions. The attached figure, Fig. 1, displays this distinction in graphical form.

Our interest here is to discuss some analytical aspects and experimental demonstrations of the latter, that is macroscopic neutron diagnostics. For reasons of technological relevance and this author's experience, the following specific areas will be discussed:

1. void fraction determination in two-phase flow,

2. neutron conversion enhancement,

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3. reconstruction of media heterrogenities,

4. temperature sensing by neutron transmission.

In keeping with the objectives of this summary, the descriptive rather than the mathematical/experimental details will be emphasized. A bibliography at the end, based on our published results, can be consulted for more detailed information.

As a point of generality, we emphasize that, although in the investigations to be reported here we have used a spectrum of neutrons, monoenergetic neutrons - if available with sufficient intensity - could similarly be used and would indeed provide a refined tool for certain aspects of research and developmental objectives.

#### Neutron Diagnostics of Two-Phase Flow

Two-phase flow conditions occur in many industrial and technological processes involving either entrainment of air for fluid mixing purposes or the generation of voids by thermal energy exchanges. The chemical process and electricity production industries in particular encounter such hydro-thermal problems. A specific and urgent subject involves the study of boiling in nuclear reactors. We illustrate the complexity of the pheonomena in the attached, Fig. 2.

Although two-phase flow conditions occur very frequently, no altogether satisfactory methods of void fraction measurement exist; techniques such as fast-acting valves, probes, and photographic methods are invariably of restricted utility. When dealing with liquids not exceeding 3 to 4 mean-free-paths in thickness, we find that neutron diagnostic methods are very accurate and easy to use.

The analysis of void fractions involves relating the incident and emerging neutron beam to the instantaneous void fraction. If we designate the former by  $I_{in}(t)$  and the latter by  $I_{out}(t)$  then we may write

$$I_{out}(t) = I_{in}(t)B[x_0, \Sigma_{\ell}, \alpha(t)]exp(-\Sigma_w 2\delta)exp[-\Sigma_{\ell} x_0(1 - \alpha(t)], (1)$$

where  $\Sigma_{W}$  and  $\Sigma_{\ell}$  are suitably energy averaged containment-wall and liquid total macroscopic cross sections,  $x_{0}$  is the channel thickness,  $B[x_{0}, \Sigma_{\ell}, \alpha(t)]$ is the neutron build-up function and  $\alpha(t)$  is the instantaneous void fraction.

We have conducted numerous tests on static and dynamic channels and developed techniques for the instantaneous and time-averaged measurement of the void fraction. The neutron beam used was extracted from the McMaster University "Swimming Pool" 2 MW Nuclear Reactor yielding a neutron flux of  $\sim 10^6$  n/cm<sup>2</sup>-s at the beamport; it consisted of a dominant Maxwellian and an epithermal component. A standard collimator encased BF<sub>3</sub> detector with a scalar/timer and a fast magnetic tape data acquisition unit was used.

Some of our experiences can be summarized as follows:

- (i) it appears most convenient, and sufficiently accurate, to measure the build-up function and cross section by calibration;
- (ii) the gating period is important to minimize the appearance of a dynamic bias in the void fraction;
- (iii) Equation (1) is best solved by iteration;
- (iv) source fluctuations effects are important but can be minimized.

The attached figures, Fig. 3 to Fig. 7, provides graphical and descriptive detail on experimental and analytical results.

# Neutron Conversion Enhancement

The application of neutron radiography in industrial nondestructive testing has in recent years proven to be of considerable significance. In areas such as the examination of radioactive nuclear fuels, low-density hydrogeneous material determination and isotopic as well as high-density

material discrimination, neutron radiography represents essentially the only effective methods of nondestructive examination.

It is apparent that such photographic uses of neutron beams could be extended substantially in industry and other applied sciences if improved techniques for the conversion of neutrons into photo-sensitive or other image-producing radiation could be established. For example, the practicality of extensive on-line radiographic study of assemblyline products and the more broadly based on-site tests of the integrity of construction components could thus be realized. Critical to this development is the attainment of a sufficiently high optical density and image sharpness for a given and generally relatively low neutron beam intensity.

To elucidate the subject, we refer to the attached figure, Fig. 8, and describe the essential physics characteristics of the neutron radiographic processes in the following abbreviated forms: a spatially homogeneous beam of neutron emerges from a suitable neutron source and penetrates an object to be radiographed. The emerging neutron beam, which has now become spatially heterogeneous in accordance with the isotopic composition of the object, is absorbed in a suitable converter material located in a neutron camera. The converter material is so chosen to yield suitable secondary radiations which contribute to the formation of a direct or indirect latent image in a suitable recorder. The latent image is eventually made visible to the unaided eye in the form of a spatially varying blackness and can be related to the material composition of the object to yield some material information.

For purpose of generality and to indicate the distinct problem areas, we consider describing the optical density on the radiograph, D(r), at some point r in functional form as an integral over all neutron energies by

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$$D(\underline{r}) = \int_{0}^{\infty} T(\underline{\varsigma}, E)C(\underline{\varsigma}, E)I(\underline{\beta}, E)dE , \qquad (2)$$

where  $T(\underline{\varsigma}, E)$  is the neutron transmission in the material specimen being examined,  $C(\underline{\varsigma}, E)$  is the neutron conversion process and  $I(\underline{\beta}, E)$  is the image formation function; the parameters  $\underline{\varsigma}$ ,  $\underline{\varsigma}$  and  $\underline{\beta}$  are the appropriate scalar or vector parameters which characterize the radiographic process; E is the incident-beam neutron energy.

The companion relationship to the optical density is the image sharpness at some position  $\underline{r}_0$  on the film and in a specified direction. This is a function of the optical density gradient and hence may be written as

$$S(\underline{r}_{0}) = f[\frac{\partial D(\underline{r})}{\partial \underline{r}}]_{\underline{r}_{0}} .$$
(3)

The detailed functional form of f( ) is governed, to some extent by convention.

The dominant area of interest for application purposes is therefore the examination of each of distinct neutron-nucleus and secondary radiation effects so as to maximize both the optical density, Eq. (2), and the image sharpness, Eq. (3). Our emphasis to date has focussed upon providing functional expressions for each of the several processes and endeavouring to identify research and developmental directions which would lead to neutron image enhancements.

Some of our results can be summarized in graphical and descriptive form as shown in Fig. 9 to Fig. 16.

# Interior Heterogenity Reconstruction

The topic of interest here involves the reconstruction of gross interior heterogenities in bulk materials using neutron transmission techniques. This is analogous to the medical diagnostic problems of

obtaining information about the state of normal and diseased tissue and organs from an x-ray radiograph. There exist numerous problems in industrial research and scientific practice where the unique neutronnucleus interaction characteristics could gainfully be used in the interior reconstruction of the interior of materials, among these we cite nondestructive testing, methods of examination of archaelogical specimen, and geophysical analysis of selected in-situ ore and soil specimen.

In the attached figure, Fig. 17, we display in graphical form the experimental set-up used in our investigation. Basically, a neutron beam is passed through a heterogeneous material specimen which is mounted so as to permit independently linear motion across the neutron beam and rotational motion on a transverse axis. The transmitted beam, along a predetermined narrow beam area and direction is recorded by digital means. The collected data obtained along several traverses for several orientation of the specimen is thereupon unfolded by computer. In our work, we have used the ART (Algebraic Reconstruction Technique) formalism which has recently been developed. Its use is based on an iterative procedure of the type

$$A^{q+1}(i,j) = A^{q}(i,j) + B^{q}_{k}(i,j) , \qquad (4)$$

where (i,j) is a cell index of the medium, q is the stage of iteration and k is a beam index; A and B are the reconstructed and corrector matrices for the material density at cell (i,j).

Our results can best be described in the attached graphical form, Fig. 17 and Fig. 18.

#### Temperature Sensing by Neutron Transmission

The determination of the bulk temperature of a medium in some materials poses extreme problems. For example, high temperature, corrosive-

ness, or purity requirements may preclude standard methods; further, the formation of slag on the surface of a material may similarly prevent the use of optical methods.

We have found that the Doppler Effect is sufficiently pronounced for epithermal neutron beam to effect the neutron transmission in some materials; this is shown in Fig. 19. As is evident, in some temperature regions and for some materials, the effort is sufficient to provide considerable sensitivity.

### Concluding Comment

As indicated previously, the description above is brief. The interested reader can find more details on this work carried out at McMaster University by reference to the Bibliography appended to this summary.







Fig. 2: Illustration showing the complexity of fluid flow conditions encountered in two-phase flow



Fig. 3: Experimental comparison between measured and actual voids of twophase test specimen. The open circles identify two sets electromagnetic radiation attenuation measurements (A,B) while the solid circles identify the neutron attenuation measurements. It is apparent that neutron transmission is more accurate for and covers a much larger range of void fractions.



Fig. 4: By gating the neutron detector - and thus simulate short interval neutron transmission measurements - it is possible to obtain void distributions. In this case we note the differences between a low void bubble flow regime. These void distributions may effectively be used to define flow characteristics.



Fig. 5: Neutron transmission analysis is sufficiently accurate to measure changes in void fraction distributions small distances apart during flow transitions. The pipe has a inside diameter of 2 cm with  $\Delta x = 9$  cm near an air inlet.



Fig. 6: The transition from bubble flow to slug and bubble can be identified with considerable precision by gating the neutron counter counting period. A distinct difference in apparent void fraction appears as the gating period is increased.



Fig. 7: The spatial void distribution in a 2 cm pipe has been studied by scanning the transmitted neutron beam radially. By mathematical unfolding methods, the parameter n and  $\alpha_c$ , which appear in two-phase flow theory, have been thus determined.



Fig. 8: Schematic depiction of neutron conversion schemes leading to the formation of an image. Commonly, only one converter and one recorder - with the converter behind the recorder - are used.



Fig. 9: Because neutron attenuation is a nuclear phenomena whereas electromagnetic attenuation depends upon atomic characteristics, the radiation attenuation and the subsequent images produced should differ. Here we show the differences in optical density associated with a rock specimen radiograph when examined by x-rays and by neutrons. These differences can be used to identify rock features such as inclusions and ore content.





Fig. 11: The optical density across a knife-edge object can be used as an indication of image sharpness of the neutron imaging system. Here we illustrate the comparison between analytical results - based on a one parameter Lorentzian representation - with experimental results of three different conversion processes. It is apparent that the Lorentzian respresentation is fully adequate



Fig. 12: While Fig. 11 illustrates image unsharpness of a stationary object, this figure shows unsharpness due to a moving (rotating) knife-edge. Again a Lorentzian representation which incorporates a steady-state component and a time-dependent component has been used to provide a satisfactory fit. It is thus apparent that unsharpness can be described, in a fundamental sense, by a compact analytical representation.



Experimental results conducted to determine the effect of isotopic enrichment in gadolinium on the optical density. It appears that isotopic enrichment is effective in optical density enhancement when thin converters are used; this would suggest its utilization in ultra high resolution neutron radiography.



Fig. 14: An analysis has been undertaken to evaluate the potential of optical density enhancement using linearly heterogeneous converters. This illustrates the enhancement factor possible by varying spatially the isotopic density,  $E_T$ , and the atomic density  $\alpha_T$ .



Fig. 15: The possibility of radiographing very fast transient phenomena was considered. The neutron Imaging system was taken to consist of a layered recorder-converter arrangement each possessing a distinct resonance absorption cross section. Thus, neutrons of different energies will require a different time interval to traverse the source-to-camera distance and hence record the transient at a different point in time. The following figure shows some results.

1.



Fig. 16: Time intervals possible using neutron energies as the timing mechanism in a neutron imaging system described in Fig. 15. As shown here, extremely fast transients can thus be radiographed.





Fig. 17: Illustration of a heterogeneous test specimen and the neutron beam directions orientations used to obtain a reconstruction of the interior inhomogenity.

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Fig. 18: Graphical display of two reconstructions of the heterogenities of the test specimen; these two reconstructions differ slightly due to the use of different convergence criteria adopted.



Variation of neutron transmission through three metallic specimen with change in specimen temperature. It is apparent that temperature transmission can serve as a temperature sensor particularly near the medium's melting point. Fig. 19:

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#### NEUTRON SMALL ANGLE SCATTERING BY COLLOIDAL SOLUTIONS OF GRAPHITE

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#### ABSTRACT

Neutron diffraction and small angle scattering have considerable potential as methods to study adsorption at the solid liquid interface, particularly in colloidal dispersions and gels. Almost no work has been done using neutron high angle diffraction, but here we present some model experiments using neutron small angle scattering and the contrast variation method to study colloidal solutions of mono-dispersed polystyrene latices, and of graphite (vulcan III) ultrasonically dispersed in water with and without peptisation by sodium dodecyl sulphate at 25°C. These effects illustrate the likely effects of polydispersity in practical applications of the small angle neutron scattering technique in this area.

The small angle scattering method gives the particle radius of gyration, mean scattering length density, and hence information about the conformation of the surfactant molecules in the adsorbed layer. The use of this information to test theories of colloid stability, as well as in practica! applications, is discussed.

#### INTRODUCTION

Despite the small scattering cross-section of neutrons by matter (typically  $10^{-24}$  cm<sup>2</sup> compared to  $10^{-16}$  cm<sup>2</sup> for atom and electron scattering experiments), considerable progress has been made in the last five years in studying adsorption on the gas solid interface by neutron methods<sup>(1)(2)</sup>.

Initially, work concentrated on systems showing BET type 1 isotherms with surface areas between  $20m^2/\text{gram}$  and several hundred square metres/ gram in order to achieve reasonable sensitivity in diffraction from the adsorbed species, but good signal to noise was obtained even for less than one monolayer coverage in such cases <sup>(3)(4)</sup>. Recently, however, it has been possible to study systems with much lower surface coverage using the high fluxes and multidetector techniques at the Institut Laue-Langevin in Grenoble, and work now in progress is concerned with systems showing BET type 2 and BET type 3 isotherms where there is a hydrophobic interaction with the surface<sup>(5)</sup>.

Typically, from these studies it has been possible by using neutron diffraction, to determine the two-dimensional (and, in the case of multilayers, three-dimensional) crystal structures of the adsorbed phases as a function of temperature, thereby giving a microscopic structure understanding of the adsorption isotherms. At the same time, by use of neutron inelastic scattering, it has been possible to determine, in favourable cases, the lattice and molecular dynamics of the adsorbed phases, and hence to make the first steps towards a discussion of their stability and interconvertibility<sup>(2)</sup>. The object of the present paper is to speculate about the possibilities for the extension of such studies to the solid liquid interfaces, and in particular to extend these to a consideration of the structure and stability of colloidal solutions and gels. The particular advantage of neutron scattering derives from the contrast that can be achieved in both diffraction and inelastic scattering because of the large variation in scattering length between different isotopes. For small angle scattering, this allows changes in the mean scattering length density of the dispersent medium so that the scattering from the colloidal particle and the adsorbate can be separated. For inelastic scattering the difference in the time scales of motion of the whole colloidal particle and the molecules adsorbed on it can be recognised since a variety of adsorption times between
approximately  $10^{-6}$  sec and  $10^{-12}$  sec is available  $^{(6)}(7)$ . The theory and practice of this contrast variation method has been well developed for determining polymer conformations in solutions and solids  $^{(8)}(9)$ , as well as the internal structure of biological macromolecules  $^{(10)}(11)(12)$  and, there-fore, only a brief summary of the more important results will be given here for a simple case.

For a certain range of small angles the intensity of scattering from isolated particles as a function of the momentum transfer  $Q = \frac{4\pi \sin\theta}{\lambda}$ where 20 is the scattering angle and  $\lambda$  the neutron wavelength can be expressed by the Guinier approximation<sup>(13)</sup>

$$I(Q) = I_o \exp\left(-\frac{Q^2 R_s^2}{3}\right)$$
(1)

where I is the scattered intensity at  $\theta = 0$ , and R is the "radius of gyration" of the particle defined as

$$R_{g}^{2} = \int_{R_{g}}^{R_{g}^{*}} R_{g}^{*}(R) dR$$

which for a sphere gives

$$R_g = \sqrt{0.6}$$
 x actual radius

From (1), a plot of  $\ln I_Q$  against  $Q^2$  gives a straight line of slope  $\frac{-R_g^2}{3}$ . For macromolecules in solution, or in our case a colloidal solution, the scattered intensity depends upon the contrast - the coherent scattering length density difference between the surrounding liquid and the solute or colloidal particle. As hydrogen and deuterium have neutron scattering lengths of -0.38 x  $10^{-12}$  cms and + 0.65 x  $10^{12}$  cms. respectively, a large range of values of  $\rho$ s, the mean scattering length density of the solvent, may be obtained by changing the relative H-D content. For example, 8% D<sub>2</sub>0

in  $H_20$  has  $\rho_s = 0$  and the small angle scattering from suspended particles is equivalent to their 'in vacuo' scattering.

Stuhrmann<sup>(12)</sup> has shown that, by using dilute solutions to eliminate inter-particle effects, the scattered intensity may be written as

$$I(Q) = \left(\rho_{m}V\right)^{2} \left(F_{s}(Q) + \frac{\rho_{m}-\rho_{s}}{\rho_{m}}F_{F}(Q)\right)^{2}$$
<sup>(2)</sup>

where V is the particle volume,  $\rho_{m}$  is the mean scattering length density of the particle, and

$$F_{s}(Q) = \frac{1}{\rho_{m}V_{m}} \int \left[\rho(R) - \rho_{m}\right] \exp(iQ \cdot R) dR$$
<sup>(3)</sup>

$$F_{F}(Q) = \frac{1}{V} \int_{V} \exp(iQ \cdot R) dR$$
<sup>(4)</sup>

The distribution of scattering le gth density withir the particle relative to the mean is given by

$$\left[\rho(R) - \rho_{m}\right]$$

From (2), the square root of the scattered intensity extrapolated to zero angle should be linearly related to  $\rho$ s and will be zero when  $\rho$ m and  $\rho$ s are equal. With intensities measured in absolute units, the gradient gives V, the particle volume. The value of the radius of gyration at infinite contrast derives from the particle shape and the variation of  $R_g^2$  with  $(\rho m - \rho s)^{-1}$  reveals inhomogeneities in the internal distribution of scattering density. For no exchange or penetration of solvent into the scattering particle<sup>(12)</sup> the slope of the plot of  $R_g^2$  versus  $(pm-ps)^{-1}$  shows qualitatively whether the density gradient from the particle centre is positive or negative.<sup>(10)(12)</sup> Determination of these quantities may be of considerable interest in the study of microporocity<sup>(14)</sup>.

Using the procedure described by  $Zimm^{(15)(16)}$ , the concentration dependence of the scattering may be incorporated into (1), giving, for low concentration, and  $QR_o^{<1}$ 

$$\frac{KC}{I(Q,C)} = \frac{1}{M \exp(-\frac{Q^2 R_g^2}{3})} + 2A_2C$$
(5)

which becomes

$$\frac{KC}{I(Q,C)} = \frac{1}{M} \left( 1 + \frac{Q^2 R_9^2}{3} \right) + 2A_2C$$
<sup>(6)</sup>

where K is a constant, proportional to contrast, M is the 'molecular' weight of the scattering particles, C is the concentration, and  $A_2$  is the second virial coefficient. Simultaneously plotting  $\frac{C}{I_Q}$  against  $Q^2$  and C at infinite contrast and extrapolating to zero angle and concentration gives a line of intercept  $\frac{1}{M}$  and initial gradient  $A_2$ . Thus the physical characteristics of particles - radius of gyration, volume and mean scattering length density are derived as well as the second virial coefficient, and may be used to test theories of the colloid stability.

In addition to studying such problems as the physical chemistry of colloid stabilisation, it seems possible, both by the use of small angle scattering and inelastic scattering, to look at questions such as the effect of mixed surfactants (17), the conformational transitions in adsorbed polymers (18), and even to study such technical questions as the mechanism of stabilising carbon dispersions in oils etc. by dispersant additives. (19) In many practical systems, however, the question of poly-

dispersity immediately arises, and therefore we present in this paper a comparison of some results from a strictly monodispersed system and their extension to a polydispersed carbon of likely technical importance.

## EXPERIMENTAL

## a) Materials

Polystyrene latices containing a single ionogenic surface species (carboxylic acid groups), and with a very small coefficient of variation in the particle size (typically less than a few percent), have been prepared by Ottewill and his collaborators<sup>(20)</sup>(21), and samples of this material in stabilised dispersed at 0.2% weight per volume, and in aqueous mixtures containing between 0% - 60% D<sub>2</sub>O at pH 9.8 were used for the neutron scattering measurements. The bead diameter was determined before experiment by electron microscopy and found to be approximately 500Å. For these experiments the samples were contained in silica sample cells and small angle scattering was measured with 10Å neutrons at the 20 metre position of the D11 small angle scattering mæhine at Grenoble. Acceptable statistics for high contrast samples were obtained in 2-hour counting times, and spectra were taken for seven D<sub>2</sub>O concentrations and blanks. The density of the polystyrene was quoted as 1.058 g/cc, giving a contrast matchpoint in H<sub>2</sub>O/D<sub>2</sub>O mixtures at 29% D<sub>2</sub>O:71% H<sub>2</sub>O.

The graphite, a sample of Vulcan III batch no. 2A/29 surface area  $71 \text{ m}^2/\text{gm}$ , obtained from the National Physical Laboratory, Teddington, U.K. <sup>(22)</sup> was ultrasonically dispersed in mixtures of  $H_20$  and  $D_20$ . Dispersions with concentrations of 0.2% to 10% by weight carbon were sonicated for 90 sec. each using an ultrasonic finger in direct contact with the solution. This time was rather less than the five minutes specified by Medalia and Heckman for complete dispersion of the graphon aggregates <sup>(23)</sup>. To one group of samples was added 35 mg of sodium dodecyl sulphate per 100 mg of carbon, equivalent to 5 monolayers if the surfactant molecules

occupy an area of  $50 \text{\AA}^{2}$  <sup>(22)</sup>. This S.D.S. concentration ratio was kept constant. The peptised samples were noticeably more stable than the dispersions in water, remaining apparently dispersed for several months. Some of the unpeptised samples, particularly at high carbon concentration, were observed to have largely flocculated even during experimental runs (i.e. up to 3 hours after dispersion). Electron micrographs of the diluted peptised suspension were taken and showed that, even in the apparently dispersed solution, clusters of graphon particles existed. Since further sonication is known to cause oxidation<sup>(24)</sup> this was not attempted.

The neutron small angle camera, DII, was used working at a sample detector distance of 20m and wavelength 16Å. Samples 1 mm thick were contained in silica cells of total wall thickness 2 mm and maintained at 25°C. Scattering patterns from individual samples were obtained in halfhour counting periods during the 20 hours instrument time available, and the results from the 64 x 64 cm<sup>2</sup> area detector were converted to radial distribution functions by integrating the counts in I cm annuli at a given radius from the beam centre. At the 20 m position with 20 m collimation, the gravity deflection of transmitted and scattered 16Å neutrons was 7 cm, and beam centre on the detector was chosen accordingly. Since the effect of wavelength spread on beam 'droop' may cause distortion of the results at low angles, vertical and horizontal sections through the pattern were compared with the radial distribution obtained to check for systematic This is shown in Figure 1 and it can be seen that the horizontal errors. section, only slightly affected by 'droop', is identical to the radial distribution for deflections of >5cm from beam centre. The experiments were all done with the main beam stop in place and the counting rate over the whole counter never exceeded 550 counts sec<sup>-1</sup> so errors due to electronic loss of counts were negligible.

RESULTS

# (a) Polystyrene Latices

The results are summarised graphically in Figures 2 and 3. Figure 2 is the Guinier plots (lnI vs.  $Q^2$ ) of the different  $D_2^{0}$  concentration sols  $(D_20/H_20$  and silica cell background subtracted). Intensities are in arbitrary normalised units, uncorrected for self absorption. As can be seen, essentially linear plots are obtained. This confirms sufficient uniformity of particle size. The unsystematic variation at low angle is explained by mismatch in the background subtraction - the silica/ ${}^{
m H}2^{0/D}2^{0}$ background scattering being very strong at low angles and weak over the rest of the spectrum. As predicted, intensities are reduced for  $D_2^0$ concentrations approaching 29%  $D_20$  and a spectrum taken at 30%  $D_20$  showed no measurable intensity above background (not shown in Figure 2). Values of radius of gyration obtained from the slope of these plots are tabulated in Table 1 along with the equivalent values of scattered intensity extrapolated to zero angle (I\_). These latter, now corrected for self absorption, are displayed in Figure 3 as a  $\sqrt{I_0}$  vs. scattering length density of solvent (=  $% D_{2}0$ ) plot. The linearity of these points shows that the homogeneity of the particles is good to within experimental accuracy. The plot also gives a mean scattering length density for the particles as 1.37  $\pm$  0.1 x 10<sup>10</sup> cm<sup>-2</sup> giving their density as 1.03 ± 0.07 g/cc (cf. 1.057 g/cc quoted). The high estimated errors are based mainly on possible uncertainty in the measurement of the small volumes involved in preparing the samples.

## (b) Dispersed Carbon

Figure 4 shows the lnI vs  $Q^2$  plots for 2% wt. Vulcan III dispersed in various  $H_2^0/D_2^0$  mixtures. The plots are markedly curved at low angles but a straight line may be drawn through the high angle region giving values for the apparent radius of gyration,  $R_g$ , and by extrapolation, the scattered intensity at zero angle  $I_0$ . These are tabulated in Table II. The

% D <sub>2</sub> 0	R <sub>g</sub> (Å)	lnI <sub>.o</sub>	$\sqrt{I_o}$ corr.
60	172	6.63	36.6
52.5	165	5.74	24.0
42	173	4.73	15.3
30	-	-	(0.6)
26.4	-	(1.3)	(3.0)
21	170	3.25	8.22
0	174	5.81	32.43

TABLE 1

TABLE II

<u>Contrast Variati</u>	on Param	eters for	Vulcan	111
carbon disp	ersed in	H20/D20	mixtures	3

%D <sub>2</sub> 0	I o	LnI <sub>o</sub>	$\sqrt{I_o}$	Rg±30Å
0	396	5.98	19.9	402
30	164	5.10	12.8	391
50	101	4.61	10.0	402
80	21.8	3.08	4.7	402
100	1.8	0.59	1.3	-

Intensities corrected for self absorption and normalised to 2.5 x  $10^5$  monitor counts

%D <sub>2</sub> 0	Io	LnIo	$\sqrt{I_o}$	Rg±30Å
30	221	5.40	14.9	406
50	105	4.65	10.2	394
80	4.0	1.39	2.0	417
100	2.7	0.99	1.6	407
			;	

<u>TABLE III</u> <u>Contrast Variation Parameters for Vulcan III</u> carbon dispersed in  $H_2O/D_2O$  mixtures with sodium dodecyl sulphate

Intensities corrected for self absorption and normalised to  $2.5 \times 10^5$  monitor counts

intensities have been suitably corrected for self absorption. Figure 5 is a plot of  $(I_0)^{1/2}$  against  $\rho$ s. As predicted, a linear relationship is observed indicating contrast matching at about 100%  $D_20$ . From this is calculated a mean scattering length density of 6.5 ± 0.7 x  $10^{10}$  cm<sup>-2</sup>. The volume of the scattering particles could not be determined since an absolute calibration of the instrument could not be done. The incoherent scattering from a 1 mm thick  $H_20$  calibration sample was too low for accuracy (<2 cts/channel/hr) and sufficient time was not available. This is a general problem for very long camera lengths such as the 20 m position and its resolution awaits the characterisation of a suitable standard low angle scattering sample.

For the peptised dispersions, the scattering curves of  $\ln I vs Q^2$ are represented in Figure 6 for 2% wt. Vulcan in 10, 30, 50, 80 and 100%  $D_20$  dispersions. The 80 and 100%  $D_20$  curves were almost superimposed are, it is assumed, to the 100%  $D_20$  giving negative contrast. Appropriate  $H_20/D_20/SDS$  blanks have been subtracted to obtain these curves, and the contrast variation results are summarised in Table III.

In Figure 7 the contrast match point is found for peptised samples from a plot of  $\sqrt{I_o}$  vs.  $\rho$ m. The 100% D<sub>2</sub>O dispersion is taken, as before, to give negative contrast and the straight line obtained indicates the validity of this assumption. The mean scattering length density of the particles and the soap layer is found to be 5.7±0.5 x 10<sup>10</sup> cm<sup>-2</sup>.

The spectra from dispersions of different concentrations, containing 0.3, 0.7, 2.0, 5.0, 10% wt of carbon, are displayed as Zimm plots in Figure 8. These solutions were stable enough to allow reproducible measurements but some sedimentation did occur for the 10% "solution" and the results are only of qualitative significance. The lowest concentration plot had a markedly smaller slope than those above c.0.5% wt/vol. Possible interpretations of this will be discussed below.

#### DISCUSSION

## (a) Polystyrene Latices

The results from the polystyrene latices have a classical behaviour coming from straight Guinier plots with an essentially constant radius of gyration for the different values of the contrast. The value of the particle radius derived from this agrees well with the electron microscope value, and the mean scattering length density is prepared for the assumed structure of the polystyrene bead. In definitive experiments with long exposure times, the accuracy of these quantities could be greatly improved, and we estimate that, by reference to the work on adsorbed surfactants of dispersed carbon, to be discussed below, the conformation and density of adsorbed surfactants and polystyrene latices, and similar monodispersed systems, could be determined with high accuracy by small angle neutron scattering.

By analogy with biological macromolecular systems, it is obvious that, for monodispersed colloids where penetration of the colloidal particle by a solvent or adsorbate occurs, there would be adequate signal to noise for following the kinetics of such processes and for determining the internal structural organisation of adsorbed molecules.

## (b) Dispersed Carbon

By comparison with the monodispersed colloid, the most obvious feature in the scattering curves for this system is the strong curvature at low momentum transfers arising from the polydispersity. This is a severe limitation of the applicability of neutron scattering when measurements are only made over two or three decades of momentum transfer. The approximation that has been used to analyse the results (namely fitting of straight line to one portion of the scattering curve) is only roughly true and the most satisfactory procedure is to simulate the scattering curve from assumed particle size distribution. This is a relatively simpler operation for colloidal dispersions than for dry powder samples, for example, because, to a large extent, interparticle scattering can be limited and because the contrast variation method allows additional information to be brought to bear in case of, for example, the presence of non-penetrable voids in the scattering material.

The analysis that has been carried above is self-consistent and can serve some practical ends as illustrated by the results obtained for the peptised and unpeptised solutions. Evidence that internal particle effects are relatively small at the dilutions studied (0.3 - 10% wt.%) is that the spectra obtained at different concentrations can be superimposed for the peptised solutions within experimental accuracy. In contrast variation, the form of the scattering curve also remains unchanged even in 'negative contrast' (Figure 6, 100% D<sub>2</sub>0) except at the contrast match point when no significant low angle pattern is observed (Figure 4, 100%  $D_2^{(0)}$ ). This further indicates that the observed diffraction is due to the carbon alone and that there is no scattering from voids or inhomogeneities. Solid particles are therefore suggested. The form of the curves is also consistent with a distribution of carbon particle sizes containing some larger (1000Å+) particles or agglomerates of particles. A quantitative determination of this distribution starting from assumptions about the form of the distribu-

tion and the shape of the particles was not possible since the range of values available was restricted. From the more linear higher angle region of the scattering curves an apparent radius of gyration for the particles of  $400 \pm 30$ Å was found (df. Table II) (corresponding to spheres of radius  $510 \pm 40$ Å). This value can be considered as characteristic of the particles over the Q range studied, though, as stated, data from higher Q values would be required to enable a mean particle size to be obtained.

The value of the radius of gyration from the high Q region of the spectrum is in approximate agreement with the values determined by electron microscope examination where it can be seen that the substance consists of carbon balls of approximately  $300\text{\AA}$  radius, generally joined together in clusters of about  $20^{(23)}$ .

The curved radius at low angles can be analysed by assuming a superposition of particles giving rise to the approximately linear Guinier plot at high Q onto a particle set with a larger radius of gyration. An estimate for this larger radius was obtained by subtracting the extrapolated high Q line from the data at smaller values of Q. This gave again a fairly good straight line with about 10 points upon it and a radius of gyration of about 1000Å. In this way, we can parameterise, in an approximate way, the size distribution in the colloidal material.

The plots of  $\sqrt{I_o}$  vs scattering length density, for both regions of the scattering curve, are plotted in Figures 5 and 7. The convergence of the lines helps determine the contrast match point which is the same for both. Since scattered intensities approach zero at the contrast match point, statistical errors increase. Due to the counting rates at the 20m detector position with 16Å neutrons, statistically significant total counts were only obtained at high contrasts. It is a disadvantage of the carbon/H<sub>2</sub>0/D<sub>2</sub>0 system that the contrast match point lies at about 100% D<sub>2</sub>0. Ideally, good positive and negative contrast data would allow accurate match points to be determined (i.e. match point around 50% D<sub>2</sub>0).

The values obtained for the match points give mean scattering length densities of 6.5 ± 0.7 x  $10^{10}$  cm<sup>-2</sup> (Figure 5) and 5.7 ± 0.5 x  $10^{10}$  cm<sup>-2</sup> (Fig.7) for the carbon particles with and without SDS respectively. The difference in these figures can be attributed to the effect of an absorbed surfactant layer surrounding the particles since the scattering length density of the  $H_2O/D_2O$  mixture is not significantly altered by the small concentration of SDS present. By assuming complete exclusion of the  $H_2O/D_2O$  by surfactant at the carbon surface, we can determine an apparent thickness of the adsorbed layer to be about 40Å. This has a large uncertainty due to the polydispersity of the colloid, poor counting statistics, and low contrast of the peptising agent. Use of a deuterated peptising agent would make a great improvement. The exact distribution of particle sizes would be required to be known and a monodispersed sample would thus greatly simplify such a study. A value of the density of the particles can be calculated from the contrast point as 1.9 ± 0.2 g/cc (cf. 1.9 - 2.6 g/cc for graphite and 2.2 g/cc calculated from crystallographic data on microcrystalline graphite<sup>(25)</sup>). This low value could indicate some pores or amorphous zones.

The Zimm plot obtained for the peptised samples (Figure 8) gives reasonably consistent positive gradients apart from the lowest concentration (0.35%C). The positive gradient shows that strong repulsive forces exist to stabilise the colloid and that these forces may be smaller at lower carbon concentrations. It is to be noted that soap concentration is a fixed ratio of carbon concentration in these experiments and that the observed abrupt change in gradient on passing from 0.7% to 0.35% of graphite also coincides with passing from above to below the critical micelle concentration for SDS in  $H_2^0$ . Since the soap scattering was always subtracted from the raw scattering curves, the results indicate that the ^arbon may be differently peptised in the two situations.

# CONCLUSIONS

For monodispersed colloids it is concluded that measurements of the radius of gyration, the particle mean scattering length density, and the intensities at zero scattering angle, by neutron small angle scattering, is an effective method of studying adsorption at the liquid solid interface. The method has adequate sensitivity to study the packing of the adsorbate over a large part of the adsorption isotherm and, when used in conjunction with contrast variation, could be used to determine the conformation of complex or polymeric adsorbates. For monodispersed systems at high concentration, where long range particle ordering has been observed, it is even conceivable that three dimensional information on the colloidal particle and surfactant packing could be obtained in the same way as has recently been found for virus crystals<sup>(26)</sup>.

For polydispersed systems the same type of information can be obtained provided measurements are made over a large range of momentum transfer and a model for the particle size distribution can be fitted. At the technical level of application, some results can be obtained by assuming a crude distribution, as has been done in the present work, and characteristics of the colloidal dispersion and of the adsorbate suggest the mean scattering length density, and hence the true particle density. The degree of packing of surfactants and qualitative changes in the nature of the peptisation as a function of concentration of the peptising agent are reasonable goals in the short term.

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# CAPTIONS TO FIGURES

Figure 1	Comparison of the normalised radial distribution
	function (full line) with a horizontal section of the
	scattering pattern through the 23rd row of detector
	elements and with two vertical sections through the
	32nd and 38th columns.
Figure 2	Guinier Plots for 0.2% wt/vol polystyrene sol for
	various H <sub>2</sub> 0; D <sub>2</sub> 0 mixtures.
Figure 3	Variation of the square root of extrapolated intensity
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	$H_2^0$ and $D_2^0$ .
Figure 5	Determination of the contrast matching point for
	unpeptised Vulcan III sol in $H_2^0/D_2^0$ . The very low
	angle pattern points come from subtracting the high
	angle Guinier line at low Q to give an approximately
	linear second region.
Figure 6	Guinier plots for 2% carbon sol peptised with sodium
	dodecyl sulphate in various concentrations of $H_2^0$ and
	D <sub>2</sub> 0.
Figure 7	Determination of the contrast matching point for
	peptised Vulcan III sol in $H_20/D_20$ . The very low angle
	points were derived as in Figure 5.
Figure 8	Zimm plots for peptised Vulcan III dispersion concentra-
	tions between 0.35% and 10% by weight in 7.5% $D_2^0/$
	92.5% H <sub>2</sub> 0.
Figure 9	Dependence of the squared radius of gyration, $R_{g}$ on
	the contrast for (a) unpeptised and (b) peptised
	Vulcan III sols.





FIGURE 2



In (SCATTERED -INTENSITY)	7 6 5 4 3 2 1 0 -1						۲ ۵ ۹					• • •	•	• •		•	■ • •			0 30 50 60 00 00 00	°/。 °/。 °/。 ¢/。 ¢/。	)))))))) • •	
	0	1		100				4	200	0				3	300	)			40	00		50	0
			(	(мо	M	EN	ΠL	M	•	TF	RA	N	SF	E	ج) <sup>:</sup>	2	[A	-2	, 10	-7	]		

2% VULCAN III IN  $H_2Q/D_2Q$  (POSITIVE CONTRAST)





۰. · · ·



2 % VULCAN III IN H20/D20 WITH S.D.S

FIGURE 6

FIGURE 7



FIGURE 8



s.D.s

ZITIM PLOT FOR VULCAN HI WITH

CONCEMBRATEON / SCATTERED INTENSITY





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#### APPLICATIONS OF NEUTRON SCATTERING IN MATERIALS SCIENCE

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## ABSTRACT

It can be expected that the application of neutron scattering in. materials science will become more widespread with increasing interaction between neutron scatterers and materials scientists. Several potential growth areas are identified, e.g., structural analysis of polycrystalline and multi-phase systems as well as amorphous substances; small-angle scattering analysis of extended defects such as vacancy clusters, precipitate zones, etc., including the kinetics of their formation, in crystalline and vitreous substances; and dynamic effects near phase transformations. Small-angle scattering methods are illustrated by two examples, the formation of voids in  $\beta'$ -NiAl and the decomposition of Al-Zn alloys.

#### INTRODUCTION

So far, neutron scattering has yet to prove its usefulness and its wide range of possibilities for major areas of materials science although some efforts, especially on polymers and on topics related to energy storage and superconductivity have been initiated a few years ago at several neutron beam research centers. As, with the existence of the Institut Laue-Langevin (ILL), intense neutron beams and various neutron scattering instruments have become available to the scientific community, the number of problems that can be studied successfully has increased considerably, and the substantial interest of materials scientists in the possibilities of neutron scattering has become an irreversible fact [1]. At present, the ILL faces requests for beam time exceeding the available time by factors of two to three on average, and an increasing demand in areas that have only recently begun to include neutron scattering as a research tool - as is the case in materials science.

It is not always the high neutron flux that makes the ILL attractive (although a high flux always represents an additional convenience) but rather frequently, the instrumentation of the ILL is either unique or thought to be unique, and the mode of access is known and not too difficult. It is very desirable that other neutron scattering facilities become available to interested scientists (similar to the spectrometers at Harwell, Great Britain). A first step for Western Europe has been made by compiling information on existing facilities [2] in Austria, Belgium, Denmark, France, Germany, Great Britain, the Netherlands, Norway, Sweden, and Switzerland. But beyond the possible use of existing devices, present and future research centers will have to provide a progressive improvement and development of scattering instruments and related facilities.

Neutron scattering will become a more commonly used method in applied research if there is more frequent interaction between the "heutron scatterer" and the scientific community involved in applied research. It seems reasonable to expect the highest degree of success where both sides are interested and contribute their special knowledge and competence to a project. In particular, materials science oriented research very often must resort to many different methods on samples frequently treated in rather intricate ways. Facilities for this type of work are not commonly available at neutron scattering centers. The resident neutron scientists, on the other hand, will usually have a high level of expertise in obtaining good scattering data, but the evaluation and interpretation will require co-operation of all parties involved. Different mechanisms are conceivable to obtain this desirable interaction, and these are presently being discussed in connection with present and future neutron scattering centers where a "user programme" is offered as a "service" to other laboratories.

There are many problems in materials science where neutron scattering can yield valuable additional or even unique information, and in the following, a few of these areas will be identified, mainly based on the author's own experience or observations at ILL, and with some emphasis on research topics which do not necessarily depend on the availability of a very high neutron flux.

## STRUCTURE

Currently, neutron crystallography is predominantly concerned with solving the structure (and spin distribution) of new substances in the form of powders or single crystals. For the materials scientist, crystalline substances are often more puzzling in polycrystalline form or as a mixture of different phases (obtained by phase separation or compaction). Neutrons offer, for the great majority of interesting materials, a fundamental advantage over X-rays as samples can be studied in bulk form, and there are no complications related to form factor corrections.

The analysis of textures of polycrystalline materials (after solidification, plastic deformation, recrystallisation, etc.) should greatly benefit from these facts, and the ease with which samples can be exposed to different temperatures, magnetic fields, pressures, stresses, etc., makes it possible to study the influence of such parameters in situ. The efforts made in this field have recently been reviewed by Szpunar [3].

In multi-phase materials, some problems of interest are : orientation relationships in systems exhibiting displacive transformations (habitus planes) or phase separation by diffusion controlled mechanisms, structure and composition of precipitates (where isotopic replacement may also be helpful), influence of other parameters (pressure, stress, temperature, etc.) on structure and orientation of precipitates, residual strains in composite materials. As a recent example in this field we quote the work of Cowlam et al. [4] who measured the interlayer spacings  $c_0$  of graphite nodules in a high-carbon steel (containing Si) in two different stages of graphitisation (with and without stress relief in the matrix). From the difference in  $c_0$ , corresponding to a compression of about 0.4 % along this axis for graphite formed without stress relief in the surrounding matrix, it was possible to estimate the pressure inside the nodules.

Precision measurements of lattice constants using single crystals, and the detailed analysis of the shape of Bragg peaks (Huang scattering, side bands, etc) are of special interest in the study of point defects and phase transformations. Lattice parameter changes can be measured with considerable accuracy ( $\sim 10^{-6}$ ) using neutrons [5], and rapid progress is being made in providing special equipment for very high temperatures [6] and high pressure [7]. Neutron diffraction topography can supplement crystallographic work and provide information on subgrain boundaries, magnetic domains, and isolated defects (see Schlenker and Baruchel [8] and references therein). Vitreous systems, metallic and non-metallic, are the subject of very active research today [9, 10]. Neutron diffraction will be particularly helpful in the analysis of amorphous ferromagnets, as large amounts can now be produced, but also in distinguishing between different structural models quite generally [11]. Although polarized neutrons will be more advantageous [12] for magnetic work (but high neutron flux would then be required), magnetic contributions to unpolarized neutron diffraction can also yield useful information on the spin distribution in comparison with the distribution of nuclei. Thus, in the relatively simple amorphous ferromagnets Co-P (prepared by electrodeposition with Co concentrations around the eutectic composition of 19 at.%), it was found [13] that Co nuclei and magnetic moments have the same distribution and that any magnetic fluctuations must be weak.

## INHOMOGENEITIES

Under this term, we summarize here structural features in crystals. vitreous and liquid substances that exceed atomic dimensions in at least one direction. Point defects, very small clusters and short-range order have been discussed previously [1, 14, 15], and we want to concentrate on larger inhomogeneities in the range of 10 to about 1000 Å which are most important in controlling many properties of materials, e.g., mechanical strength of alloys, critical currents in hard superconductors, coercive forces in magnetic materials, optical properties of glasses, etc. Neutrons will reveal fluctuations in scattering length density on a scale of 10 to 1000 Å in real space by diffraction with correspondingly small momentum transfer, i.e., small-angle scattering. It can be anticipated that smallangle neutron scattering will become one of the most outstanding research tools for materials scientists, as it is and will be instrumental in studying polymer conformation, decomposition of alloys and glasses, clustering of point defects and spins, dislocation arrangements, pores and microcracks, critical fluctuations, even interfaces and surfaces. The importance of this method is also documented in several other contributions to this conference, and the paper by Galotto et al. [16] describes technological studies on high temperature alloys using a small-angle scattering instrument at a rather small reactor.

In order to illustrate the type of information that can be obtained from small-angle neutron scattering, two research programmes currently performed at ILL in collaboration with laboratories in the three partner countries will be presented.

The first example stands for problems that can be easily studied at room temperature, i.e., the thermal treatment that is important in such a case can be carried out separately, before the small-angle scattering is measured. The stoichiometric  $\beta'$  compound NiAl can retain a high concentration of vacancies when quenched from about 1600°C to room temperature [17]. No major change of vacancy concentration or arrangement can be observed at room temperature but if such samples are heated to above ~ 300°C, vacancies will cluster and finally form rather large, facetted voids which can be easily observed in the electron microscope. Small-angle neutron scattering is used to get reliable information on the early stages of vacancy clustering at different temperatures and precise values on the number and average size of voids, also at later stages where the shape is known from electron microscopy, Results obtained on the instrument D11 at ILL for some of the single-crystalline samples are plotted in Fig. 1 as a function of the scattering vector Q =  $4\pi \sin \theta / \lambda$  where  $\theta$  is half the scattering angle and  $\lambda$  the wavelength of the incident neutrons. Macroscopic cross-sections were calculated using vanadium as a reference scatterer (there may be some deviations at the smaller angles as there was some small angle scattering

for vanadium, too), and all plotted points correspond to radial averages taken at 1 cm intervals on the two-dimensional position-sensitive detector of D11 as long as there was no measurable anisotropy of the scattering pattern. From Guinier plots of the data shown in Fig. 1, one further obtains the radii of gyration Rc indicated in the figure. It can be seen that the as-quenched sample shows already a measurable small-angle scattering which does not, however, reveal any facetting, and gives no well-defined void size. Subsequent aging leads to a considerable increase in small-angle cross-sections and void sizes. Facetting leads to anisotropic scattering at somewhat larger angles, as shown in Fig. 2 for the sample aged at 400°C. In this case, anisotropy is observed for  $Q \gtrsim 0.04$  Å<sup>-1</sup>. The pattern reflects the projection of {110} facets in a {110} plane with possible trunca-tion of the voids in <111> directions. This research [18] will continue and results combined with transmission electron microscopy will make it possible to better understand the physical properties of the material. Similar phenomena as reported here on thermal vacancies also occur after irradiation of materials. Facetted voids in neutron-irradiated aluminum single crystals have been studied with small-angle neutron scattering by Hendricks et al. [19] using the Jülich instrument, and an investigation of radiation damage in GaAs single crystals has recently been terminated [20]. revealing the shape of the oriented displacement spikes after fast neutron irradiation.

Obviously, it is very convenient if measurements can be performed at room temperature as there will be no special sample containment, at least for solid samples. As almost all substances exhibit more or less intense small-angle scattering, data reduction is greatly simplified if there are no window effects. There are, however, cases, most prominently in the study of alloy decomposition, where either a rapid quench to temperatures well below room temperature for subsequent measurements in a cryostat, or in situ measurements at the temperature of interest are indicated. The former method will be limited by available quench rates and undesirable byproducts whereas the latter will work well for kinetic studies in a temperature range where the process to be studied is slow enough so that significant scattering data can be accumulated in time intervals smaller than the time constant of the process. Both methods have been used in an attempt to contribute towards an understanding of the kinetics of zone formation in Al rich Al-Zn alloys. This binary system has been the subject of several recent papers where different methods have been applied to determine the position of the coherent spinodal. Fig. 3 shows part of the Al-Zn phase diagram with the stable and the metastable (Guinier-Preston zone) solvus. The theoretically expected position of the spinodal and the points suggested by Junqua et al. [21] do not agree very well at lower concentrations. Our neutron scattering results for aging of an Al-12 at. % Zn alloy at room temperature (scattering measured at 4.2 K) [22] and at 175°C (in situ aging) [1] reveal interparticle interference effects at both aging temperatures, as the small-angle scattering intensity exhibits a maximum at angles different from zero in both cases. At room temperature, for a sample quenched from 380°C, this peak position can be seen to move from  $Q_m = 0.12 \text{ Å}^{-1}$  to  $Q_m \approx 0.04 \text{ Å}^{-1}$ during the first 100 min of aging with a simultaneous increase of the radius of gyration from about 4 Å (measured after only a few minutes of aging) to 35 Å [22]. At 175°C (corresponding to the cross in Fig. 3), a slowly cooled alloy shows a peak at  $Q_m \simeq 0.02$  Å<sup>-1</sup> that is only slightly shifted to smaller angles for aging times exceeding about 20 min. At higher aging temperatures, the kinetics of decomposition is considerably slower, and the Poitiers group [21, 23] infer that the fast kinetics and the appearance of a small-angle scattering peak correspond to spinodal decomposition whereas phase separation by nucleation and growth occurs at

higher temperatures. Some of the arguments are based on results in the more thoroughly investigated alloy AL-6.8 at.% Zn [23], and we have recently [24] carried out small-angle neutron scattering experiments on this alloy aged in situ at  $T \ge 133^{\circ}$ C, a temperature that is definitely above the maximum spinodal temperature (132°C) proposed by Junqua et al. [21] Fig. 4 shows the scattered intensity as a function of Q<sup>2</sup> for different aging times. Radii of gyration R<sub>G</sub> can be extracted from these plots, and the values are also given in the figure. There is some precipitation after 13 hours but the most important change occurs between 15 and 30 hours. At the position marked by an arrow, deviations from the expected single-particle scattering function (which yields a straight line down to Q = 0) are found and must be taken as evidence for interparticle interference [24]. At least one of the criteria offered for a distinction of different modes of decomposition must therefore be modified.

These examples will have given some indication of the possibilities of small-angle neutron scattering. There are many crystalline systems where the details of phase separation are not well understood. Favorable scattering contrasts often exist even for much lower incident neutron intensities, and of course, magnetic domains, e.g., in amorphous magnets, and phase separation in vitreous systems [10] can also be examined. Concerning the latter topic,  $SiO_2-Al_2O_3$  [25] and silicates containing titania [26] are currently being studied. In both cases, it has been possible to prepare and investigate sets of samples corresponding to different stages of decomposition.

# PHASE TRANSFORMATIONS

Apart from the more "macroscopic" aspects of the products of phase transformations as discussed above, there is considerable interest in the fundamental microscopic mechanisms and the physical origin of phase transformations, and neutron scattering can be considered a very important technique in this field.

As the concept of the soft mode is becoming more familiar to materials scientists [27], the role of phonons in the more difficult first-order structural transformations will be analyzed more closely. The neutron scattering experiments of Axe et al. [28] relating to the  $\omega$  transformation in Zr-Nb and of Mori et al. [29] on AuCuZn<sub>2</sub> (which undergoes a martensitic phase change from a b.c.c. to a f.c.c. based structure' show striking phenomena that are difficult to interpret in detail, but will stimulate progress in the microscopic explanation of displacive transformations[30,31]. It has also been suggested that the soft-mode concept could prove useful in the study of spinodal decomposition [27, 32].

Critical scattering of neutrons, associated with magnetic and structural transformations has been observed, e.g., in Au-Fe alloys near the onset of ferromagnetism [33], in A&-Zn [34] and Nb-H [35] when approaching the temperature of the coherent spinodal at the critical composition. Some of these experiments require rather low momentum transfers, i.e., long neutron flight paths or very slow neutrons. There remains, however, a wide variety of critical phenomena that can be investigated with current instrumentation. The influence of parameters other than temperature on critical scattering in Ni is being studied by Stierstadt and co-workers [36, 37]. Whereas the effects of uniaxial stress on the critical fluctuations are very difficult to reveal even with the D11 instrument at ILL [36], the influence of dislocation networks [37] should be more easily detectable.

#### CONCLUSIONS

This paper is not to be considered a complete review of applications of neutron scattering in materials science. It is hoped, however, that the potential of elastic and inelastic thermal neutron scattering in this scientific domain has been indicated. The study of problems similar to those described above represents a good example of interdisciplinary cooperation where the sometimes very complex "microstructure" skillfully prepared by the materials scientist and characterized with his more classical research tools presents a challenge to even the most experienced neutron scatterer who has in the past proven the value of his methods in studying more ideal substances such as good single crystals and simple liquids.

#### ACKNOWLEDGMENTS

Discussion with Drs. J. Blétry, P. Guyot, G. Laslaz and A. Wright are gratefully acknowledged.

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FIG. 1. Isotropic macroscopic small-angle neutron scattering cross-sections as a function of scattering vector Q for single crystals of NiAl quenched from 1600°C to room temperature and heat-treated as indicated.



FIG. 2. Iso-intensity lines on the two-dimensional position sensitive detector (of the small-angle neutron scattering instrument D11 at ILL) corresponding to the scattering from facetted voids in NiAL.



FIG. 3. Partial phase diagram of AL-Zn. The calculated coherent spinodal (dashed curve) and the suggested experimental spinodal temperatures are shown [21].



FIG. 4. Small-angle scattering intensity as a function of the square of the scattering vector for Al-6.8 at.% Zn aged in situ at  $T \ge 133$ °C for 13 to 39 hours. The radii of gyration R<sub>G</sub> obtained from these curves are also given.
## ON TEXTURE STUDIES BY NEUTRON SCATTERING

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In recent years scientific communities have paid ever more attention to problems of applied character. This holds also for people working in the field of neutron scattering.

A problem of general interest which can be studied by neutron scattering methods is the texture formation in metals and alloys. Neutron scattering is preferable to X-ray techniques when information on the bulk is needed, when large grains are present in the material or when magnetic properties are studied. The function which is needed for describing the studied problem is the spatial distribution of scattered neutron intensity for monochromatic ingoing neutrons fulfilling Bragg's law for a particular scattering plane of the crystal in question. The function can be measured by fixing the detector at an angle satisfying the law

 $2d \sin \theta = n\lambda_0$ 

where d is the distance between the selected planes,  $\vartheta$  is the scattering angle,  $\lambda_0$  is the ingoing neutron wave-length and  $n = 1, 2, 3, \ldots$ , while the sample is being rotated into all possible directions.

The mathematics used in this method are well known. Therefore we do not want to go into details, such as corrections for apparative functions and for crystal properties. Moreover, wit is easy to prove that in the case of spherical samples these corrections are of minor importance.

A special problem, formation and properties of the texture in ball bearings made of steel was chosen to illustrate the possibilities of neutron scattering methods. Since definite conclusions can be drawn directly from scattering data, for illustration the distributions of scattered neutron intensity obtained for samples rotating around fixed axes are presented. These measurements are part of a systematic study which is still in progress.

The original aim of our work was to clear the problem of ageing of ball bearings. For this reason new, used and artificially fatiqued balls were investigated by neutron diffraction using the /110/ reflection of  $\propto$  -Fe. Fig.l shows the intensity of this reflection. The slightly higher and narrower intensity distribution is significant for new balls in all our data as compared with the data on used balls. This is an indication of the change in mosaic structure during ageing.

In order to study the expected changes in the texture of the balls, rocking curves were measured. A strong anisotropy was found in the scattered intensity also in the case of new balls. The anisotropy showed a 60° periodicity, as to be seen in Fig.2a. By changing the axis of rotation, the intensity distribution could be symmetrized /Fig.2b/ i.e. the axis of symmetry could be found. If the ball was rotated around this axis, the periodicity changed to 90°, as shown in Fig.3, but with a smaller modulation depth. In contrast with expectations, ageing did not lead to marked changes in the scattering pattern /see Fig.4/. In some cases the 90° periodicity curve changed to a greater extent, however, even this change was not always observed. Artificial fatiguing was carried out in the geometry shown in Fig.5. The studied balls were turned during this treatment to a definite orientation with the 60° symmetry axis in the z-direction. The equivalent rocking curve for a perpendicular axis where 90° periodicity can be observed.

The experimental results suggest that the observed texture can be connected with the technology of ball production. For the manufacturing of balls first a wire is pulled from steel, then this wire is chopped into pieces and pressed in the direction of the wire axis to form balls.

In order to clear the formation of texture in the production process, chopped wires made of D8 steel were also studied by neutron diffraction. As to be seen in Fig.7,  $60^{\circ}$  periodicity of the rocking curve could be observed if the axis of the wire was rotated in the scattering plane. The  $90^{\circ}$  periodicity texture could not be seen in this case, as apparent from the same figure. This texture is formed later during the pressing of the balls.

The non-isotropic distribution of crystallites in the studied samples results in a non-isotropic abrasion and, as shown in Fig.6, in a preferential orientation of the balls. This fact could be observed also from the previous experiments. The geometry shown in Fig.5 uned for fatiguing led to an annular wear on the surface of the balls. The symmetry axis /60°/ was observed to be perpendicular to the plane of this wear. This implies that the texture of balls in ball bearings may lead to non-isotropic wear and therefore to a shorter lifetime.

Summarizing, the results show that neutron scattering seems to be a potential tool for the study of practical problems similar to that discussed in the present report.

## FIGURE CAPTIONS

- Fig.l Intensity of the /110/ reflection of new, used and fatigued balls.
- Fig.2 60<sup>0</sup> periodicity of neutron intensity when rocking the sample:
  - а.
  - b. :the symmetry axis perpendicular to the scattering plane.
- Fig.3 90° periodicity of scattered intensity /new balls/.
- Fig.4 60° periodicity /a/ and 90° periodicity /b/ after ageing.
- Fig.5 Lay-out of fatiguing.
- Fig.6 The fatigued balls turned into definite orientation with the 60<sup>0</sup> periodicity axis in the z-direction /a/. The intensity for rotation the sample around a perpendicular axis is also given /b/.
- Fig.7 Rocking curve for cilinders of & -Fe before pressing balls from them.









ROCKING ANGLE

FIG. 3



FTG. 4



FIG. 5



(STINU (ARBITRARY INTENSITY

FIG. 6





# SUMMARY OF MITRE REPORT: "APPLICATIONS OF HIGH FLUX NEUTRON SOURCES IN TECHNOLOGY AND BLOLOGY"

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Argonne National Laboratory is planning to construct an intense pulsed neutron source to be used as a new research tool in basic and applied research in the fields of materials science, chemistry and biology. As part of an effort to explore the base upon which neutron research stands, in early 1976 Argonne commissioned the MITRE corporation to conduct a survey of the possible uses of neutron sources in technology and biology. The report was completed in November 1976 and a copy may be obtained by writing to Dr. J.M. Carpenter, Solid State Science Division, Argonne Nat. Laboratory, Argonne, Illinois 60439, USA. As a first step a number of documents containing information on advantages and uses of neutrons was assembled and sent to a variety of research laboratories funded by U.S. industrial firms and government. At the same time a review was made of European attempts to diversify neutron research. In particular, at Harwell a ve-year effort has been made to encourage industrial circles to use the government's research reactors. Although slow at first, the effort is beginning to reap benefits, with about 40% of the effort at the reactors now having a direct link to industry or technological departments of universities. A number of responses were received from US industrial firms and gov. departments not presently engaged in neutron research, and these were followed up with more information and a workshop held in Sept. 1976.

The main body of the report contains tables and responses by companies and agencies identifying problem areas in which neutrons might have application. The responses, in general, fall into one of three categories; Materials Science, Chemistry, and Biology. No attempt will be made here to cover even a

representative from each subsection within a group, since the Report contains extensive tables. A few general examples are all that this short summary can attempt to cover.

1) Materials Science. Problems here include areas such as new alloy development, structural materials for new energy technologies, fusion reactor materials, radiation damage in metals, embrittlement, cracks, voids and corrosion in different environments. For example, the Martin-Marietta company has an interest in the correlation of material properties with the structure of Ti  $_{X}^{V}(1-x)^{C}$ . Other problems concern the electrical and electronic industries, such as structural integrity of semiconductors, ceramic materials, amorphous films.

In the field of Materials Science a great number of problems clearly are suitable to the technique of small-angle and wide-angle neutron diffraction. Reference should be made to the contributions of Walther, Kostorz, and Schelten in IAEA report.

- 2) Chemistry. In this field the industrial problems that might benefit from neutron research concern catalysis, bonding forces, i.e. cure state of adhesives, radiation damage, emulsions, and the dynamics of chemical reactions. Two fields seem particularly appropriate, polymer chemistry, and the study of bound and free water. Both these problems are being studied extensively at various neutron installations and a direct contact between this work and industry already exists.
- 3) Biology. The report states that there is general interest in using neutron sources to determine the structure and properties of molecules in biological materials, major areas of research include; information of nuclease fragments, properties of fibrous muscle proteins, protein structure of ribonuclease, investigation of nucleic acid, and structure of viruses. In this section most of the organizations contacted were non-profit institutions (e.g. government

or university research hospitals) and their main interest is thus in basic research. However, many areas are associated with applied topics and this application is quite new for neutrons.

A second section of the report is concerned with the possible use of neutrons in energy related programs. This is a direct response to the mission of the Energy Research and Development Administration (ERDA), which also operates the National Laboratories in the US. An examination of these problems shows, as expected, that there is an overlap between ERDA's objectives and the problems stated by the industry as applicable to neutron scattering. However, some additional problems, such as those connected with fossil fuel utilization, magneto-hydrodynamics, coal gasification, storage batteries, supercon sting systems, and nuclear fuel, also appear. In many of these the problems center on materials limitations and there, again, small-angle and wide-angle neutron diffraction appear to be of direct use. Another area of importance is the measurement of fast diffusion rates (principally H diffusion) and this subject is already covered in the IAEA report by Springer and Skold. In nuclear fuels (and indeed in many industrial problems involving complex installations) neutron radiography is especially useful and is already routinely used.

## Conclusions

During the study period the Mitre Corporation contacted 137 organizations, 81 from the private sector and the remaining 56 being government laboratories and universities. (This, of course, excludes the "regular" users of neutrons and those universities etc. who have staff members involved in some aspect of neutron research in basic science). Positive interest in using high flux neutron sources was indicated by 23 sources, 19 from the private sector,

4 other. Some interest, and the desire to be kept informed, was expressed by an additional 22 sources. 13 sources expressed no interest and the rest did not respond.

It should be stressed that this contacting, and searching for possible neutron applications, was conducted by people with no expertise in neutron research (Although the initial package was prepared by ANL staff and questions were referred to ANL.) The workshop, an account of which will appear separately, was a point of direct contact. Nevertheless, in spite of this problem and the short period of time available to put the report together, it does contain a number of important conclusions and recommendations.

The report demonstrates that a strong interest exists in using neutrons in certain areas of applied research. In addition to showing the existence of substantial interest in neutron research in US industry and other organizations, the report is useful in establishing : (1) The need to educate potential users regarding neutron techniques and (2) the need to organize within each neutron source facility a staff to take care of the problems of outside users, and to build and operate the equipment suited to their research needs.

## NEUTRON SMALL ANGLE AND DIFFUSE SCATTERING TOWARDS APPLIED RESEARCH

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## Abstract

A variety of favourable neutron properties is the basis on which neutron scattering could become a helpful tool to solve applied research problems and to test materials nondestructively. These properties are the low absorption of thermal and subthermal neutrons, the irregular change of the nuclear scattering length from atom to atom and from isotope to isotope, the existence of a magnetic interaction and the suitable wave length range between 1 and 20 Å which allows to measure fluctuationlengths ranging from 0.5 Å to 5000 Å. A broad field of applied research can be expected for SANS since in the fundamental research this technique had been successfully used to investigate dislocations, grain boundaries, voids, precipitates, segregations, spinodal decompositions, solutions, suspensions and magnetic fluctuations as Bloch and Neel walls, magnetic precipitates, magnetic phase transformations and flux lines in type II superconductors.

As typical examples four shall angle neutron scattering problems are reviewed. They are related to applied research in so far as either commercial products or technologically important phenomena are investigated. In these examples the ragnetic haronesses of Ticonal and Koerflex, void parameters in neutron irradiated Al, dislocation densities in Ni and Cu, and the pinning mechanism in superconductors are investigated. Finally beam time and the proportionate costs are estimated for a reference scatterer demonstrating that the use of neutrons can even be inexpensive.

#### Introduction

During the last ten years, neutron small angle and diffuse scattering has been developed into an important method for the investigation of structural problems. A large number of problems of fundamental research has been successfully investigated by these techniques using the instruments at the HFR in Grenoble or at other less powerful reactors. The high amount of small angle neutron scattering (SANS)' experiments has been reviewed recently [1,2]. Solid-state investigations by diffuse neutron scattering (DNS) were reviewed in [3,4,5]. These reviews demonstrate that the field of application is wide for both techniques and is based on a few very favourable properties of neutron interaction with matter.

In contrast to this broad application in fundamental research up to now only a few problems which are of technological importance have been investigated by these neutron techniques. This situation is partly caused by the circumstance that the people who are dealing with technological problems have not been informed well enough about the characteristic features of these techniques. With the present contribution we hope to improve this situation.

We see two possibilities for utilizing both neutron scattering techniques in technology: (i) to solve applied research problems and (ii) to test materials nondestructively. Because of the favourable transmission properties of neutrons the second possibility seems to be very promising. First steps in this direction are done in the FIAT-laboratories [6,7] where turbine blades, various types of steels and other materials have been investigated in order to correlate small angle scattering parameters with technologically important material parameters. However, even from this laboratory no routine control by use of SANS is known to us. On the other hand examples exist for the use of neutron small angle scattering in applied research problems. By this we mean that either the investigated materials are of technological importance or that the subject studied with a model substance is technological. We will present in this paper four examples of SANS in applied research. This

part is preceded by a brief review of the most important properties of neutron interaction with matter, including a challenging proposal for the use of diffuse neutron scattering.

In the last part of this paper we will discuss the restricted availability of neutron beams and estimate the beam-time and cost to measure the SANS pattern of a well-defined, representative reference scatterer. We hope this estimate will encourage people to consider more seriously SANS and DNS as a useful tool to solve technological problems.

## Neutron Properties

Thermal and subthermal neutron beams easily penetrate matter of cm thickness [8]. For instance, for customary steels based on Fe or Ni the absorption is such that a neutron beam of 6 Å wavelength is attenuated to about 50 % in a 1 cm thick sample. The absorption is considerably larger in Co rich alloys. In such alloys a 50 % attenuation of a 6 Å neutron beam is already achieved over a thickness of 1 to 2 mm depending on the exact composition of the alloy. In this case one may take into consideration that the absorption cross-section is inversely proportional to the neutron wave length and that therefore at least for small wavelength neutrons the necessary penetration may be achieved. As a second example it is mentioned, that for the Aluminum alloys in use the penetration depth of 6 Å neutrons is exceptionally more than 1 cm.

This low absorption of thermal and subthermal neutrons is for various reasons required in order that neutron scattering can become a material testing tool. Certainly, because of high penetration a destructive thinning of the investigated material is not required. Besides this, the illuminated volume will be in the order of a few cm<sup>3</sup> and therefore surface effects are usually unimportant. As a consequence polishing, etching, or any other surface treatment can mostly be omitted. In addition, it should be noted that because of the large illuminated volume the scattering data represent a good bulk average of the investigated material.

In the following we will describe the structural changes which can be investigated by neutron scattering. One will see that almost every structural change is coupled with a fluctuation of a scattering length or of a scattering length density and gives therefore rise to neutron scattering. This neutron scattering can be measured either in a DNS or a SANS facility provided that the characteristic lengths for these fluctuations are in the range between 0.5 Å and 5000 Å.

Typical problems investigated by diffuse neutron scattering are substitutional and interstitial defects, magnetic impurities or small clusters of these defects and of magnetic atoms [3,4]. For a statistical distribution of substitutional defects with coherent scattering length  $b_D$  in a host lattice of atoms with coherent scattering length  $b_H$  the scattering cross-section per atom is given by

$$\frac{\mathrm{d}\mathbf{G}}{\mathrm{d}\mathbf{Q}}(\mathbf{x}) = c (1-c) (\mathbf{b}_{\mathrm{D}} - \mathbf{b}_{\mathrm{H}})^{2}$$
(1)

where c is the atomic concentration of the defects. For the assumed statistical distribution of defects the scattering cross-section is independent of the scattering vector  $\mathbf{x} =$  $2k_{o} \sin \frac{\sqrt{2}}{2}$  where k is the wave vector of the incoming neutron wave and  $^{\mathfrak{H}}$  is the scattering angle. One sees that the magnitude of the defect scattering is essentially determined by the difference of the scattering lengths of the two constituents. In fig. 1 scattering lengths of atoms and isotopes are shown as a function of the atomic weight. One sees that the scattering lengths vary irregularly and drastically from atom to atom and even from isotope to isotope. Because of this irregularity the scattering length difference of two components frequently is above 0.5  $10^{-12}$  cm. About this difference is required to measure the Laue monatoric scattering of an alloy component of 10 % concentration. For this estimate a representative background of an incoherent scattering of 500 wharn has been assumed.

Certainly, there are practical cases known in which the Laue scattering is stronger and the background weaker, Thus,

we get the opportunity to investigate structural changes in materials via the diffuse scattering, since any deviation from the initially assumed statistical distribution causes structure in the  $\times$ -dependence of the scattering cross-sections.



Fig. 1: Nuclear coherent scattering lengths b and some magnetic scattering lengths  $b_{mag}$  for neutrons as a function of atomic weight smaller than 100. X-ray scattering lengths are shown as dashed line.

Such frequently occurring structural changes are based upon formations of small clusters or upon ordering phenomena. Despite these encouraging aspects so far, due to our knowledge diffuse neutron scattering has not been used as a material testing tool nor in an applied research project. Hence we will suggest one special project and will thereafter discuss important features of small angle scattering.

Very soft magnetic materials are special iron-nickel alloys containing about 50 to 80 % Ni. They are called Permalloys and are chiefly characterized by very high permeability at low applied fields [9]. At and near the composition of FeNi<sub>3</sub> long range ordering frequently occurs below a temperature of 503°C. The magnetic properties of the ordered alloys are inferior to those of the disordered. Indirect evidence for the influence of ordering on the permeability is shown in fig. 2 where the maximum permeability  $\mu_m$  is plotted versus the Ni-concentration. One sees that  $\mu_m$  of the alloys with 78 % Ni concentration is very sensitive to the heat treatment. In addition, by x-ray and neutron diffraction it was shown that long-range order occurs by slow cooling. However, it is not known how strongly



Fig. 2: Maximum permeabilities of iron-nickel alloys.

a remaining short-range ordering in the quenched alloys limits the permeability. Diffuse neutron scattering from Permalloys could provide the necessary information which should be correlated with magnetic properties in order to estimate an upper limit for the permeability and to find ways to approach these values. The diffuse scattering from Ni<sub>3</sub>Fe is unfortunately very weak because the scattering lengths of natural iron and nickel are similar. Their difference is about 0.1  $10^{-12}$  cm. This shortcoming can however effectively circumvented if the neutron experiments are performed with alloys of Ni<sup>62</sup> instead of natural Ni. In this case the scattering length difference is 1.6  $10^{-12}$ .

In SANS experiments one observes the scattering of thermal or subthermal neutrons from long wave length fluctuations of

mass density, chemical composition, isotope distribution, and of magnetization. The scattering occurs at scattering angles of the order of  $\lambda/\phi$  where  $\lambda$  is the neutron wave length and  $\phi$ the characteristic length of the long wave length fluctuation, e.g. the diameter of a precipitate. Since in long instruments [10]  $\vartheta$  can be varied from 10<sup>-4</sup> to 10<sup>-1</sup> radian fluctuations ranging from 10 to 5000 Å can be investigated. For a further discussion of the magnitude of the scattering cross-section we assume a two phase system of statistically distributed particles of volume  $V_1$  and scattering length density  $\rho_1$  in a matrix of scattering length density  $\rho_2$ . For this simplest case the differential scattering cross-section per unit volume is given by

$$\frac{d\Sigma}{d\Omega} = n_1 v_1^2 (\rho_1 - \rho_2)^2 |F(x)|^2$$
(2)

where  $n_1$  is the number density of particles and  $F(\chi)^2$  is the particle form factor normalized to 1 at  $\chi = 0$ . A useful relation is  $p = n_1 \vee v_1$  with p the volume fraction of particles. One sees that any two phase system gives rise to small angle scattering provided that  $\rho_1$  differs from  $\rho_2$ . This can occur due to a mass density fluctuation in chemically homogeneous systems produced by the strain field of dislocations, by grain boundaries, by voids, cracks and crazes. In more than one componental systems  $\rho_1$  can differ from  $\rho_2$  due to composition fluctuations caused by precipitation, segregation, or spinodal decomposition and in liquids by dissolved molecules or suspended particles. Examples of two phase systems with different  $\rho_1$  and  $\rho_2$  due to isotope fluctuations are, as mentioned above, mixtures of protonated polymers with a few percent deuterated polymer molecules. Such mixtures have been deliberately produced in order to investigate the configuration of the polymer molecules via the small angle scattering from the tagged molecules. Because of the magnetic interaction for magnetic atoms a magnetic scattering length and a scattering length density exist which are proportional to the magnetization and which depend on the angle between the scattering vector and the magnetization vector [11]. Hence,  $\rho_1$  and  $\rho_2$  can differ in a magnetic two phase system due to magnetization fluctuations with respect to

direction and magnitude. They are caused by magnetic precipitates in zero field or in saturation field, by Bloch and Meel walls, magnetic domains, flux lines in type II superconductors and by magnetic phase transformations.

All these different types of fluctuations usually have characteristic fluctuation lengths between 10 and 5000 Å which can be resolved in SANS facilities with high resolution. The huge number of various small angle scattering experiments done so far in Grenoble but also at other less powerfull reactors as they are in Jülich, Saclay and Munich has shown that one usually can measure within a few hours the small angle scattering patterns caused by these fluctuations [1]. The estimated time of a reference sample given at the end of this paper will confirm this conclusion, and should encourage people to consider SANS as a new tool in the applied research field.

## Applications of small angle neutron scattering

(I) One of the most important and frequently used hard magnetic materials is TICONAL. The good magnetic properties chiefly characterized by a (B H)  $_{max}$  value in the order of 100 KWs/m<sup>3</sup> have been achieved by various heat treatments. By these heat treatments needle-shaped magnetic precipitates with a prevered orientation of the needle axes are grown in a weakly magnetic matrix. The linear dimensions of the precipitates are diameters of about 300 Å x 300 Å x 1500 Å. Because of their small linear dimensions perpendicular to the field direction which is usually applied parallel to the prevered orientation of the needle axes it is presumed that the magnetization is reversed by homogeneous rotation. If furthermore it is assumed that magnetization reversal in a particle is not influenced by reversals in neighbouring particles one estimates for (B H)  $_{max}$  an upper limit which is about three times higher than the best value which is reached today [12].

Bitter patterns seen to indicate that the magnetization is reversed cooperatively within groups of particles. If that would be the case the estimate has no realistic meaning. SANS

experiments with TICONAL X single crystals have shown that in the demagnetized state correlations do not exist between the magnetization vectors of the particles, thus statistically for one half of all particles a magnetization reversal had taken place. Maier (1969) [13] obtained this result by comparing the scattering pattern of TICONAL X in a saturation field with that after demagnetization (see fig. 3). Combining both results obtained by the Bitter method and by SANS it is likely that cooperative magnetization reversals occur at the surface but not in the bulk and hence, the above estimate about the best (B H)<sub>max</sub> value in TICONAL is based upon correct assumptions, i.e. there is a realistic chance to increase the B H value of TICONAL.



Fig. 3: Contour lines of the correlation function of the magnetization as deduced from scattering at a Ticonal X sample in the magnetized and demagnetized state.

Much easier producable hard magnetic materials are vicalloys. These materials have (B H) walues of about 30 kWs/m<sup>3</sup>. The alloys consist mainly of Fe and Co with small concentrations of Cr and V. Millions of small magnets are produed every year out of Koerflex which is the German name of vicalloy [14]. However, the reason for the magnetic hardening of Koerflex achieved by annealing at  $500^{\circ}$ C for 2 hours after cold rolling is not satisfactorily known. Recently we performed SANS experiments on Koerflex in order to obtain more combined information on the metallurgical and magnetic properties of these alloys. It is the purpose of these experiments to understand better the complexity of these magnetic materials in order to suggest ways to improve their quality.

(II) In materials which are irradiated at 300 K in reactors with neutron fluences in the order of  $10^{21}$  neutrons per cm<sup>2</sup> voids are formed. A consequence of this void formation is a swelling of the material. Volume changes  $\Delta v/v$  larger than 10 % have been observed in high flux reactors at the highest fluences. This swelling causes serious problems for the construction of future reactors. Therefore projects have been started to produce alloys which are radiation resistant and which still have good mechanical properties. For such projects one needs a rapid and reliable method to determine representative parameters of the formation of voids. Those parameters are the number density of voids, their mean size and their total volume fraction (swelling). Representative values for all these parameters are directly obtained by a small angle scattering pattern measured for instance with neutrons. In addition, such a method is for various reasons superior to transmission electron microscopy (TEM) which is the method used so far to characterize the void formation. The main advantages are that after irradiation not any preparation of the hot samples is required and that good statistical average values are obtained since in the order of 10<sup>14</sup> voids are investigated in the scattering experiments. By TEM, however, after a proper thinning, for practical reasons only a few thousand voids can be counted. These considerations have been demonstrated to be valid by scattering experiments on neutron irradiated aluminum specimens [15]. Fig. 4 shows a Guinier plot of the small angle scattering patterns from voids in Al (swelling 0.8 %) measured in Jülich in less than an hour. In fig. 5 it is demonstrated that SANS, immersion density measurements and TEM gave the same values for the swelling.

(III) It is not only a tedious but also a delicate problem to determine in absolute units the number density of dislocations by electron microscopy. Early neutron scattering studies in Munich and in Jülich have shown that dislocation densities can be obtained by SANS. The results from these experiments are



Fig. 4: Guinier plot of neutron scattering data from neutron irradiated aluminum measured with three different detectors D1, D2 and D3.



Fig. 5: Swelling  $\Delta v/v$  versus specimen position in the irradiation tube as determined by small angle neutron scattering, transmission electron microscopy and by immersion density measurements.

summarized in fig. 6 where dislocation densities ranging between  $10^9$  to  $10^{11}$  cm<sup>-2</sup> measured in Ni and Cu were plotted versus the ratio T/G b where T is the shear stress applied during plastic deformation and b and G are the Burgers vector and shear modulus, respectively. Again, as in the void study one gets in a nondestructive way representative and good statisti-



Fig. 6: Dislocation densities in single and polycrystals determined by neutron scattering versus  $\mathcal{T}/(b \ G)$ .  $\mathcal{T}$  is the shear stress, b the Burgers vector and G the shear modulus. For further details see [1,16].

cal average values for a parameter by which the condition of a material is characterized.

(IV) Finally, we will refer to an example where a technologically immortant problem, the flux pinning in type II superconductors, is investigated in a model substance. Type II superconductors with very high upper critical fields are technically useful provided the flux lines can be strongly pinned. The effect of pinning is that up to a critical current density  $\delta_c$  transport currents can flow without energy dissipation. The methods used so far for investigating pinning mechanism were all based on the validity of the critical state model and gave on a rather indirect way information on the basic interaction force exerted to flux lines. By neutron diffraction from flux lines it was possible to measure the flux line bending caused by the basic interaction forces and to determine so rather directly these forces without using the hypothesis of the critical state model [13].

In fig. 7 the mean basic interaction force  $\langle f^2 \rangle^{1/2}$  as determined from neutron scattering data is compared with the



Fig. 7: Pinning forces as a function of the reduced flux density in Nb with Nb<sub>2</sub>N precipitates acting as pinning centers.  $\langle f^2 \rangle^{1/2}$  determined from flux bending measurements by neutron diffraction and k from volume pinning measurements.

maximum pinning force as determined from macroscopic data using the critical state model. The comparison gives us confidence in the hypothesis of the critical state model.

## Technical Remarks

The preceding two parts of this paper have shown that SANS could be applied to very different technological problems as a material testing method. Certainly there are some obvious difficulties to use a small angle scattering technique in such a way. They will be discussed now. The scattering experiments must be performed at research reactors with medium or even high flux of thermal neutrons. In addition, in many cases it is desirable that a cold source is installed in the reactor and that a very long instrument for high resolution and a multidetector for fast measurements can be used. Such a complete instrumentation exists only at very few places in the world and this

means that the application of neutron scattering involves usually a transportation over large distances. A powerful reactor with a good instrumentation which is solely used for material testing purposes is probably too expensive and therefore one should consider the possibility of renting beam time at an international high flux reactor or at a national medium flux reactor in connection with the use of a small angle scattering facility. How expensive is in this case a routinely performed material test? To answer this question let us define a reference scatterer, a 1 m long steel rod which should be examined at 10 different positions by illuminating  $F = 1 \text{ cm}^2$  areas. The thickness of the rod may be t = 1 cm and such that the transmission of  $\lambda = 10$  Å neutrons is T = e<sup>-1</sup>. We assume further that there are spherical precipitates for  $\phi = 500$  Å diameter with a volume fraction p = 5 % in the material, that the scattering length difference per atom between precipitate and matrix is b = 0.2  $10^{-12}$  cm, and that the atom density is n =  $6 \cdot 10^{22}$  cm<sup>-3</sup>. For the characteristic scattering angle  $\Im_c = \lambda/\phi$  one gets  $\Im_c = 2.10^{-2}$  radian. Thus, we set the angular resolution of collimator and analysator to  $\Delta A = 3 \cdot 10^{-3}$  radian and adapted to that the wave length resolution to  $\Delta N_{\lambda} = 0.15$ . Concerning the neutron sources we consider the two cases, first a high flux reactor with a thermal flux of  $\phi_n = 5 \cdot 10^{14}$  n/sec cm<sup>2</sup> and a gain factor of g = 30 for the Cold Source and second, a small reac-tor with  $\phi_n = 2 \cdot 10^{13}$  n/sec cm<sup>2</sup> without a cold source. For both cases it has been taken into account an attenuation factor f = 0.1 due to absorption scattering and other losses in guiding the neutron beam. With all these figures we can calculate the exposure time required to measure the Guinier region of the small angle scattering pattern within a desired accuracy (see Appendix 1). This allows us then to give an estimate of the costs since we can assume that the proportionate cost per hour of a beam is about 48 \$ at the high flux reactor and about 15 \$ for the small reactor (see Appendix 2).

If an accuracy of  $\sim 3$  % is required to determine diameter and volume fraction of the precipitates the 10 positions of our reference scatterer are examined by a position sensitive counter within 10 seconds at the high flux reactor and within

2 hours at the small reactor. These measurement times correspond to proportionate beam time costs of 0.15 \$ and 30 \$, respectively for the two reactors. It should be mentioned that the use of a twodimensional multidetector can bring down the prices by a factor of three to five. Thus, we can state that the use of neutrons can even be inexpensive and that the exposure times can be short enough in order that a material testing in large numbers can be put forward.

## Appendix 1

(1) The required beam time to meet the desired accuracy is calculated from the following formula. The neutron intensity  $\Lambda I$  at the detector is given by

$$\Delta I = \frac{\phi_n}{2\pi} f \frac{\exp(-k_0^2/k_T^2)}{k_T^4} g_4 k_0 \cdot \Delta k_0 \cdot \frac{\Delta k_0}{k_0} \cdot T \cdot t \cdot F \cdot$$

$$p \cdot t (n \cdot \Delta b)^2 \exp(-\frac{1}{3}\chi^2 R_g^2) \cdot \Delta k_1 \cdot \Delta k_1$$

In this equation  $\phi_n$  is the thermal neutron flux, f the attenuation factor, g the gain factor of the cold source,  $k_o = 2^{n/\lambda}$  and  $k_T = 3.7 \ {A}^{-1}$ . Because of the angular divergence  $\Delta A$  it holds  $\Delta k_o = \Delta k_o = \Delta k_1 = \Delta k_1 = \Delta A + \delta_0$ . Furthermore T is the transmission of the scatterer and t the specimen thickness, F the illuminated area, p the volume fraction of precipitates of volume v and the scattering length density difference between precipitate and matrix is  $n \cdot \Delta b$ . With the precipitate diameter  $\phi$  the volume is  $v = n/6 \ \beta^{-3}$  and the radius of gyration is:  $R_g = \sqrt{3/20^2} \phi$ . Using the data for reactor, instrument, and reference specimen as described in the text one gets 150 and 0.2 scattered neutrons per second at the scattering vector  $\times_{1/e} = \sqrt{3}/R_g$  for the two different reactors. - With a position sensitive counter centered with respect to the primary beam the small angle scattering pattern down to an intensity drop of  $e^{-2}$  is recorded simultaneously in  $\vartheta = 4 \frac{\Lambda_1}{1/e}/\Delta^2 = 18$  effective channels. In order to obtain from these  $\vartheta$  data points two parameters with an accuracy a = 3 % the data points must be measured with an accuracy of at least  $\sqrt{\vartheta/2} a = \pm 9$  % corresponding to 125 counts per channel. Thus the minimum beam time for 10 runs is 8.3 sec at the high flux reactor and 1.74 hours for the small reactor.

## Appendix 2

In the table 1 some prices are listed from which the proportionate costs per instrument and hour were calculated. The prices are estimated for a high flux reactor with cold source as the Grenoble reactor and for a small reactor as the Munich reactor.

## Table 1: Purchase and operating costs of reactors

Reactor	HFR + cold source	small reactor
Flux of thermal neutrons	$5 \cdot 10^{14} \text{ cm}^{-2} \text{ sec}^{-1}$	$2 \cdot 10^{13} \text{ cm}^{-2} \text{sec}^{-1}$
Annual operating costs	8 Mi \$	1 Mi ß
Annual depreciation over 20 years	1 Mi \$	0.2 Mi \$
Number of instruments	35	14
Number of operating hours per year (70 %)	6000	6000
Proportionate costs per instrument and hour	48 \$	15 ø

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# DETERMINATION OF HYDROGEN SELFDIFFUSION COEFFICIENTS BY MEANS OF QUASIELASTIC NEUTRON SCATTERING

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#### ABSTRACT

Quasielastic Neutron Scattering on hydrogen diffusing in metals yields information on the diffusive motion. In particular, from the quasielastic width at small scattering vectors, the selfdiffusion coefficient can be evaluated with good reliability. Three kinds of experiments are discussed in more detail, namely (i) hydrogen diffusion in Nb for a wide range of temperatures and concentrations; (ii) hydrogen diffusion in Nb with dissolved interstitial impurities which act as traps for the diffusing hydrogen atoms; and (iii) hydrogen diffusion in molten lithium.

#### 1. INTRODUCTION

The solubility of hydrogen in metals plays an important technical role, for instance in view of energy storage problems, and also with respect to hydrogen embrittlement in metals. For this kind of problems the selfdiffusion coefficient for hydrogen dissolved in metals as a

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function of temperature and concentration is an important parameter. In particular, a number of such problems also arise in connection with fusion reactor design. In the following we will demonstrate in a number of examples that quasielastic scattering of slow neutrons is a reliable and relatively fast method for the determination of selfdiffusion coefficients. We restrict the presented results essentially to investigations which were carried out at the FRJ-2 reactor at Jülich, at the Grenoble high flux reactor, and at the CP-5 reactor at Argonne National Laboratory.

### 2. THE METHOD

If slow neutrons are scattered on a metal loaded with hydrogen, the scattering intensity is determined by incoherent scattering processes on the protons, provided that the scattering on the host metal atoms can be neglected. The incoherent scattering probability is then proportional to the scattering law  $S_{inc}(\underline{Q},\omega)$  where  $\underline{hQ} = \underline{h}(\underline{k}_0 - \underline{k}_1)$  and  $\underline{hw} = \underline{E}_0 - \underline{E}_1$  are the momentum and energy transfer during scattering, respectively.  $S_{inc}(\underline{Q},\omega)$  can be calculated by means of a Fourier transformation in space and time of the van Hove autocorrelation function  $G(\underline{r},t)$  for the protonic motion [1] and one gets

$$S_{inc}(\underline{Q},\omega) = (1/2\pi) \int \int e^{i(\underline{Qr} - \omega t)} G_{s}(\underline{r},t) d\underline{r} dt \qquad (1)$$

For interstitial hydrogen diffusion,  $G_{s}(\underline{r},t)$  can be easily calculated in terms of a simple rate equation (or a system of rate equations), neglecting effects such as correlations, delocalization, and finite flight time (Chudley-Elliott-model [2], see also [3]). After Fourier transformation the resulting scattering law is, in general, a sum of Lorentzians centered at energy transfer h $\omega = 0$ , whose widths

depend on the mean rest time of the proton on its interstitial site, and on the interstitial lattice geometry. For sufficiently small Q, S<sub>inc</sub> approaches a single Lorentzian, namely

$$S_{inc}(Q,\omega) = \frac{\Gamma/\pi}{\omega^2 + \Gamma^2} e^{-Q^2 < u^2 >}$$
(2)

where the width (FWHM) of the quasielastic spectrum is given by

$$2\Gamma = 2Q^2D$$
 (3)

Small Q means  $Q < 2\pi/d$  where d is a typical distance between sites. This requires that Q should be smaller than 0.3..0.5 Å<sup>-1</sup>. D is the macroscopic selfdiffusion coefficient. The Debye-Waller factor in Eq. (2) takes into account the vibrations of the hydrogen on its interstitial site ( $\langle u^2 \rangle$  = mean square amplitude of the thermal motion of the proton).

There are two essential differences between a determination of D from the quasielastic width  $\Gamma$ , and a "macroscopic" measurement of the diffusion coefficient, such as Gorski-effect [4] or permeation experiments [5]. First, a quasielestic scattering process "observes" the path of the diffusing proton over distances of the order of, say, Q = 1..30 Å whereas the other experiments sample the motion over macroscopic distances. This aspect could become important if the diffusion occurs along dislocations or grain boundaries. For instance, assume that the mobility of a proton on a grain boundary is considerably higher than in the bulk, and that the proton spends, in a certain temperature region, only part of its time on the grain boundary. Under these circumstances one would expect a composite spectrum or, if only a narrow range of energy is measured, a reduction of the observed quasielastic intensity.

The second difference is related to the driving force acting on the diffusing particle. In a Gorski-effect experiment the diffusion coefficient  $(D^G)$  is determined from the time constant of the mechanical relaxation in the sample caused by hydrogen diffusion, after an external stress has been applied. In this method the decay of a concentration gradient is actually measured and the chemical potential  $\mu$  of the interacting protons enters. The corresponding diffusion coefficient is then

$$D^{G} = (\delta \mu / \delta c)_{T} cM_{\mu}(c,T)$$
(4)

where  $(\delta \mu / \delta c)_T$  is the derivative of  $\mu$  with respect to the hydrogen concentration c, and  $M_H$  is the mobility of the dissolved protons. On the other hand, the selfdiffusion coefficient from <u>incoherent</u> neutron scattering is related to the motion of an <u>individual</u> proton in an equilibrium distribution. Under these circumstances, the mutual interaction of the protons is not the driving force, and  $\delta \mu / \delta c$  has to be replaced by its value for a dilute system,  $c \neq \sigma$ , namely  $k_BT/c$ . This leads to [6]

$$D^{\mathbf{x}} = D_{\mathbf{G}}(\delta \mu / \delta c) \xrightarrow{} 0 / (\delta \mu / \delta c) \xrightarrow{} 0$$
 (5)

The reduced diffusion coefficient  $D^*$  is expected to be identical to the diffusion constant D as measured from quasielastic neutron scattering. It should be pointed out that the quantity  $D^*$  is also obtained from other "single particle" methods, namely nmr field-gradient measurements (or isotope/tracer measurements if there were no isotope effect).

The range of hydrogen concentrations which can be studied by the neutron scattering method is restricted by the available sample size, and by the absorption and incoherent scattering cross sections of the host

lattice,  $\sigma_a$  and  $\sigma_{inc}$ . In this regard NbH<sub>x</sub> is the most favourable system for such investigations ( $\sigma_{inc} = 2-5 \cdot 10^{-3}$  barns), and hydrogen concentrations of the order of a few 0.1 at.% can be investigated with a high flux reactor. In substances where  $\sigma_{inc}$  is of the order of a few 0.1 barns, measurements with about 5 to 10 at.% hydrogen are still feasible. The availability of backscattering spectrometers (energy resolution 0.3...) µeV) has extended largely the accessible range of such measurements. D-values between  $10^{-7}$  and  $10^{-5}$  cm<sup>2</sup>/sec can be investigated with such instruments, whereas conventional spectrometers cannot be used below  $10^{-5}$  cm<sup>2</sup>/sec. Unfortunately, the diffusion of deuterium cannot be easily investigated by neutrons due to its small incoherent cross section, except at large concentrations. Here, however, coherency effects will complicate the interpretation of the spectra in 'terms of a diffusion constant. However, the coherent component in the scattering can, in principle, be used to obtain information about inter-particle correlations if a more elaborate scheme of analysis is adopted.

#### 3. EXPERIMENTAL RESULTS

## Experiments on hydrogen diffusion in pure materials

Selfdiffusion coefficients were determined from t-o-f spectra on  $\alpha$ NbH<sub>x</sub> [7] for x = 0.03 and x = 0.33 which is the critical concentration of this system. The quasielastic width was determined at Q = 0.5 and 1.1 Å<sup>-1</sup>, the resulting (resolution-corrected) values of  $\Gamma$  were of the order of 1 - 2  $i 10^{-4}$  eV. <u>Figure 1</u> compares D-values from these measurements with the Gorski-effect experiments. At low concentration there is very good agreement. However, at the critical concentration, c = 0.33, the function D<sup>G</sup> yields a critical slowing down due to the singularity of  $(\delta c / \delta \mu)_T$ , which does not appear in the quasielastic scattering data. Figure 1 also shows the reduced value D<sup>\*</sup> from Eq. (5)
where  $(\delta \mu / \delta c)_T$  was also evaluated from the Gorski-effect experiments. As can be seen,  $D^*$  agrees with D from the neutron data. Detailed experiments were carried out in particular close to  $T_c$ , and no critical behaviour of  $D^*$ , and therefore of the mobility  $M_H$  was observed [7].

Quasielastic scattering experiments were also performed at lower temperatures on a dilute system  $NbH'_{0.012}$ , in order to investigate the change of the activation energy near 250°K which was for the first time observed in Gorski-effect experiments [4]. This change of activation energy has caused some controversy and, therefore, it was remeasured by a careful quasielastic scattering experiment at the Grenoble reactor, with an energy resolution of 1 µeV [8]. For all temperatures, the ordinate scale of the measured spectra was normalized from a measurement at 180K where the quasielastic spectrum falls entirely within the resolution window of the backscattering spectrometer. For each temperature the spectra at three different Q-values (0.15..0.56  $Å^{-1}$ ) were fitted simultaneously with D as the only disposable parameter (Eq. (3)). Figure 2 demonstrates the excellent agreement between the two methods. These results yield an independent proof of the observed change in activation energy which might be due to a transition from a classical jump diffusion, to a temperature region where hopping due to phonon-induced tunneling takes place [9,10].

Finally, we mention briefly unpublished work dealing with hydrogen diffusion in powders of the titanium alloy TiFeH<sub>x</sub> (0.1  $\leq$  x  $\leq$  0.8) [11]. From hydrogen charging and discharging times, and from the measured grain size, the apparent hydrogen diffusion coefficient was estimated to have a value of about 10<sup>-6</sup> cm<sup>2</sup>/sec at 70°C. On the other hand, quasielastic scattering experiments at the Jülich backscattering spectrometer revealed no measurable quasielastic width, leading to a lower limit of  $D < 5 \cdot 10^{-8}$  cm<sup>2</sup>/sec. Metallographic studies explain this discrepancy which is caused by diffusion on sub-grain boundaries, or on microcracks.

#### Hydrogen diffusion with traps

It is well established that interstitial impurities like nitrogen, oxygen, or carbon in transition metals act as traps for the dissolved hydrogen atoms. An interesting problem is the influence of such trapping centers on hydrogen diffusion. This effect has been studied by experiment and theory on a dilute model system, namely  $NbH_{0.004}N_{0.007}$  [12]. The experiments were carried out at the Grenoble backscattering spectrometer with a resolution of about 1 µeV.

At small values of Q, the observed quasielastic spectrum consists of a single Lorentzian whose width is approximately proportional to  $Q^2$ . Since, at small Q, the scattering process averages over many diffusive steps, this width is expected to be determined by the effective selfdiffusion constant  $D_{eff}$  of the H in the N-doped niobium, with  $\Gamma = Q^2 D_{eff}$ . At larger Q a drastic decrease of the observed quasielastic intensity with increasing temperature is found, and the corresponding line-width is much smaller (10..100 times) than the width for hydrogen diffusion in pure niobium. This can be understood as follows: For larger Q, a single diffusive step is observed, and, correspondingly, the spectrum is expected to consist of two components: a narrow line due to protons trapped close to an impurity; the width of this line is determined by the mean trapping time  $\tau_{T}$ . In addition, there should appear a broad line from protons diffusing in the undisturbed lattice sufficiently far from the interstitial. This component is so broad that it was not observable directly. However, this part of the spectrum was recognized by the reduction of the observed intensity ratio  $I_1/I_0$  for the <u>marrow</u> line as shown in figure 3. Figure 4 shows  $1/T_T$  and  $D_{eff}$ as obtained from the spectra.

The spectra could be quantitatively interpreted by a <u>two-step random</u> walk model [13] which is based on ideas similar to the Singwi-Sjölander model [15]<sup>(1)</sup>: it is assumed that the diffusing protons alternate randomly between a trapped "state" (with a mean trapping time  $\tau_T$ ) and a free "state" (with a mean lifetime  $\tau_1$ ). In the free state, diffusion takes place in the same way as in the pure host metal (diffusion coefficient D). It can be shown that the scattering law consists, in general, of two Lorentzians whose widths  $\Gamma_1$ ,  $\Gamma_2$  and weights  $R_1$ ,  $(1-R_1)$ are simple functions of  $\tau_T$ ,  $\tau_1$ , and D. For small Q, <u>one</u> Lorentzian dominates ( $R_1 = Q$ ) with

$$\Gamma_2 = Q^2 D \tau_1 / (\tau_T + \tau_1) = Q^2 D_{eff}$$
(6)

For larger Q (at the zone boundary) one gets approximately

$$\Gamma_2 \simeq \tau_T^{-1}$$
 and  $\Gamma_1 \simeq \Gamma_0 + \tau_1^{-1}$ , (7)

$$R_{1} = \tau_{1} / (\tau_{T} + \tau_{1})$$
(8)

where  $\Gamma_0(\underline{Q})$  is the width for trap concentration equal to zero. Figure 5 shows  $\tau_T$  and  $\tau_1$  in an Arrhenius plot. The activation energy for  $\tau_1$ ,  $E_{act} = 90$  meV, agrees approximately with the activation energy for D (70 meV), as it should, since, obviously one has  $\tau_1 = s^2/6D$ where s is the mean distance between the traps. The agreement is improved if the saturation of the traps is taken into account which makes s temperature dependent  $(1/\tau_1'$  in <u>figure 5</u>). The activation energy for  $\tau_T$  is 180 meV. Therefore, the lowering of the binding energy due to interstitial atoms is about 180 meV -  $E_{act}^D \cong 0.1$  eV. This value agrees with results from resistivity measurements [16] and elastic

(1) For a justification of these models see [14].

theory [17]. The solid curves shown in <u>figures 3 and 4</u> are based on more detailed <u>atomistic</u> theories for the trapping process, describing the interaction between the dissolved N and H in terms of elastic strain fields [17]. A detailed analysis of all measured data has shown that the two-step random-walk model allows a consistent, accurate, and also quite simple analytical description of this problem. This theory might be of general use for the theoretical interpretation in other cases of diffusion in impure materials, except for large Q where the detailed structure of the trap comes into play.

#### Hydrogen diffusion in molten lithium

In order to evaluate methods for the recovery of tritium from the lithium blanket in the fusion reactor it is essential to understand the transport of tritium in molten lithium. The transport of tritium and of the other isotopes of hydrogen through the blanket and through the structural components is also important for the evaluation of possible deterioration in material properties due to hydrogen embrittlement. These problems are conveniently studied by quasielastic neutron scattering which measures directly the diffusion constant of the hydrogen isotopes. In the following we report briefly on preliminary results obtained for the diffusion of H in molten  $\text{LiH}_{0.2}$  at 700°C by means of quasielastic scattering as described in Section 2.

The scattering spectrum was measured for 18 values of Q in the region where the  $Q^2$ -behaviour is observed. In order to isolate the hydrogen scattering, measurements were made with and without H in the sample, and the difference was taken as the scattering from H alone. Because the scattering from H is much stronger than the scattering from Li, and as the interference scattering is weak at the small values of Q of interest here, this procedure does not introduce any errors. A detailed discussion of this will be given in a full paper in the near future. The values of D<sub>H</sub> obtained from the values of Q measured are

shown in <u>Fig. 6</u>. These were obtained by dividing the measured width at each Q by  $Q^2$ , and the results show that we are in the region where the quasielastic scattering is described by the simple diffusion model, i.e. according to Eq. (3). The value obtained for  $D_H$  is (4.1 x 0.5) x  $10^{-4}$  cm<sup>2</sup>/sec, where the error is estimated from the scatter of the values at the individual values of Q. It is interesting to note that  $D_H$  is only 40% larger than  $D_{Li}$  and that simple mass scaling according to  $D_H/D_{Li} = (m_{Li}/m_H)^{1/2}$  does not apply in this case.

In Fig. 7 we compare the present result with the results obtained recently from conventional permeability measurements by Alire [18] at three temperatures. The samples measured by Alire are LiH<sub>0.08</sub>, LiH<sub>0.02</sub> and LiH<sub>0.005</sub> at  $T = 805^{\circ}C$ ,  $855^{\circ}C$  and  $905^{\circ}C$ , respectively. Assuming that concentration effects are not too important we must conclude that the two sets of experiments are inconsistent. Although we are not able to explain this discrepancy it is worth noting that the permeability measurements are less direct. For example, they are very sensitive to a proper correction for the rate of permeation through the container material. On the other hand, the neutron measurement is made under equilibrium conditions and does not suffer from this difficulty. We plan to repeat the neutron experiment at lower concentrations and at several temperatures in the near future. We also plan to determine the diffusion constant for D in LiD<sub>y</sub>. Due to the relatively weak scattering from tritium, a direct measurement on LiT is difficult. However, the results for H and D should yield enough information regarding the isotope effect to allow an extrapolation to the case of tritium.

# RESUMÉ

We could demonstrate that quasielastic scattering is a rather accurate method for the determination of D for hydrogen in metals

(better than 10% if resolution corrections are properly carried out). The method is particularly advantageous for cases where only powder samples are available so that other methods are difficult to apply, and for diffusion in liquids.

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#### FIGURE CAPTIONS

- Fig. 1 Selfdiffusion coefficient for hydrogen in NbH<sub>c</sub> vs. temperature T for different concentrations c, by Gorski-effect experiments [4] and by neutron quasielastic scattering [7].  $D^{*}$  = reduced selfdiffusion coefficient from Eq. (5) with  $D^{G}$  and  $(\delta \mu / \delta c)_{T}$  from Gorski-effect experiments (from [6]).
- Fig. 2 Selfdiffusion coefficient for hydrogen in NbH<sub>0.012</sub>. Circles: quasielastic scattering experiments (Richter et al. [8]); Solid line: Gorski-effect experiments; Dashed: extrapolation of the high temperature curve in [4].
- Fig. 3 Intensity  $I_1$  of the narrow component in the quasielastic spectrum for NbN<sub>0.007</sub>H<sub>0.004</sub>, in units of the total intensity  $I_0$  (as determined at small temperature) [12]. Points: experiments (Q in Å<sup>-1</sup>); Solid lines: theory (see text,  $r_0$  = distance of closest approach used in the theory).

- Fig. 4Width  $\Gamma_T$  of the quasielastic spectrum for NbN<sub>0.007</sub>H<sub>0.004</sub>measured at large Q (due to the trapped protons), andselfdiffusion coefficient  $D_{eff} = \Gamma/Q^2$  from the width  $\Gamma(Q)$ at small Q, vs. temperature [12].Solid line: atomistic theory.RWM: random-walk model calculation with the parameters fromfigure 5.
- Fig. 5 Interpretation of the results on NbN<sub>0.007</sub>H<sub>0.004</sub> in terms of the random walk model. Crosses: (mean trapping time)<sup>-1</sup>; Triangles : (Mean time between trapping events)<sup>-1</sup>. Circles: mean time between trapping events, corrected for saturation, from [17].
- Fig. 6 Selfdiffusion coefficient  $D_H$  for hydrogen in molten LiH<sub>0.2</sub> at 100°C obtained from the quasielastic width at different values of the scattering vector Q using Eq. (3).
- Fig. 7 Present result for D<sub>H</sub> compared to the results obtained by Alire [18].

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FIG. 4





FIG. 6



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## 1. INTRODUCTION

During the last 10 - 12 years, small angle neutron scattering (SANS) became an important tool for the investigation of structural problems in solid state physics, chemistry and biology /1/. More recently, sin ce about 5 years, the unique possibilities of SANS in view of non destructive testing have been investigated by the FIAT - Research Laboratories /2, 3, 4/. During this time a SANS device has been designed and built /5/ and entirely destinated to the development of technological applications.

As it is shown in Tab. I, SANS can be positioned between two intensively used classical methods, radiography and Bragg scattering. In this positionSANS covers a gap which is not accessible by any other non destructive method.

Infact, intermediate are the interation phenomena and the observation angles: radiography observes at zero angles the attenuation of the direct beam, multiple small angle refraction its line broadening, small angle diffraction the intensity near the direct beam and Bragg scattering single peaks at wide angles. Dimensions of the concerned inhomoge neities are also intermediate in a range of about 4 orders of megnitude.

Intermediate are last but not least the prospected applications; whilst Bragg scattering is not concerned with mechanical failure and radiogra phy with failure in its final stage, SANS should allow one to characterize the evolution of such structural details which could determine a failure process.

Present research with SANS in the field of non destructive testing deals with correlations between scattering effects and various fabrication or degeneration processes. Such processes can be divided in mechanical (fatigue, cold work) - thermal (aging, phase transition, recristallization) and thermomechanical ones (creep, thermal fatigue etc) and depend on structure (precipitates, grain boundaries...) and defects (dislocation, uvoids 'A cracks).

Final objectives of SANS work in this field are essentially the following ones:

- a) to achieve more reliable and economical project criteria by exploring better the "ignorance part" in the so called safety factors.
- b) to control for the correct execution of complicated thermomechanical fabrication procedure of mechanical components.
- c) to control for excessively severe service conditions of a material by observing its degeneration in an early stage.

d) to determine the residual lifetime of components in the final stage of the degeneration process.

The results so far obtained in the FIAT labs are very encouraging; they demonstrate in many examples that such objectives are already achievable or that they may be achieved in the near future. After a short consideration of the theoretical background of the methods, the experimental basis is described elsewhere /4/, a series of possible applications is illustrated.

#### 2. THEORETICAL BASIS AND INTERPRETATION,

Although neutron scattering often requires somewhat complicated considerations, the theoretical basis of the here considered applications can however be summarized rather simply. SANS analysis is in general based on the comparison of the experimentally obtained structure-dependent scattering crossection with the one calculated from a model structure. Fig. 1 shows schematically such a model structure with a dislocation, a woid and a precipitate embedded in a cristal matrix. An incident pla ne wave can be considered to create at any single point characterized by its (nuclear + magnetic) scattering length  $b_k$  and its positional vector  $r_k$  a spherical wave. The total amplitude A of the scattered wave, observed at a direction defined by the scattering vector k (ved. fig. 1), is the sum of the single spherical waves or the Fourier transform of the scattering length density  $\gamma(\mathbf{r})$  over the sample volume V

$$A(\vec{k}) = \int \eta(\vec{r}) e^{-i\vec{k}\cdot\vec{r}} dV(r) \qquad (1)$$

The scattering cross section is then obtained as

$$\frac{d\Sigma_s}{d\Omega} = AA^*$$
 (2)

Experimentally it is determined by measuring the intensity d3, scattered in the solid angle interval d.  $\Omega$  and by normalizing for the incident intensity  $\mathbf{J}_{\mathbf{c}}$ , the sample thickness and the beam attenuation by absorption and scattering  $(\Sigma_{\mathbf{a}}, \Sigma_{\mathbf{s}} = \text{absorption}, \text{ scattering cross section})$ :

$$\frac{d\Sigma_s}{d\Omega} = \frac{dJ}{J_o d\Omega} \frac{\overline{e^{(\Sigma_a + Z_s)D}}}{D}$$
(3)

The here desired informations concern positional and compositional fluctuations  $\Delta \eta(r)$  with respect to the scattering length density

 $\eta_c(\vec{r})$  of the ideal cristallite matrix.

a can infact be neglected in

$$\eta = \Delta \eta + \eta_0 \tag{4}$$

at scattering angles which are too small for satisfying the Bragg relation. For avoiding multiple Bragg scattering into the small an gle region, a sufficiently long wavelength (e.g. 8  $\Re$ ) has to be <u>u</u> sed for SANS - work in metals /6/.

A series of calculated cross sections which are the ones more frequently used in technological SANS-work, are listed in Tab.II. These are first of all the ones for isotropic particle seattering (N = particle density). At very small angles they have a common form, the well known"Guinier Approximation". Using this form, a dimension of the scatterers, the radius of gyration Rg is easily obtained in many cases (diluited monodispersion). /7, 8, 9/

Further scattering functions are the ones for linear dislocations (Q = dislocation density) and random fluctuations of the scattering length density ( $l_c$  = correlation length)./1,7,9,10/

At wider angles, the different asymptotic form of such functions can be often used to identify easily the type of a scatterer. This is conveniently done by plotting the results on log-log paper

to read the slope.

It is important to note, that multiple refraction, obtained when the neutrons pass successively through zones of different refraction index (A = constant, n = number of refractions), can be identified and in certain cases separated from particle scattering./11,12/ This is possible by repeating the measurement with a different wave hength and plotting the results in function of K.

For all 'the reported examples, the results will depend on  $\lambda$  only in the case of multiple refraction where  $\lambda$  influences the line broadening.

Superposition of scattering contributions from different scatters is not so serious as it might seem; the single effects normally are pre dominant in different angular regions. Interpretation is however always performed by a kind of trial error procedure and a good knowledge of the examined material is essential as much as the possibility of using, when necessary, the electronmicroscopy.

#### 3. RESULTS

The here reported examples concern 3 different fields, where non destructive control by SANS is possible:thermal treatment, fatigue and creep processes, and degeneration fenomena in turbine blades.

# 3.1. Thermal treatments

A series of carbon steels have been examined according to fig. 2 which are characterized by their increasing carbon content and consequent tly by the ratio of plate to lath martensite. Such morphology diffe rences evidently influence the number of refractions from magnetic domains and therefore the linebroadening.

The figure shows both, the dependence on heat treatment and carbon content. It is remarble that a similar linear dependence exist for the strength in function of carbon content and grain size, the important quantities to be controlled.

Fig. 3 concernes a maraging steel 17.4 PH which assumes, after suitable heat treatements, a martensitic structure with various fractions of ferrite, austenite and copper precipitates. A superposition of different scattering contributions is clearly seen from the figure. At the lower scattering angles multiple refraction from the magnetic domains is important, whilst particle scattering from the Cu-precipitates of ~ 100 Å is predominant at the wider ones. This became evident by comparing the slopes for different uavelenth's as indicated in the figure. The control of precipitation is one possible application, the other one is better shown in fig. 4 where the obtained multiple refraction is interpreted.

The corresponding linebroadening is plotted there ar function of the tempering temperature and compared with the percent of pustenite measured on the same material with the conventional X-ray method. The excellent agreement indicates a possibility to control the residual austenite in a non destructive way.

Ni - superalloys as INCONEL X-750 have been intensively studied with SANS. The strengthening phase in such alloys is constituted by  $\gamma'$ -precipitates, an intermetallic Ni<sub>3</sub> (Al, Ti) compound. SANS allowes to measure the size distribution of these precipitates. A typical result is shown in fig. 5 where the respective results from electron microscopy are also indicated.

The size evolution of f-s during aging (at 843°C), measured by SANS is shown in fig. 6. The result agrees well with the theory of 1/3. Wagner Lifshitz which foresees infact a linear dependence with t.

INCOLOY 800, an austenitic high temperature steel can be strengthened by the same precipitates as the Ni-alloys. Important is also the carbon content and carbide formation.

The electron micrographs of fig. 7 show that the structure before heat treatment, is characterized by a high dislocation density and after heattreatment by carbides. SANS gives in both cases the correct asymptotic slopes (-3 for dislocation and -4 for particle scattering).

# 3.2. Creep and Fatigue

Creep in INCOLOY 800 has been examined with SANS according to fig. 8 where the total scattering cross section is plotted, as well as the apparent radius of gynation. A rapid and uniform increase of these quantities is observed first as a conseguence of heat treatment (see effect of fig. 7); lateron a further increase takes place, evidently caused by creep degradation and interpretable by the formation of microvoids.
Armco iron specimens, have been submitted to fatigue at different peak stresses.

Fig. 9 shows the consequent variations of the average magnetic domain dimensions d\_ indicated by multiple refraction. Fig. 10 illustrates how such results can be applied. Plotting the variations of d\_ obtained near the rupture point in function of the applied stress, the fatigue limit ( $\sim 16 \text{ kg/mm}^2$ ) is obtained by extrapolation.

- A further example on fatigue has been obtained with polycristalline Hi. Fig. 11 reports the increase of scattering when samples are fatigued at different stresses  $\mathbf{v}$  up to cycle numbers N which were still far away (at lifetimes lower than  $\sim 10\%$ ) from rupture. The incremental scattering curves are due to disperation scattering.

Plotting in fig. 12 the deduced dislocation density  $\rho$  in function of  $\sigma^2$ ; the square of the applied periodic peak stress, the results show that  $\rho$  is proportional to  $\sigma$  as theoretically predicted,/13/ and the intercept value  $\sigma^2 = 24,5 \text{ kg/mm}^2$  (at  $\rho = 0$ ) is in good agreement with the fatigue limit of Ni. SANS prospects in this way a non distructive way of controlling if a component works below or above the fatigue limit.

## 3.3. Degradation in turbine blades

Very interesting examples of SANS applications are given by the control of the **y** evolution during the service of turbine blades. Fig. 13 shows this evolution for power station gas turbine blades, firstly during the aging process and during service after 16.000, 60000 and finally at 65.000 h where failure occured. A similar evolution is observed in (accelerated) creep-rupture tests, as also reported in Fig. 13. It is important to note that no degradation is observed at the base of the blades where the temperature remain rather low. Similar effects are obtained in blades of aircraft engines as shown in fig. 14. One can observe the time evolution of the **y** radius, which is maximum in the middle of the blades, but also control for possible temperatu re excursions and their contributing effect on the final lifetime.

#### 4. CONCLUDING REMARKS

Scope of the present article was to demonstrate the possibility of applying the non destructive G.A.N.S. method in practical problems of industrial metallurgy.

Such applications are already convenient on an economical basis, when one or more of the following key problems exist:

- routine examination of the degradation processes in rather expensive mechanical component: (gas turbine blades may cost more than 1000 \$/Kg)
- optimization of heat treatment processes (age hardening) and statistical control on components of the industrial process.
- investigation or characterization of the structulat legradation process (oreep fet que) in single samples or components, where the destructive routine analy is (e.g. by electronmicroscopy) would require excessive test capacities.

Neutron fluxes in common university research reactors (5MW) are sufficient for such applications and it seems that many of such reactors are presently underoccupied. The required S.A.N.S instrumentation would cost about 200.000 \$ and its rational use would seem to be a problem resolvable by a well organized industrial joint venture, perhaps supported by national or international public subvention.

Application of  $S_A.N_S$  in the mentioned field further requires a combination of personal expertise in neutron scattering and industrial metallurgy.

Such a combination is not commonly evailable. For convincing metallurgists in front of S.A.N.S results electron micrographs are extreme ly useful besides of the cases where they are really necessary for experimental support. The neutron physisists on the other hand tend to consider metallurgy sometimes as a disciplin not useful enough for their university career.

Looking to these present problems in an optimistic way, one may say that application of S.A.N.S. for non destructive testing however constitutes an excellent example of how to close the gap which exists in many fields bet ween industrial (applied) research and fundamental research.

Looking more in the future especially towords the problems of limiting the increase of energy and material consumption, one may predict an increasing interest in methods like S.A.N.S. Such problems infact require structural materials to become stronger, (lighter) and applicable at higher temperatures. They furthermore require to use those materials much closer to the real techni cal limits of applicability without decreasing safety. All these problems necessitate a better and more quantitative knowledge and control of degradation processes. Only by increasing this knowledge can one hope to eliminate gradually the "ignorance part" of the so called safety factors and to substitute it by probabilistic failure considerations.

Great industries have enough interest in resolving such problems and consequently in applying S.A.N.S.

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fig.1



fig. 2









fig.5

**INCONEL X-750** 











fig.9

# **ARMCO IRON**



NOITAIRAY NIAMOD BVITAJAR









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fig.14
	RADIOGRAPHY	SMALL ANG	LE SCATTERING	BRAGG-SCATT.
Phenomena	TRANSMISSION	REFRACTION	DIFFRACTION	DIFFRACTION
ANGLES OF OBSERVATION	ZERO	VERY SMALL	SMALL	WIDE
HETEROGENEINES	MACROSCOPIC FLAWS, ETC.	DISPERSED PHASES, ETC	PRECIPITATES, MICROVOIDS, DISLOCATIONS	ATOMS
DIMENSIONS	10 <sup>6</sup> A	10 <sup>5</sup> A	10 <sup>4</sup> ÷10 A	~ 5A
PARAMETERS	SINGLE SECTION AND THICKNESS	CONCENTRATION	CONCENTRATION, DIMENSIONS, DISTANCES	INTERATOMIC DISTANCE, CRYSTALLITE DIMENSIONS
APPLICATIONS	QUALITY-CON TROL, MAINTE NANCE	CONTROL OF HEAT TREAT- MENTS AND DEGENERATION - PROCESSES, RESIDUAL LIFE- TIME DETERMINATION		ANALYSES OF PHASES, COMPOSI TION, ANISO TROPHY AND STRESS
RADIATION	X and X-RAYS, NEUTRONS	NEUTRONS	,(X-RAYS)	X-RAYS, ELECTRONS, HEUTRONS

Tab. I - Positioning of the neutron small angle scattering technique between two conventional methods: radiography and bragg-scattering

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## TAB. II : Commonly used scattering cross sections in technological SANS - WORK.

N = density of scatterers, V = scatterer volume, l = correlationlength,  $\rho = disclocation density, b = Burgers vector, v = Poisson$  $ration V = atomic volume, G = interference function, <math>\eta = number$ of refractions

SCATTERER	SCATTERING $\frac{d \Sigma}{d \Omega}$ CROSS - SECTION $\frac{d \Omega}{d \Omega}$	A SYMPT FORM
SPHERE ( 2R:diom.)	$NV^{2} \Delta \eta^{2} \left[ \frac{J_{3/2}(KR)}{(KR)^{3/2}} \right]^{2}$	K
THIN DISK (2R=diam.)	$\frac{N^2 V^2}{K^2 R^2} \Delta \eta^2 \left[1 - \frac{1}{KR} J_1(2KR)\right]$	1 K <sup>2</sup>
THIN CYLINDER (2H=length)	$NV^{2} \Delta \eta^{2} \left[ \frac{sh(2KH)}{KH} - \frac{sen^{2}(KH)}{K^{2}H^{2}} \right]$	<u> </u>
SPHERICAL SHELLS	$N^{2}V^{2}A\eta^{2}\left(\frac{\sin KR}{KR}\right)^{2}$	<u>1</u> K <sup>2</sup>
GUINIER APPROXIMAT.	$NV^{2}A \eta^{2} \exp\left(-\frac{K^{2}R_{p}^{2}}{3}\right)$	
R ANDOM FLUCTUATIONS	$NV^{2}\Delta \eta^{2} \frac{1}{(1+K^{2}l_{*}^{2})^{2}}$	$\frac{1}{K^4}$
LINE DISLOCATIONS	$\frac{f}{V_{A}^{2}}a_{ab}^{2}b^{2}\frac{r}{2}\left(\frac{1-2i^{2}}{1-\sqrt{2}}\right)^{2}\frac{G\left(KR_{0}\right)}{K^{3}}$	1 K <sup>3</sup>
MULTIPLE REFRACTIONS	$ \begin{array}{c} \bullet \mathbf{x} \mathbf{p}  \left[ -\frac{\Theta^2}{\beta n \lambda^4 \Delta \eta^2} \right] \end{array} $	

LIST OF OTHER PAPERS PRESENTED AT THE ADVISORY CROUP MEETING

Neutron scattering studies of polymers: cellulose-I and cellulose-II N.M. Butt Josef Stefan Institute and neutron scattering studies at the TRIGA reactor V. Dimic Liquid crystal studies by neutron scattering N. Kroo, L. Bata, I. Vizi Neutron studies of molecular solids K.R. Rao Industrial material research and elastic neutron scattering J. Szpunar Biological applications of thermal neutron scattering: A bibliography, AERE Harwell Report MPD/NBS (1976). Available from HMSO. D.L. Worcester

Copies of the above papers can be obtained on request from the Physics Section, International Atomic Energy Agency, P.O. Box 590, A-1011 Vienna, Austria

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