INDC(IND)-039/GI INT(87)-3



INTERNATIONAL NUCLEAR DATA COMMITTEE

CHEMICAL EFFECTS ON THE EDXRF AND PIXE STUDIES

S.K. Kataria, Nuclear Physics Division B.A.R.C., Trombay, Bombay 400 085, India

NDS LIBRARY COPY

June 1987

IAEA NUCLEAR DATA SECTION, WAGRAMERSTRASSE 5, A-1400 VIENNA

<u>INDC(IND)-039/GI</u> INT(87)-3

CHEMICAL EFFECTS ON THE EDXRF AND PIXE STUDIES S.K. Kataria, Nuclear Physics Division B.A.R.C., Trombay, Bombay 400 085, India

June 1987

Reproduced by the IAEA in Austria June 1987

87-02505

S.K.Kataria , Nuclear Physics Division B A R C ,Trombay, Bombay 400 085

The energy dispersive x-ray fluorescence analysis (EDXRF) and proton induced X-ray emission (PIXE) analysis are being widely used in the elemental analysis of a variety of samples due to their rapid and simultaneous multi-element capabilities. The wide acceptance of these X-Ray methods is due to implicit simplified assumptions that the absorption and emission of characteristic xrays are independent of the physical and chemical environment of the elements in the samples. In the past few years, a number of experimental studies have been carried out to estimate the validity of these assumptions both for PIXE as well as EDXRF applications. The $K\beta/K\alpha$ intensity ratios for Cr and Mn were found to be significantly influenced by the chemical state of these elements in the sample by Tamaki et al (1). In another study (2) using wavelength x-ray spectrometer, chemical effects in Cr compounds were confirmed. For Mn compounds, Kataria et al (3) found that not only the $K\beta/K\alpha$ ratio but even the absolute K x-ray yields depends on the chemical nature. The dependences of $K\beta/K\alpha$ ratios in PIXE analysis have also been carried out recently. The phenomenon of multiple ionisation of the inner shells by heavy ions has been studied extensively and has been reviewed by Burhop (4). However, the influence of multiple ionisations in the outer shells by the lighter ions p,α which can significantly alter the $K\beta$ / K\alpha ratio as well the fluorescence yield w have not received much attention.

A few direct measurements of absolute fluorescent K X-rays yields have been reported so far in the literature. In 1974, Matsumara (5)reported that the slope of the calibration curve for S ,Si and P concentrations in pig-iron is different by about 10 % depending on the metullargical state of the gray and white iron .

In another study of Mn compounds by EDXRF technique (3), significant variation (\approx 10 %) of the absolute yield of fluorescent K α X-rays have been reported. Yoshihara et al (6) measured the ratio of K-X rays from MoO₂ and Mo and the 140 KeV γ -



Fig.1. Calibration curves for sulphur by x-ray fluorescence

ray in a radioactive decay and found the value of the relative ratios $(K\beta/\gamma = 1.034 \pm 0.007 \text{ and } K\alpha/\gamma = 1.012\pm0.007)$. Similiar effects had been observed earlier in radio-active decay studies (7) for Sn, Fe, Tm and Te. Collins et al (8) have used the observed 10% differences in K $\beta/K\alpha$ ratios for the cases of Cr (0.1316), Cr³⁺ (0.1382) and Cr⁴⁺ (0.147) in the study of annealing processes in the Chromium doped solids by carrying out the K-Xrays measurements at different temperatures.

It is well known that K and L photo-absorption edges of an element are dependent on the atomic environment of the absorbing atom. The observed chemical shifts in the K and L absorption edges are of the order of 10 - 20 eV. In addition the shape and height of these edges are dependent on the molecular bonding and the chemical and crystalline environment of the absorbing atom (9-11). In fact, the extended fine structure in the photo-absorption edges is used to obtain information about the crystal structure as well as nature of molecular bonding.

The near edge structure in the vicinity of the absorption discontinuity in compounds has been reasonably attributed to the empty molecular orbits (11). On the other hand, the structure in the emission spectra reveal the nature of the occupied Molecular Orbital. Thus the x-ray emission and absorption spectra of compounds provide complementary information about the molecular

TADIE I	T	a	b	1	e	1	
---------	---	---	---	---	---	---	--

· · · · · · · · · · · · · · · · · · ·	MnKα	MnKβ	Κβ/Κα
Mn SO4	29880 <u>+</u> 90	4090 <u>+</u> 29	0.137 ± 0.0011
MnC0 ₃	30170 <u>+</u> 90	4140 <u>+</u> 37	0.137 <u>+</u> 0.0011
Mn0 ₂	22940 <u>+</u> 70	3180 <u>+</u> 22	0.139 <u>+</u> 0.001
KMn04	25100 <u>+</u> 75	3600 <u>+</u> 25	0.144 <u>+</u> 0.0011

Normalised Mn K X-rays: counts/gm of Mn also corrected for absorption effects. Samples in boric acid and counting time 5000 seconds.

Excitation with Cu X-Rays / 3 /

structure. The structure lying beyond this molecular region in EXAFS spectra are explained very well with the scattering model given by the theory of Lytle et al (9). It is very well known that these extended structures helps in the determination of interatomic distances accurately. In this class of studies it will be interesting to have absolute measurements of the absorption cross-sections as well and for a wider energy range. As a result of these measurements, it will be possible to identify whether the observed chemical effects in XRF studies are due to the ionisation process or due to the competition between the radiative and nonradiative emission processes.

The natural line widths of characteristic x-rays have been extensively studied using high resolution wave length spectrometery. The K-X ray line width is sum of decay widths of Kshell and of the L-shell participating in the transition. These decay width includes the contribution from radiative transitions as well as non-radiative Auger transitions of the outer-shell electrons. Therefore, the variation of the line widths with chemical state of the emitting atom is anticipated. In a study of the line widths of K-X rays of transition elements Hn, Cr, Fe (12), the line width of Ka, x-ray was found to vary from 2.25 eV to 4.0 eV when the oxidation state of Mn²⁺ to Mn⁷⁺. In view of







Fig. 3. Iron $K\beta_1\beta'$ - lines (n- number of unpaired electrons)



Fig.4 The Chlorine K β spectrum of CH₃Cl showing the prsence and location of multiple vacancy transition. The solid line is the emission with primary radiation from a Ag anode, the circles from a Pd anode. The spectra are normalised to the strongest peak intensity.

these observations, the fluoroscence efficiency for K-X ray emission (in other words K-X ray yields per incident photon) is also likely to significantly altered for these elements.

In a recent study with synchrotron radiation source, Chevallier et al (13) found that the line width of Fe K α_{i} line increases from 2.70 eV to 2.90 eV when the energy of the incident photon was increased from the K-edge energy E_k to E_k 500 eV. the occurence of multiple ionisation in Thus showing the absorption of incident photons and its subsequent effect on decay widths and branching ratios. For low atomic number elements, simliar results have been obtained with X-Ray Tube excitation. For example, the change in the line shape of Chlorine K β x-rays when excited with different target x-ray tubes (Ag/) Pd) has been ` explained due to the multiple ionisation in the outermost shells (see Fig. 4.).



Fig.5. $K\beta/K\alpha$ intensity ratio for photo-ionisation relative to electron conversion. o Paic and Pecar x Arndt, Brunner abd Hartmann

In another experiment on the role of multiple ionisation, 197 Au the the energy of various K-X ray lines were measured, for atoms in two cases (i) when excited by electron capture in 197 Hg, (ii) when directly excited in EDXRF studies. In the electron capture , the outer electrons do not see any change in the effective nuclear charge, so that a K vacancy unaccompanied by outer-shell vacancies due to shake-up and shake-off processes-can be obtained. It was found by Borchert et al (14) that the energies of K-Xray lines excited by photo-ionisation are about \approx 0.6 eV larger than when excited by electron capture, reflecting the effect of the unresolved satellite lines arising from the photoionisation process. In an earlier study, Tamaki et al (1) found that $K\beta/K\alpha$ ratio in K-capture excitation of Cr and V K-X rays is about 0.12 as compared to the value of 0.134 observed in the X-ray excitaion. In another set of measurements by Paic and Pecar (15) similiar results were obtained for a number of elements and it was also found that the relative ratio of KB/Kg in the two cases increases from 0.9 to 1.0 in the range with 22 < Z < 30 (see Fig. 5). Attempts have been made to explain these results on the basis of shake-off process (16).



Fig. 6. The L-absorption edges of Pt metal. The zero of energy corresponds to the onset of absorption of the L_{III} - edge.

In EDXRF analysis of thick samples, the accuracy of quantitative estimates are directly dependent on the accuracy of the attenuation co-efficients for incident radiations as well as for the fluoroscent radiations used in the matrix absorptin correction factors. Generally one estimates the absorption coefficient for the sample matrix using the tabulated values (17) and using Bragg's law of additivity.

 μ (Compound/ mixture) = Σ n, $\mu(i)$

Significant deviations from this rule have been observed in the case of stopping power measurements of charged particles p, α etc. for the multielement targets and have been reviewed recently by Thwaites (18). Jackson (19) have pointed out the

possibilities of significant deviations from this rule for the case of photon absorption for energies < 20 KeV.

Photo-electric cross-sections sensitively on the binding energy of the shell involved, particularly when the photon energy is near the photo-absorption edge. It is also well known that the B.E. of different shells are also changed by the chemical state of the atoms. ESCA as well as EXAFS studies are based on this effect. These effects are greatest at the lower energies < 10 KeV encountered in EDXRF studies, when the outgoing photo electron's energy is in the neighbourhood of valence state energies and the wave length of these photo-electrons is of the order of molecular dimensions.

It is mainly because of these chemical effects that large uncertainities of the order of 20-50 % exists in the photon

	· · · · · · · · · · · · · · · · · · ·			Mn	Кβ
Sample	Thickness mg/cm ²	Exp. (Calc.	Exp.	Calc.
MnS0,	68.2	30.2 <u>+</u> 0.14	32.0	23.6 <u>+</u> 0.19	25.0
•		30.5 <u>+</u> 0.14		23.1 <u>+</u> 0.18	
		30.0 <u>+</u> 0.14		23.1 <u>+</u> 0.18	h.
Mn 0 ₂	68.6	23.6 <u>+</u> 0.11	25.7	17.7 <u>+</u> 0.14	20.0
2		23.8 <u>+</u> 0.11	^	17.8 <u>+</u> 0.14	,
		23.9 <u>+</u> 0.12		17.9 <u>+</u> 0.14	
Mn0	62.4	23.2 <u>+</u> 0.10	27.3	17.6 <u>+</u> 0.14	21.3
۷		23.5 <u>+</u> 0.15		17.5 <u>+</u> 0.14	
		23.4 <u>+</u> 0.10		17.7 <u>+</u> 0.14	
KMn0,	68.7	30.8 <u>+</u> 0.14	37.4	23.3 <u>+</u> 0.19	29.5
•		30.3 <u>+</u> 0.14		23.5 <u>+</u> 0.19	
		30.8 <u>+</u> 0.14		23.1 <u>+</u> 0.18	1

Table 2.

Mass absorption co-efficient μ (cm²/mg) for Mn K α and Mn K β for Boric acid pellets containing Mn compounds.

absorption cross-sections as well as in the photo-electric jump ratios in the vicinity of edge energies. For energies far away from these edges, the experimental uncertainities are quoted to be of the order of 1% i.e. limit of the uncertainities of the experimental technique (20).

The experimental determination of the attenuation coefficients μ (3) of different Mn compounds for Mn K α and K β Xray lines showed very large dependences on the atomic environment of the Mn atoms. In a recent set of measurements for the photoelectric cross-sections of L-shells in Pt-Rh alloys etc; the deviations of the order of 3 to 8 % from pure element values were observed (21).

The basic theories of photoionisation of inner shells, Auger electron emission and Coster Kronig transitions and radiative transitions have been undergoing continued refinements in the last two decades (22). With the availability of tunable Xrays from Synchroton Radiation Sources, precise measurements of photo-ionisation processes as well as de-excitaion processes are becoming available and are being used for testing the various proposed models. A brief description of these models is given below.

In the photoelectric absorption process, within the limits of observations, one photon is observed by an isolated atom or an ion, and one atomic electron ejected.

 γ + atom + e + ion

Such a description is an idealisation in view of the fact that the multiple excitation and ionisation of the absorbing atom is usually ignored. There is a second set of model assumptions for theoretical calculations: Excited states are unstable and do decay; the two step description of absorption and decay is a model assumption whose limits of validity are being investigated. In most cases the lifetime of the vacancy is long enough to make this a good approximation. If however, the vacancy is produced by a photon of energy very close to the threshold, the ejected electron will be moving very slowly and may not have got clear of the atomic system before an Auger electron is ejected or X-ray photon

is emitted. In such cases, one should treat the formation and decay as apart of the same process. In recent model by Niehaus (23), this is taken into account by post collision interaction (PCI) between the two electron in Auger process.

Another such model assumption is the description of the photoabsorption as a single electron transition in a screened central potential, neglecting the electron-electron interactions (correlations) except as to define an average potential in which all the electrons move without interacting. Howat et al (24) have introduced orbital relaxation (Configuration Interaction CI), and Inter Continuum Coupling (ICC) between the final states of the outgoing electrons. Howat et al applied their model for the calculations of the Mg K-LL Auger transitions and found the magnitude of these effects upto 30 %.

These ICC corrections depends very sensitively on the atomic environment of the atom undergoing the transition. These models for isolated atoms have to be extended to take into account the changes in the electronic wavefunction when the atoms form chemical compounds or solid structure. Due to additional compression of the constituent atoms in the solid bodies and

Final LL State	Without CI or ICC	With CI	With both CI & ICC	Experiment
$(2s)^{-2}$ 1S	10.03	7.34	5.41	6.32 <u>+</u> 0.67
(2s) ⁻¹ (2p) ⁻¹	¹ P 21.94	22.03	18.80	17.44 <u>+</u> 1.58
(2s) ⁻¹ (2p) ⁻¹	³ P 8.82	8.80	8.20	8.40 <u>+</u> 0.88
(2p) ^{-2 1} S	4.37	6.20	7.82	8.97 <u>+</u> 1.37
(2p) ^{-2 1} D	54.83	55.63	59.77	57.61 <u>+</u> 3.52

Table 3.

Relative Transition Rates for K-LL Transitions in Mg

compounds, it is also reasonable to expect that inter-shell correlations and collective effects play even stronger role than in an isolated atom which have been seen (24).

has been successfully applied to the Shake theory interpretation of the satellite structure in the x-ray photoelectron spectra of a variety of atomic systems (25). Recently these calculations have been extended to the estimates of $K\beta$ x-ray emission spectrum of Argon (26). Shake theory proceeds on the assumption that the primary ejected electron is removed sufficiently rapidly that it does not disturb the other electrons : sudden approximation. The (N-1) electron wave function is simply formed by deleting one electron from the N-ground state wave function: This wave function $|\Psi_n(N-1)\rangle$ is not an eigenfunction of the (N-1) hamiltonian, but it can be expressed as a linear combination of them. The system relaxes in response to the sudden change in the potential into the (N-1) electron eigenstates with the probabilities determined by the overlap integral of the initial wavefunction and the final state eigenfunctions $|\phi_n(N-1)\rangle$

 $Pn = |\langle | n(N-1) \rangle | \Psi_0(N-1) \rangle |^2 \qquad ... (2)$

In this approximation, $|\langle \psi | \psi \rangle|^2$ can be identified as the probability that an electron in the orbital i will remain in that orbital. Similiarly the probability of raising the outershell electrons to higher unoccupied levels (shake-up probability) can be estimated. The overlap integrals with the unbound i.e. positive energy eigen-states denoting the probability of multiple ionisation (shake-off probability) can be estimated.

During the photoionisation by X-rays, due to shake-up processes, shake-theory predicts considerable percentage of Argon atoms to be excited in the valence shells in addition to the Kshell vacancy. In addition, it also predicts that significant fraction of Argon atoms are doubly ionised as a result of shakeoff process. The contribution of the K β x-rays from the doubly ionised Argon atoms has been estimated to be about 10 %. The results of these calculations are in good agreement with the experimental data on Κβ satellite lines. However these calculations can not be simply extended for estimating the effects of the atomic environment but they bring out the role of electronelectron correlations and thus of atomic environment in the X-ray emission process. Further developments in the calculations are needed before they can be used in any practical EDXRF analysis.

In summary, the available experimental evidence on all basic aspects of photo-absorption, Auger electron emission and xray emission and attenuation show that the effect of the outer electrons on the inner-shell processes is significant and shell cannot be neglected. The photo-absorption cross-section. absolute electron yields and X-ray yields as well as KB/Kg ratio Auger depend on the atomice environment. Similiar effects on the L-shell transitions and L-X rays are expected to be much larger, though experimental data have not been reported yet. It is therefore. necessary to carry out direct measurements of the chemical effects on the K,L-Xray yields per incident photon for commonly used Photon Sources in EDXRF work for accurate quantitative analysis.

In PIXE analysis, the effect of the atomic environment on the K and L X-ray yields per incident proton or alpha particle can arise due to any of the following reasons.

- (i) Physical and chemical effects on the stopping power dE/dx
- (ii) Variation of the K-shell vacancy production cross-section, in particular the probability of multiple ionisation in the outer-shells changing with the atomic environments.
- (iii) Variation of the fluorescence efficiency for the K and L X-rays.

However, very little direct experimental data exist on the effect of atomic environments on the PIXE results. Recently Brunner (27) have reported about 5 % variation of K β /K α ratios for the transition elements Cr, Mn,Fe and Cu elements in the 2.55 proton induced PIXE spectra.

Further these K β /K α ratios were found to be similiar in the EDXRF as well as for PIXE spectra by them. The shift in the difference (K β - K α) energies from its value in atomic form was also measured to be about 2.7 \pm 0.5 eV . In a study to measure the accuracy in PIXE studies, Richter and Watzen (28) observed discrepancy of the order of \approx 20 % introduced due different sample preparation methods involving chemical treatment etc.

Table 4. Relative $K\beta/K\alpha$ intensity ratios; the quoted errors mean the standard deviative reliability for PIXE, including different sample preparations; precision of the fluorescence, thick samples only.

Element	Constituents	PIXE results	EDXRF results	Calculated
Chromium	Cr /K Cr 0,	0.977 <u>+</u> 0.007	0.969 <u>+</u> 0.010	0.976
Manganese	MnS/KMn0 ₄	0.950 <u>+</u> 0.007	0.953 <u>+</u> 0.008	0.974
	MnSO ₄ /KMnO ₄	0.965 <u>+</u> 0.008	0.965 <u>+</u> 0.021	0.983
	MnSO4/MnSO4*	0.997 <u>+</u> 0.006	-	1.00
Iron	Fe /FeSO	0.987 <u>+</u> 0.005	0.986 <u>+</u> 0.023	0.984
Fe	SO ₄ /Fe ₂ (SO ₄) ₃	0.996 <u>+</u> 0.004	-	0.992
Fe ₂ (SO ₄) ₃ /Fe ₂ (SO ₄) _{3*}	0.993<u>+</u>0.005	- ·	1.0
Copper	cu mja	0.973 <u>+</u> 0.011	-	0.997

In PIXE analysis of thick samples, the accuracy of quantitative estimates are strongly dependent on the accuracy of the stopping power dE/dx for the sample matrix. This arises essentially due to the fact that X-ray production cross-sections are steep functions of the energy of the incident charged particles. Generally for estimating dE/dx for the sample matrix, one uses Bragg's rule of additivity;

dE/dx (Compound) = Σ n, dE/dx (i)

Implicit in the Bragg's rule of additivity are the assumptions that the physical phase of the sample and the chemical nature of bonding in the compounds have negligible effects on the stopping power dE/dx. Infact large deviations have been observed in dE/dx due to differences in the electronic structure of the free atoms and the same atoms bonded in molecules or associated into condensed media (18). The effects are greatest at lower



Fig.7. The stopping cross sections of He⁺ ions in as-quenched (filled circles), relaxed (open circles), and crystullized (squares) $Fe_{B2}B_{18}$ metallic glass as a function of energy. The continuous curve represents stopping cross sections based on Bragg's rule. The error bar in the figure depicts an error of $\pm 5\%$.

energies 0.5- 3.0 MeV generally encountered in PIXE studies. A of large body of experimental data for stopping power D and α particles (0.5 to 5.0 MeV) in a variety of samples show significant dependence on the chemical environment varying upto 50 I from the corresponding values in the atomic form for low Z elements. The effects of the physical environment, though smaller, are also clearly visible . In a recent study of metallic glass (29) consisting of Fenna B_{α} the variation in the stopping power was found to vary 10% and 20% depending on the fact whether the by sample was as-quenched, relaxed or crystallized. These effects are also expected to be greatest for light elements whose valence electrons are a major fraction of the total electrons (30).

ion induced X-ray emission HIXE, the multiple For heavy ionisation of inner shells KK, KL KL² etc is well known. The shell ionisation has marked degree of inner effect on both Auger transition rates and thus on radiative and the mean fluorescence yields w by an order of magnitude (4), and have been extensively studied experimentally. For proton and alpha particle induced x-ray emission, the multiple ionisation of L shells have also been found to occur though to a lesser degree (31).



Fig.8. The K X-Ray spectra of 1 H, He and 16 O on Ti demonstrating the variation in multiple ionisation with increasing projectile Z.

The probability of L-shell ionisation is orders of magnitude greater than that of K shell (31) simply because of the larger effective radii of L-shells and also due to larger impact parameters that are involved.

It has been pointed out earlier, that for photo-ionisation process, this probability is rather significant (10%) on account of shake-off processes. For PIXE, on account of slowness of the secondary electrons, the potential adaptation is assumed to be of more adiabtic nature, and therefore it is not unreasonable to assume that the shake-off is of minor importance. However, in view of the observed multiple ionisation in the L-shell orbit as seen



Fig.9. The probability of K- and L shell ionisation versus impact parameter for 0.9 MeV p on Ca.

in the satellite structures for α induced x-rays (31) , for other outer-shells in the atoms these are expected to be still larger. In fact if a charged particle ionises the atom in the K-shell, the probability of its ionising the outer shell is further enhanced. It will be much greater due to longer range of the Coulomb Interaction involved and the small amount of the energy transfer involved in this process. Due to this multiple ionisation processes, the fluorescence efficiency (31) has been estimated to change by a factor of nearly 2-4 . Therefore, the fluorescence efficiency in EDXRF and PIXE processes will be different. In the absence of any systematic experimental data on the w values. one uses the fluorescence efficiency w measured in the EDXRF studies for the PIXE work also. This can lead to large errors in the PIXE results. As in the case of EDXRF, the atomic environments will also greatly influence the multiple ionisation and hence the wvalues and Auger transition rates etc.

Therefore, absolute measurements in the case of PIXE studies have to be carried out keeping in view the significant deviations expected due to the large dependence of the stopping power dE/dx on the physical and chemical environment of the samples as well as the X-ray yields per proton. This work on PIXE technique is in progress.

Significant variation of $K\beta/K\alpha$ intensity ratios for elements (18 < Z < 30) in the PIXE and EDXRF studies, even of the order of a few percent on the chemical nature of the fluorescent



Fig. 10. The variation of mean K shell fluorescence yield for Ne with different mean numbers n of L vacancies due to different modes of excitation.(after Burhop).

atoms, can introduce large uncertainities in the PIXE and EDXRF results due to unfolding procedures used in the estimation of the peak intensities in a given spectrum. Therefore, it is necessary to have good estimates of the dependence of $K\beta/K\alpha$ ratios on the incident photon energy as well as on the atomic environment of the fluorescent atom.

REFERENCES

- 1. Y.Tamaki, T. Omori and T. Shiokawa, Radiochem. Radioanal. Lett. <u>37</u>, 39 (1979).
- B. Paci-Mazzilli and D.S.Urch, Inner Shell and X-Ray Physics of Atoms and Molecules, p 741, Plenum Press, NewYork (1981).
- 3. S.K.Kataria, R.Govil, A.Saxena and H.N.Bajpei, X-Ray Spetrom. <u>15</u>, 49-53 (1986).

- E.H.S.Burhop, Advances in Atomic and Molecular Physics, Vol <u>15</u>, 329 (1979).
- T. Matsumara, N. Kotani, T. Goto and K.Norita, Tetsu to Hagane, <u>60</u>, 1799-1804 (1978); Brutcher Translations 9462.
 R. Gast, Adv. in X-Ray Anal. <u>21</u>, 38 (1978).
- K. Yoshihara , A. Hibino, I. Yamoto and H. Kaji Radiochem Radioanal. Lett. <u>48</u>, 303-10 (1981).
- 7. R.Martin and R.Shule ; Phys. Lett. <u>46B</u> , 367 (1973).
- 8. K.E.Collins, C.H.Collins and C. Heitz, Rdiochimica Acta <u>28</u> 17, (1981)
- 9. F.W.Lytle, D.E.sayers and E.A.Stern, Phys.Rev. B11 4825 (1975) and Advances in X-Ray Spectroscopy, Pergamon Press, Oxford 1982.
- 10. C.Mande and V.B.Sapre, Advances in X-Ray Spectroscopy, Pergamon Press, Oxford 1982.
- 11. M.V.Apte and C. Mande, J.Phy. Chem. Solids, <u>42</u>, 605-610 (1981)
- 12. Yo. Gohshi and A. Ohtsuka, Spectrochimica. Acta <u>28B</u>, 179 (1973).
- 13. P.Chevalier, M.Travernier and J.P.Briand, J.Phys. B <u>11</u>, L171, (1978).
- 13b R.R.Lavilla, Advances in X-Ray Spectroscopy, Pergamon Press, Oxford 1982.
- 14. C.L.Borchert et al, Phys.Lett A65, 297 (1978).
- 15. G. Paic and V Pecar Phys.Rev A14, 2190-2 (1976).
- 16. E. Arndt, G Brunner and E. Hartmann, J.Phys <u>B15</u>, L887-889 (1982)

- 17. W.H.McMaster, N.K.Del-Grande, J.H.Mallet and J.H.Hubbel University of California Report UCRL 50174 (1969).
 - 18. D.I.Thwaites, Rad.Res. <u>95</u>, 495-518 (1983).
 - 19. D.F.Jackson, NIM 193, 387 (1982).
 - 20. V.Lakschminarayana, Ind. J. Phys. <u>58A</u>, 49-57 (1984).
 - 21. G.Nageswara Rao, Ph.D. Thesis Waltair Thesis 1983.
 - 22. B. Crasemann, Atomic Inner Shell Processes, Academic Press NewYork, 1975.
- 23. A. Niehaus, J. Phys. <u>B10</u>, 1845 (1977).
 - 24. G.Howat, T.Aberg and O. Goscinski, J.Phys. <u>811</u>,1575 (1978).
 - 25. K.G.Dyall, J. Phys. <u>B16</u>, 3137-3147 (1983).
 - 26. K.G.Dyall and I.P.Grant, <u>817</u>, 1281-1300 (194).
 - 27. G. Brunner, M.Nagel, E.Hartmann and E. Arndt; J. Phys. <u>B15</u>, 4517 (1982).
 - 28. Richter and Watjen, NIM <u>161</u>, 189 (1981)
 - 29. Kuldeep and Animesh Jain N I H B15, 101 (1986)
 - 30. D.Powers, H.G.Olson and R. Gowda, J. Appl. Phys. <u>55</u>, 1274 (1984) and S. Matteson et al Phys. Rev. <u>A14</u>, 169 (1976).
 - 31. P.Richard, " Atomic Inner Shell Processes, Academic Press NewYork, 1975 ed.B. Crasemann