

STRUCTURAL INVESTIGATIONS BY EXAFS†

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Extended X-ray Absorption Fine Structure (EXAFS) analysis is a relatively new technique for structural investigations. It is specially suited for structural studies where short range order is important as in disordered materials. It is an atom-specific technique which makes it extremely useful in the study of a variety of complex materials such as catalysts, glasses and biological systems. In this article, the theory and practice of EXAFS analysis are briefly presented along with several chosen applications.

Keywords : Extended X-ray Absorption Fine Structure (EXAFS); Amorphous Materials.

INTRODUCTION

THE observation of fine structure beyond the K-absorption edges of materials dates back to the early 1920's when it was called 'Kronig structure' (Kronig, 1931, 1932a, b). Although it was recognised even then that such fine structure was due to the presence of neighbouring atoms (Lytle, 1965; and Azaroff & Pease, 1971), it was not clear whether long-range order was essential for the phenomenon to occur (Stern, 1974; and Lytle *et al.*, 1975). It is only since 1965 that much advance has been made in this area and the undulations have come to be known as 'Extended X-ray Absorption Fine Structure' or EXAFS (Lytle, 1965). It is now recognized that EXAFS is essentially a consequence of short-range order. It is precisely the sensitivity of this technique to the local structure that renders it a unique structural tool (Stern *et al.*, 1978; Sayers, 1970; Sandstrom & Lytle, 1979; and Teo, 1980).

The K-absorption edge itself is a characteristic feature of an element and EXAFS is a consequence of (low energy) electron diffraction that occurs locally. In a sense, EXAFS can be considered to be a LEED experiment 'conducted with an electron gun and a phase sensitive detector located within the sample itself.' (Sandstrom & Lytle, 1979). It is evident that a study of the EXAFS of different elements in a given material results in the complete definition of the local structure. This is tantamount to a knowledge of the (short-range) partial structure factor for each component element.

Recent developments in EXAFS owe much to the availability of synchrotron radiation (Teo, 1980; and Winick & Bienenstock, 1978). Its use obviates much of the tedium of the experiment and also permits EXAFS analysis of dilute samples.

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Preliminary studies of soft X-ray sources indicate that EXAFS of light (low Z) elements will also soon be accessible (Mallozzi *et al.*, 1979*a, b*), which will complement data from synchrotron sources. In this article, we shall first briefly describe the theory and instrumentation and then present select applications of EXAFS in a variety of areas of physical and biological sciences to illustrate recent developments in this important technique.

THEORY OF EXAFS

We noted earlier that EXAFS is a result of two fundamental processes: (a) K-(or L-) absorption of an X-ray photon which is the photoelectric effect; and (b) an effective diffraction of the electron so emitted. In the case of an isolated absorbing atom (absorber) one sees only the characteristic rise in absorbance, $\mu (= \ln I_0/I)$, at the energy corresponding to the edge and an exponential decrease thereafter (Kincaid, 1975). When the absorber is surrounded by other atoms, μ exhibits undulations sometimes upto 2000eV beyond the edge. Undulations starting 30eV beyond the edge constitute the EXAFS. As an example, the EXAFS of GeO_2 is shown in Fig. 1.

Photoelectrons are emitted following the absorption of the X-ray photon, by the absorber atoms. The outgoing (spherical) photoelectron wave emitted by the absorber is reflected by the surrounding 'scatterers.' The phase of the reflected wave is dependent on the photoelectron wavelength, the atomic number of the scatterer and the distance between absorber and scatterer atoms. The reflected (phase-shifted) wave undergoes self-interference with the outgoing wave at the emitter site. That

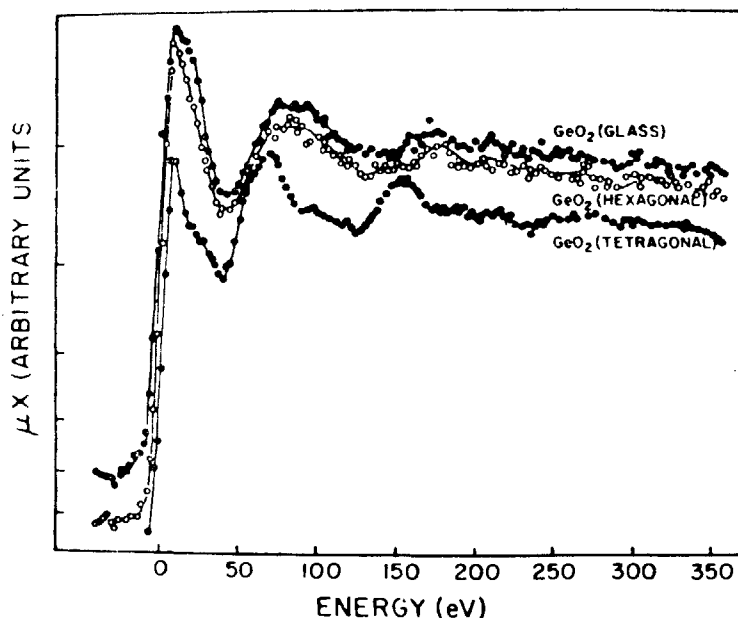


FIG. 1. EXAFS spectra of three forms of GeO_2 (after Nelson *et al.*, 1962).

this self-interference is responsible for the EXAFS may be seen as follows. (Stern *et al.*, 1978; Ashley & Doniach, 1975; and Lee & Beni, 1977). The probability, W , of X-ray absorption (i.e., photoemission) is governed by the golden rule (Bethe & Salpeter, 1959) which shows that

$$W = 2\pi^2 e^2 (\omega c^2 m)^{-1} |M_{fs}|^2 \rho(E_f) \quad \dots(1)$$

where $M_{fs} = \langle f | \underline{p} \cdot \underline{\epsilon} | s \rangle$, e is the charge of the electron, $2\pi\omega$ is the frequency of the X-ray photon, c is the velocity of light, m is the mass of the electron and \underline{p} its momentum vector, $\underline{\epsilon}$ is the electric field vector of the radiation and $\rho(E_f)$ is the density of final states. $|s\rangle$ is the K-shell wave function and $\langle f|$ is the wave-function of the final state to which the electron is excited. The selection rule requires that $\langle f|$ have p -character.

For $E \gtrsim 30\text{eV}$ the final state is essentially a continuum state. It is at once obvious from equation (1) that the only term which can cause the fine structure is $|M_{fs}|$ since the other term, $\rho(E_f)$ is a monotonically varying function. The $|s\rangle$ state in $|M_{fs}|$ corresponds to very low potential energy and hence remains unaffected; thus it is only the $\langle f|$ state that can cause the undulations. The final state of a photoelectron which corresponds to a spherical wave propagating away from the absorber is shown schematically in Fig. 2 along with the back-scattered wave which, we may recall, is generally phase-shifted with respect to the outgoing wave. The reflected wave is further phase-shifted at the absorber atom and interference between this wave and the outgoing one at the K-shell (which is a tenth or a fiftieth of the atomic radius) causes alterations in $\langle f|$.

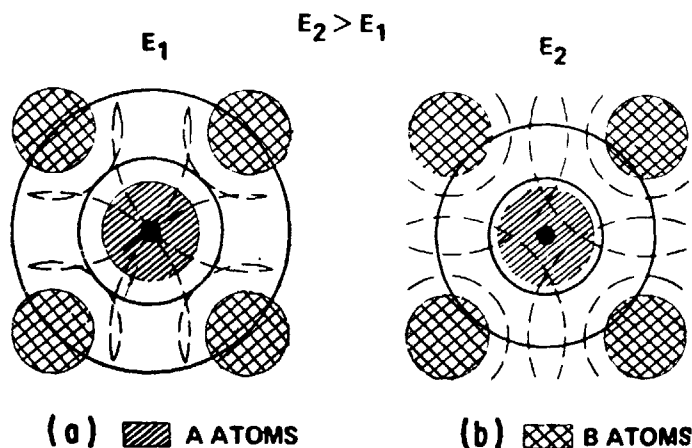


FIG. 2. A schematic representation of the EXAFS process. the solid circles denote outgoing waves centred about absorber atoms A and broken circles denote reflected waves centred about scatterer atoms B. Constructive interference is depicted in (a) and destructive interference in (b) (after Wong, 1980).

Stern and coworkers (Stern, 1974; Lytle *et al.*, 1975; and Stern *et al.*, 1978) have treated the effect of such self-interference on the final state with the inclusion of relevant phase-shifts and have shown that the EXAFS, $\chi(k)$, can be written as

$$\chi(k) = \sum_j A_j(k) \sin [2kR_j + \xi_j(k)] \quad \dots(2)$$

where $k = |k|$, summation is over j coordination shells and R_j is the distance from the absorber to the j th shell while $\xi_j(k)$ is the total phase-shift due to the j th shell ($\eta_j(k)$) and the absorber ion potential ($\delta(k)$). $\xi_j(k)$ can be fitted to a second order polynomial

$$\xi_j(k) = \xi_0 + \xi_1 k + \xi_2 k^2 \quad \dots(3)$$

$A_j(k)$ represents the total j th shell scattering amplitude and can be written (Sandstrom & Lytle, 1979)

$$A_j(k) = \frac{N_j}{kR_j^2} F_j(k) \exp - (2\sigma_j^2 k^2) \quad \dots(4)$$

N_j and σ_j in equation (4) represent the number of atoms in the j th shell and root-mean-square deviation of the interatomic distances over R_j which results both from static and dynamic (thermal) disordering effects respectively. The scattering amplitude, $F_j(k)$ is given by (Sandstrom & Lytle, 1979),

$$F_j(k) = f_j(\pi, k) \exp (-2R_j/\lambda) \quad \dots(5)$$

where $f_j(\pi, k)$ is the the back-scattering amplitude (which is equivalent to an electron back-scattering form factor) and λ is the mean free path of the photoelectron. Equation (2) explains why monoatomic gases do not exhibit EXAFS and shows very simply that the absorbance undulations arise from the sine term.

It is at once obvious that fourier transformation of equation (2) should yield information about all the j shells in direct space that contribute to the EXAFS. The R_j 's so obtained are, however, shortened by ξ_1 the k -dependent part of $\xi_j(k)$ (we discuss methods to obtain $\xi_j(k)$ later). Since the intensity of the outgoing spherical wave decreases very rapidly with increasing R , distant atoms contribute very little to the fine structure. Multiple scattering effects are also relatively unimportant and these have indeed been ignored in the derivation of eqn. (2). EXAFS should contain no information about 'shadowed' or eclipsed atoms, but there are exceptions to this as exemplified in the discussion of the 'focusing' effect to be presented later (Cramer, 1978; and Teo, 1981).

Other theoretical approaches such as those due to Ashley and Doniach (Ashley & Doniach, 1975) and Lee and Beni (Lee & Beni, 1977) use similar interference effects to explain the EXAFS. These approaches also explore the effects of alternative phase-shift expressions and multiple scattering. Since their conclusions are similar to those described above, we shall not discuss them any further.

Since the Fourier transformation of equation (2) yields only a radial distribution function about the absorber, we note that information obtained from EXAFS is limited to an average, one-dimensional representation of structure. Furthermore, in order that the transform be comparatively free of ripples, the data should extend to at least $\sim 500\text{eV}$ beyond the edge. Other limitations of the Fourier method such as termination error, are shortcomings that EXAFS shares with other cognate techniques, though use may be made of window functions (such as a Hanning function) (Wong & Lytle, 1980a) in order to minimize their effects.

The most important parameter involved in the transformation is the total phase-shift function $\xi_j(k)$. Several *ab initio* methods of evaluating $\xi_j(k)$ have been developed and values of $\xi_j(k)$ have been tabulated (Teo & Lee, 1979), but their accuracy is limited by the many approximations involved in the calculations. Often phase-shift corrections are estimated experimentally (as discussed later) by making use of structural information available from other techniques on related compounds.

An alternative method that does not involve Fourier transformation has also been proposed by Lytle *et al.* (Lytle *et al.*, 1975). In this approach one notes that the EXAFS oscillations can arise only from the sine term in equation (2). Denoting the crests and troughs in the EXAFS by even and odd values of n , one plots n vs. k . The resulting line given by

$$\frac{n\pi}{2} = 2k(R_1 - \alpha_1) + 2\beta_1 \quad \dots(6)$$

has a slope equal to $4(R_1 - \alpha_1)/\pi$ so that R_1 may be calculated for a known α_1 . This method has also been used (Apte & Mande, 1980, 1981) but it can yield values only for R_1 (that too not very accurately, especially when the first shell itself is split) and the trend has been to use the more powerful Fourier transform approach.

ANALYSIS OF EXAFS DATA

In Fig. 3, we show the various stages of processing of EXAFS data to obtain radial structure functions (RSF's). In the first stage various non-EXAFS components are subtracted from the data. Pre-edge absorption is removed using the Victoreen correction (International Tables for crystallography, 1969) of the form $A\lambda^3 + B\lambda^4$. The monotonic decrease of absorbance beyond the edge, which is known as the photoelectric decay, μ_0 , is subtracted out after approximating it either by a second degree polynomial or a spline-function (Eccles, 1978). Inadequate correction for μ_0 , especially at high k , tends to produce unphysical peaks at low R in the RSF. Normalized $\chi(k)$ is then expressed

$$\chi(k) = (\mu - \mu_0)/\mu_0 \quad \dots(7)$$

The photoelectron wave-vector k is evaluated using $\hbar^2 k^2 = 2m(E - E_0)$ where E is the energy of the X-ray photon, E_0 is a reference energy (to be discussed later) and m is the mass of the electron. $\chi(k)$ is multiplied by k^n ($n = 2$ or 3 usually) to

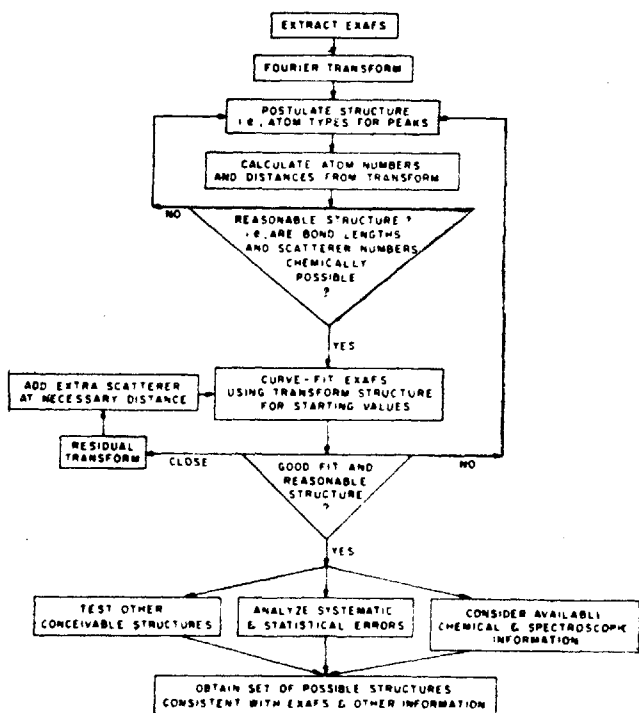


FIG. 3. A flowchart for EXAFS data analysis (After Cramer *et al.*, 1978c).

magnify the faint EXAFS at large k (Lytle *et al.*, 1975). $k^n \chi(k)$ is Fourier transformed to yield the RSF, $\phi(R)$. In the model compound, the first peak at a distance R_1 represents the distance to the nearest neighbour shell and may be compared to R'_1 , the known distance. We can then define α^* as $(R'_1 - R)$ which represents the experimentally determined phase correction. In principle, $2\alpha^*$ should be equal to the theoretically estimated k -dependent part of $\xi_j(k)$, viz., ξ_1 , if the identity of the scatterer environment has been correctly assumed. It must be emphasized that wherever scatterer identities are obscure (e.g., in several covalently bonded and disordered systems) use of α^* (and not ξ_1) is advisable. Further, the k -dependence of $\xi_j(k)$ introduces an intrinsic limitation to its quantitative accuracy.

The second stage of improvement in the EXAFS data is achieved through Fourier filtering (Eccles, 1978). Here, a particular peak in $\phi(R)$, corresponding to the i th scattering shell, is transformed back to k -space and the transformed function is fitted to a parameterized expression for EXAFS (Eccles, 1978; and Cramer 1978)

$$\chi'(k) = \frac{k^n C_1 \exp(-C_2 k^2)}{k C_3} \sin \{C_4 + (C_5 + 2R_i)k + C_6 k^2\} \quad \dots(8)$$

$\chi'(k)$ has six adjustable parameters (the C 's) and consists of both phase and amplitude terms, cf. equation (3). R_i may be treated as an adjustable parameter.

It is now recognized that $\xi_j(k)$ is a property of the absorber (A)-scatterer (B) couple only and is not dependent upon details of chemical bonding (Citrin *et al.*, 1978). Consequently, $\xi_j(k)$ is believed to be transferable from compound to compound. We may note that an EXAFS experiment can yield a value only for $\xi_j(k)$ and cannot, in any case, separate the contributions, $\eta_j(k)$ and $\delta(k)$. In a simple case Citrin *et al.* (1976) have shown that $\xi_{jA-B}(k)$ may be obtained even from compounds which do not contain simple A-B bonds. Indeed, such transferability of $\xi_j(k)$ from a model to an unknown compound provides a convenient procedure for obtaining corrected values of R_j .

In the Fourier filter method, α^* for the absorber - i th shell couple is given by $\alpha^* = R_i - R'_i$ where R_i is the curve fitted distance to the i th shell and R'_i is the corresponding peak in the RFS. Using this method it is possible to avoid ambiguities due to contributions from different shells to the estimated phase-shifts. The disorder parameter σ_j (represented by C_2) is a measure of the spread of interatomic distances in the j th shell (Lytle *et al.*, 1975). In a given shell, j , σ_j is made up of contributions from static disorder, σ_{stat} , and vibrational or dynamic disorder, σ_{vib} (related to the Debye-Waller factor) (Beni & Paltzmann 1976; and Sevillano *et al.*, 1979) and can be written $\sigma_j^2 = \sigma_{\text{stat}}^2 + \sigma_{\text{vib}}^2$. By investigating the temperature dependence of σ_j , estimates of the individual contributions may be obtained. A comparison of the EXAFS expression and the X-ray diffraction (XRD) intensity expression suggests that EXAFS is much more [$\exp(-3\mu_{\text{vib}}^2 k^2)$ times] sensitive than XRD is to disorder. This is because EXAFS involves a two-centre average and hence $\sigma_{\text{vib}}^2 = (2\mu)^2$ (Wong, 1980). Distances evaluated from EXAFS can be accurate to $\pm 0.02\text{\AA}$ but such accuracy is crucially dependent on the quality of the input data. N_j , which represents the coordination number, is estimated by a comparison of C_1 in known and unknown situations (*see* Hunter *et al.*, 1977, for an alternative method). Its accuracy is generally poor and interpretations based solely on such N_j values must be made with caution. The mean free path (*see* equation 3) is represented by C_3 , but its treatment appears unsatisfactory and its influence upon final results is not clearly established.

INSTRUMENTATION

EXAFS is commonly recorded in the transmission mode. In special situations, however, as in the EXAFS of dilute samples, other modes (e.g., fluorescence) are employed (Jaklevic *et al.*, 1977; and Stern & Heald, 1979). For surface EXAFS (SEXAFS), Auger electron spectroscopy, electron energy loss and partial electron yield measurements have been used (Citrin *et al.*, 1978; Stohr *et al.*, 1978; and Joy & Maher, 1979).

An EXAFS experimental set-up has three primary components: (i) a source of X-rays, (ii) a monochromator (and collimator) and (iii) a detector. Synchrotron

radiation is being widely used for EXAFS studies in advanced countries. Synchrotron sources produce collimated nearly polarized, tunable and intense monochromatic beams whose energies range from 3 to 25keV. Both the energy range and intensity may be further increased using 'wiggler' techniques, (Winick & Knight, 1977). EXAFS of low atomic number elements (C to S) can be measured with high-intensity nanosecond pulsed soft X-ray (53keV) sources from laser heated pulses (Mallozzi *et al.*, 1979).

For a laboratory EXAFS facility, a rotating anode source is most suitable (del Cueto & Shevchik, 1978*a, b*; and Knapp *et al.*, 1978). In this device, the anode is made of a refractory and high atomic number metal which is kept spinning at very high speeds (3000–6000rpm) in order to prevent local melting under intense electron bombardment. In addition, the geometry of the anode is designed so as to provide a sharply focussed beam of X-rays.

A comprehensive review of the progress in EXAFS instrumentation has recently been published in *AIP Proceedings* (1980). The current trend is to fully automate energy scanning, data acquisition and preliminary data manipulation. Hardware and software for these purposes are also commercially available.

APPLICATIONS

As pointed out earlier, EXAFS is a very powerful technique for the study of local structure in a variety of materials. Hence, the literature on the applications of EXAFS has been growing very rapidly in recent years. A variety of solids both crystalline and non-crystalline have been investigated using this technique. In this section we review briefly some significant reports of such structural studies.

Simple Chemical Systems

In order to elucidate the more subtle details of EXAFS theory, a host of studies have been carried out on metals, simple salts and their aqueous solutions.

Copper is one of the widely investigated metals since its simple structure is a very useful check on the technique itself (Lytle *et al.*, 1975; Stern *et al.*, 1975; Ashley & Doniach, 1975; Beni *et al.*, 1976; Gregor & Lytle, 1979; Sevillano *et al.*, 1979; Lee & Pendry 1975; and Bohmer & Rabe, 1979). Nonetheless, there is some controversy about the origin of the fourth peak in the RSF of this metal. It is likely that multiple scattering plays an important role in this case, but conclusive evidence for this has so far not been adduced. Studies of elements such as Ge (Lytle *et al.*, 1975; and Lee & Beni, 1977) and other elements using polarized X-rays (Beni & Platzman, 1976; and Brown *et al.*, 1977*a, b*) have also been performed.

KMnO₄ and other manganese salts have been studied both in the crystalline state and in aqueous solutions (Rabe *et al.*, 1979*a, b*). The idea of employing beats in order to detect small differences in bond-lengths has been used successfully by these workers. Aqueous solutions of Ni(II) salts have been studied by Sandstrom (Sandstrom *et al.*, 1977) using Ni_K EXAFS. In concentrated solutions, unequal distances to the first shell were inferred from the presence of 'beats'. A Ni-Cl distance

of 3.1 Å has also been reported. These conclusions have, nonetheless, been questioned by Licheri *et al.* (1981). Compounds of copper have been extensively investigated in this laboratory (Fig. 4) and elsewhere (Sham *et al.*, 1981; and Martens *et al.*, 1978). EXAFS studies in this laboratory of the square-planar complexes of Cu have yielded RSF's in which a wealth of detail is evident (Fig. 4). In La_2CuO_4 , one clearly sees the presence of unequal Cu-O bondlengths while the metal-metal bondlength in the acetate manifests itself as a sharp peak. In the magnesium copper glucuronate and related derivatives, we see only a single peak due to the Cu-O bond around 1.96Å: the coordination number of Cu is 4 thereby establishing the square planar geometry of the complex. None of the studies so far reported has shown the presence of Jahn-Teller distortion or even of significantly different disorder terms in the equatorial and axial bonds (Sham *et al.*, 1981).

Biological Molecules

EXAFS has been used in this area in order to elucidate nuances of structural detail that normally elude other structural techniques. EXAFS of metal ions have been studied in enzymes throwing much light on the nature of protein-substrate binding. Details of these compounds and a summary of the work done to date are available in many reviews (Holm, 1977; Shulman *et al.*, 1978; Cramer & Hodgson 1979; and Teo, 1980). It is in the investigation of biological molecules that the importance of the choice of model compounds (in order to fully exploit the capabilities of EXAFS analysis) is best borne out (Cramer, 1978). Indeed, the transferability of EXAFS parameters which has been successfully demonstrated in the case of biological molecules vindicates the validity of the assumptions underlying the EXAFS theory.

Table I summarizes some of the work undertaken on biological materials. In rubredoxin, iron is known to be coordinated to four cystein-thiolate ligands. It was thought that there were shorter and longer Fe-S bonds that modulated the redox potential at the iron site but EXAFS studies show the absence of such bond length differences (Shulman *et al.*, 1978). It now seems that $\text{Fe}(\text{SR})_4$ does not involve an entatic state. A similar study of haemoglobin has revealed that iron-ligand bond within 0.02Å. The between haemoglobin-Kempsey and deoxyhaemoglobin-A are length differences origin of the differences in oxygen affinity between the two forms may therefore not be related to the iron site (Eisenberger *et al.*, 1976, 1978). An investigation of azurin, a copper containing blue protein, has revealed the presence of the shortest yet reported Cu-S distance of 2.10Å (Tullius *et al.*, 1978). Furthermore, this is consistent with the strong absorption at 400 cm^{-1} in the Raman spectra of these proteins. EXAFS study of nitrogenase has revealed the presence of Mo in the dinitrogen reduction site (Wolff *et al.*, 1978). A novel Fe-S cluster seems to be present in this enzyme with several Fe atoms at 2.72Å from Mo. The clusters do not seem to contain oxo-groups.

In this laboratory, we have investigated the structure of the copper complex formed in the slime of the bacterium *Pseudomonas aeruginosa* (Fig. 4). The study has revealed that copper is four coordinated with a Cu-O distance of 1.96Å. It

TABLE I
A summary of some recent EXAFS studies

No.	Material	Edge ^a	Data obtained ^b			References
			Bond-length	Coordn. No.	Dis-order	
A. Salts and Aqueous Solutions						
1.	NaBr, KBr	Br _K	Y	Y	—	Lagarde (1976)
2.	RbCl, SrS, SrF ₂ , SrCl ₂	Rb _K , Sr _K	Y	Y	Y	Bohmer & Rabe (1974)
3.	KMnO ₄ crystalline and aq. soln.	Mn _K	Y	Y	Y	Rabe <i>et al.</i> (1979a)
4.	CuBr ₂ aq. soln.	Cu _K , Br _K	Y	Y	Y	Fontaine <i>et al.</i> (1978)
5.	Cu compounds	Cu _K	Y	Y	Y	Martens <i>et al.</i> (1978)
6.	NiNO ₃ .6H ₂ O & aq. soln.	Ni _K	Y	Y	Y	Sandstrom <i>et al.</i> (1977)
7.	NiNO ₃ .6H ₂ O & aq. soln.	Ni _K	Y	Y	Y	Licheri <i>et al.</i> (1981)
8.	Cu salts aq. soln.	Cu _K	Y	Y	Y	Sham <i>et al.</i> (1981)
9.	RhBr ₃	Rh _K , Br _K	Y	Y	Y	Reed and Eisenberger (1978)
10.	Fe, Mo and Co Complexes					Cramer <i>et al.</i> (1976, 1978c.)
B. Metals and Alloys						
1.	Cu, Co	Metal _K	Y	Y	—	Greegor and Lytle (1979) (<i>see text for others</i>)
2.	Cu	Cu _K (F)	—	—	—	del Cueto and Shevchick (1978a)
3.	Zn single crystal	Zn _K	Y	—	—	Brown <i>et al.</i> (1977a)
4.	Fe-Cu alloy	Fe _K (F)	Y	Y	Y	Hastings <i>et al.</i> (1979)
5.	(La _x Gd _{1-x})Os ₂	La _{LIII} Gd _{LIII} Os _{LIII}	Y	Y	Y	Boyce and Baberschke (1981)
6.	Al	Al _K	Y	—	—	Fontaine <i>et al.</i> (1979)
7.	Ge	Ge _K				Lytle <i>et al.</i> (1975) and Lee and Beni (1977)
8.	Fe in argon	Fe _K	Y	—	—	Montaine and Shenoy (1980)
C. Biological Materials						
1.	Copper etioporphyrin	Cu _K	Y	—	—	Sayers <i>et al.</i> (1977)
2.	Nitrogenase	Mo _K	Y	Y	Y	Wolff <i>et al.</i> (1978); and Cramer <i>et al.</i> (1978b)
3.	Cytochrome P 450	Fe _K	Y	Y	Y	Cramer <i>et al.</i> (1978a)
4.	Rubredoxin	Fe _K	Y	Y	Y	Shulman <i>et al.</i> (1978); and Bunker and Stern (1977)
5.	Pt-uridine complexes	Pt	Y	Y	—	Teo <i>et al.</i> (1978a)
6.	Pt-compd-calf thymus complexes	Pt _{LI}	Y	Y	Y	Teo <i>et al.</i> (1978b)
7.	Haemoglobin	Fe _K (F)	Y	Y	Y	Eisenberger <i>et al.</i> (1976, 1978)

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No.	Material	Edge ^a	Data obtained ^b			References
			Bond-length	Coordn No.	Dis-order	
D. Amorphous Materials						
1.	GeO ₂	Ge _K	Y	Y	Y	Sayers <i>et al.</i> (1975)
2.	Se	Se _K	Y	—	—	Parthasarathy <i>et al.</i> (1981)
3.	As ₂ S ₃ , As ₂ Se ₃ , GeSe ₂	As _K , Se _K	Y	—	—	Sayers <i>et al.</i> (1974)
		Ge _K				
4.	As ₂ (S, Se ₃), As ₂ (Se, Te) ₃	As _K	Y	Y	Y	Parthasarathy <i>et al.</i> (1982)
5.	As ₂ O ₃	As _K	Y	Y	Y	Gurman and Pettifer (1979)
6.	ZnCl ₂ & GeO ₂	Zn _K , Ge _K	Y	Y	Y	Wong and Lytle (1980a)
7.	GaAs, GaP	Ga _K , As _K	Y	Y	Y	Theye <i>et al.</i> (1980)
8.	GaAs	Ga _K , As _K	Y	Y	—	del Cueto and Shevchik (1978)
9.	Cu-As-Se	Cu _K	Y	Y	Y	Hunter <i>et al.</i> (1977)
10.	As ₂ Te ₃	As _K	Y	Y	Y	Pettifer <i>et al.</i> (1977)
11.	CoSO ₄ -ZnSO ₄ -Na ₂ SO ₄ -K ₂ SO ₄ ; CoO-B ₂ O ₃	Co _K	Y	Y	—	Results from I. I.Sc. Laboratory
12.	Fe ₄₀ Ni ₄₀ P ₂₀₋₂ B ₂	Fe _K , Ni _K	Y	—	Y	Wong (1980)
13.	Fe ₈₀ B ₁₀ Ge ₁₀	Ge _K	Y	Y	—	Wong (1910)
14.	Nb ₃ Ge	Ge _K	Y	Y	Y	Brown <i>et al.</i> (1977)
15.	Pd ₈₀ Ge ₂₀	Ge _K	Y	Y	Y	Hayes <i>et al.</i> (1978)
16.	TiO ₂ -SiO ₂	Ti _K	Y	Y	Y	Sandstrom <i>et al.</i> (1980)
17.	RFe ₂ (R = Rare Earth)	R _L , Fe _K	Y	Y	—	Stern <i>et al.</i> (1978)
18.	CrO ₂ gel	Cr _K	Y	—	—	Results from I. I. Sc. laboratory
E. Fast Ion Conductors						
1.	AgI	Ag _K	Y	Y	Y	Boyce <i>et al.</i> (1977)
2.	CuI	Cu _K	Y	Y	Y	Boyce <i>et al.</i> (1980)
3.	RbAg ₄ I ₅	Ag _K	Y	Y	Y	Stutius <i>et al.</i> (1979)
F. Catalysts						
1.	Cu-Ni	Cu _K , Ni _K (F)	Y	Y	Y	Apai <i>et al.</i> (1979)
2.	Os, Ir & Pt/SiO ₂ , Al ₂ O ₃	Metal _K (F)	Y	Y	Y	Via <i>et al.</i> (1979)
G. Miscellaneous						
1.	Br ₂ /graphite	Br _K	Y	Y	Y	Heald and Stern (1978)
2.	Rb/NbSe ₂	Rb _K , Nb _K	Y	—	—	Bourdillon <i>et al.</i> (1980)
3.	KC ₈ and KC ₁₂	K _K	Y	—	—	Caswell <i>et al.</i> (1980)
4.	Ni impurity in diamond	Ni _K	Y	—	—	Wong and Lytle (1980b)

a : Subscripts indicate edges at which EXAFS was studied. Fluorescence experiments are denoted by (F). The rest have been carried out in the absorption mode.

b : 'Y' indicates that data related to this parameter are available.

would have been impossible to obtain this information by any other technique since we can get this complex only in the form of fine powder. Other spectroscopic studies support square planar coordination in this complex. Comparison of the EXAFS results and the spectroscopic data with those obtained for the model glucuronates shows that the natural complex is very similar to magnesium copper glucuronate (Fig. 4).

The work of Teo *et al.*, (1978a) on the interactions between DNA and Pt-containing compounds is very interesting. It is one of the few studies using L-edge EXAFS.

Amorphous Materials

Significant number of applications of EXAFS are to be found in this area where conventional structural tools (e.g., X-ray diffraction and probe ion spectroscopy) suffer from well-known limitations. We have earlier referred to the EXAFS study of crystalline and amorphous GeO_2 where the sensitivity of EXAFS to local structure (a vindication of the SRO theory) was clearly demonstrated.

In recent years, Gurman and Pettifer (1977) and Pettifer and McMillan (1977) have investigated the As_K EXAFS of crystalline and glassy As_2O_3 . In the latter, they have found that disorder increases with distance from As, and have therefore con-

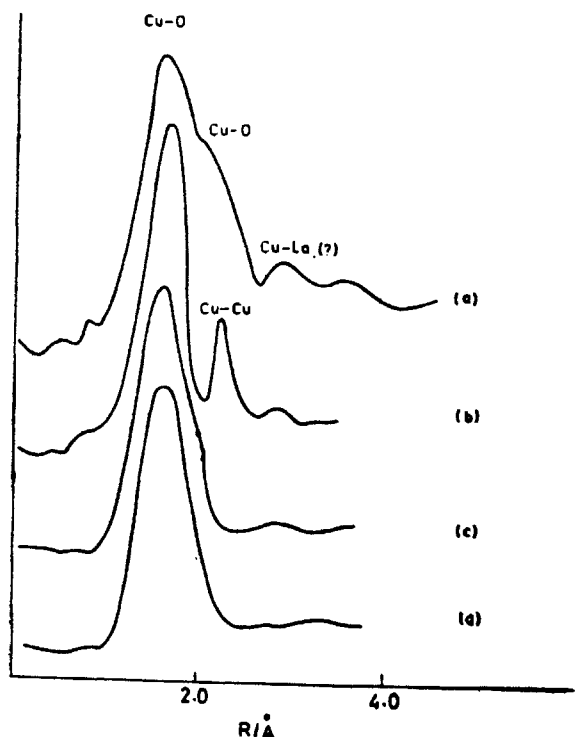


FIG. 4. RSF's of some square-planar copper compounds (a) La_2CuO_4 (b) $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$ (c) Magnesium copper glucuronate (d) Copper complex formed by the slime of *Pseudomonas aeruginosa*. (unpublished work from this laboratory).

cluded that As_4O_6 units are absent in the glass. Knights *et al.* (1977) have studied the As EXAFS of Si-H alloy films doped with As and have found that As is present as a substitutional impurity in these materials.

Wong and Lytle (1980a) have studied Zn EXAFS in $ZnCl_2$ glass through the glass transition (T_g) and have found that there is no sudden increase in disorder at T_g in this materials as there appears to be in glassy GeO_2 . Nonetheless, $ZnCl_2$ glass, which is a weak analogue of glassy GeO_2 , shows higher disorder than the latter in the temperature range studied. Theye *et al.* (1980) have studied disorder in flash evaporated amorphous films of III-V compounds. In amorphous GaAs, K-edge EXAFS of both the elements were studied whereas only the Ga edge EXAFS was investigated in GaP. In contrast to the findings of del Cueto and Shevchik (1978b) who studied sputtered films of GaAs, Theye *et al.* have found no evidence of chemical disorder in GaAs; in GaP, however, they conclude that a fraction of the bonds about Ga are likely to be Ga-Ga bonds. Since homo- and hetero-atom bond energies are similar in GaP rather than in GaAs, the conclusions of Theye *et al.* appear to support the hypothesis of chemical ordering (Rao & Mohan, 1981).

Se is a very ready glass former and the RSF of Se glass (Fig. 5) has been found to contain a very interesting short distance at 1.98\AA (Parthasarathy *et al.*, 1981). This could possibly represent the bonds at chain terminations where the penultimate and ultimate Se atoms are likely to be linked by a π -bond. The EXAFS of glassy chalcogenides have been studied by a number of workers (Gurman & Pettifer, 1979; Pettifer & McMillan, 1977; Pettifer *et al.*, 1977; and Sayers *et al.*, 1974) and coordination numbers and distances have been ascertained. Pettifer *et al.* (1977) have found evidence for a higher degree of short range order in As_2Te_3 glass than in the crystal which they have attributed to increased covalency in the glass. The present authors have studied glasses in the pseudo-binary systems As_2S_3 - As_2Se_3 and As_2Se_3 - As_2Te_3 (Parthasarathy *et al.*, 1982). The RSF's of these glasses are shown in Figs. 6 and the distributions of R_i values about the mean distance, as reflected by the full width at half maxima (FWHM) of the peaks, are shown in Fig. 7. Non-nearest

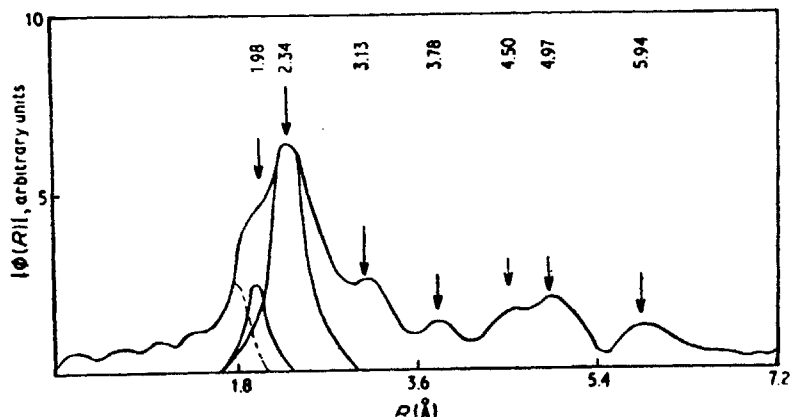


FIG. 5. RSF of selenium glass (after Parthasarathy *et al.*, 1981).

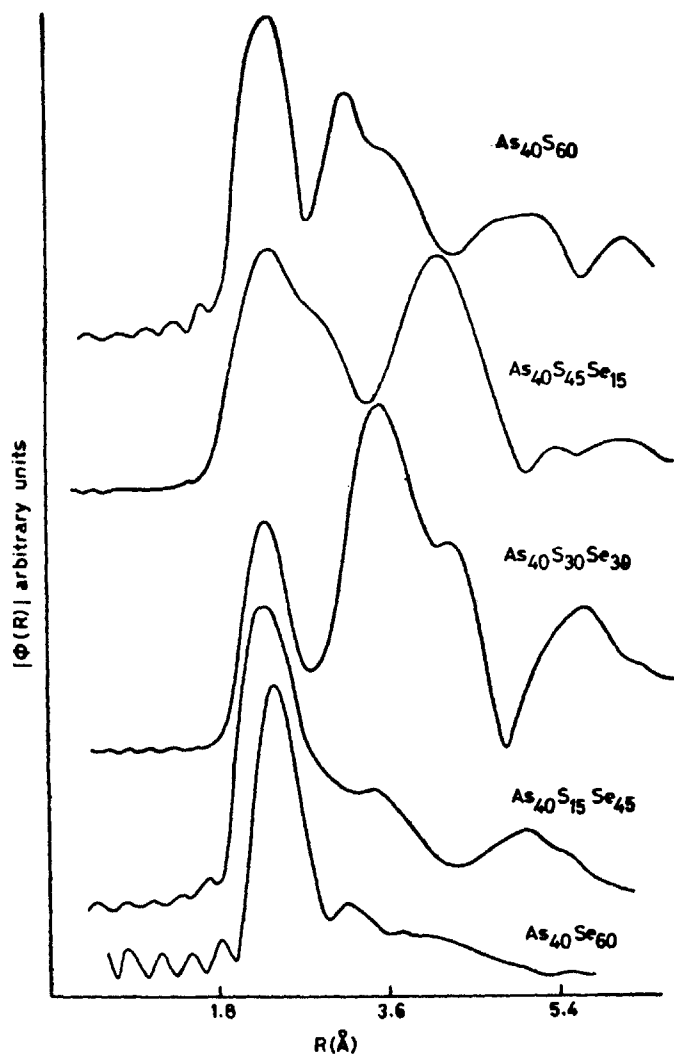


FIG. 6a. RSF's of (a) $\text{As}_2(\text{S, Se})_3$ glasses (after Parthasarathy *et al.*, 1982).

neighbour distances in As_2Se_3 - As_2Te_3 vary in agreement with earlier evidence for increased ionicity in intermediate compositions (Sarode *et al.*, 1979; and Vaipolin & Porai-Koshits, 1963). In As_2S_3 - As_2Se_3 glasses, however, the spread of second shell bond-lengths appears to suggest the presence of homoatomic bonding, possibly because of the similarity of various bond energies in this system.

The possibility of using probe ion EXAFS for structural studies in glasses has been explored by us in this laboratory for the first time. EXAFS of Co^{2+} in sulphate glasses and in borate glass have been analysed. Co-O distances were found to be very similar in crystals and in the glasses (Fig. 8). The value of the experimental phase shift, however, appears to be strikingly low.

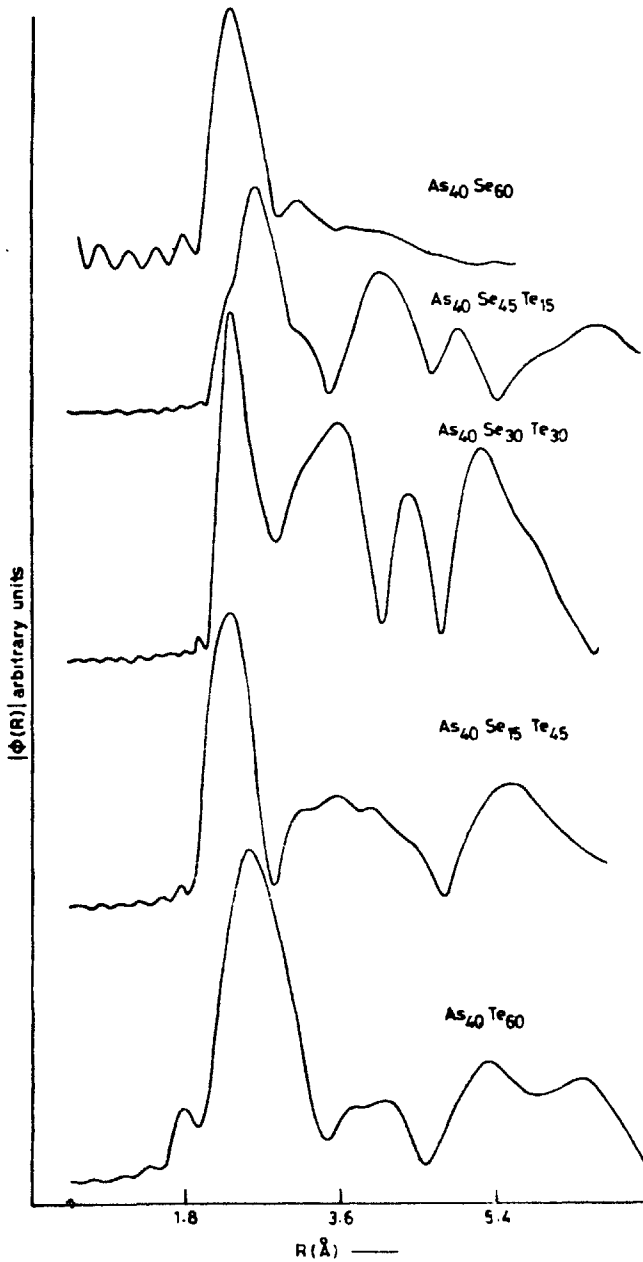


FIG. 6b. RSF's of $\text{As}_2(\text{Se,Te})_3$ glasses (after Parthasarathy *et al.*, 1982).

A large number of metallic glasses have been investigated using EXAFS and the work has been reviewed by Wong (1980). The amorphous ferromagnet $(\text{Fe, Ni})_{80}(\text{P, B})_{20}$ has been investigated exploiting the atom selectivity of EXAFS (Wong, 1980). It has been found that more than 10 per cent P enhances the dynamic

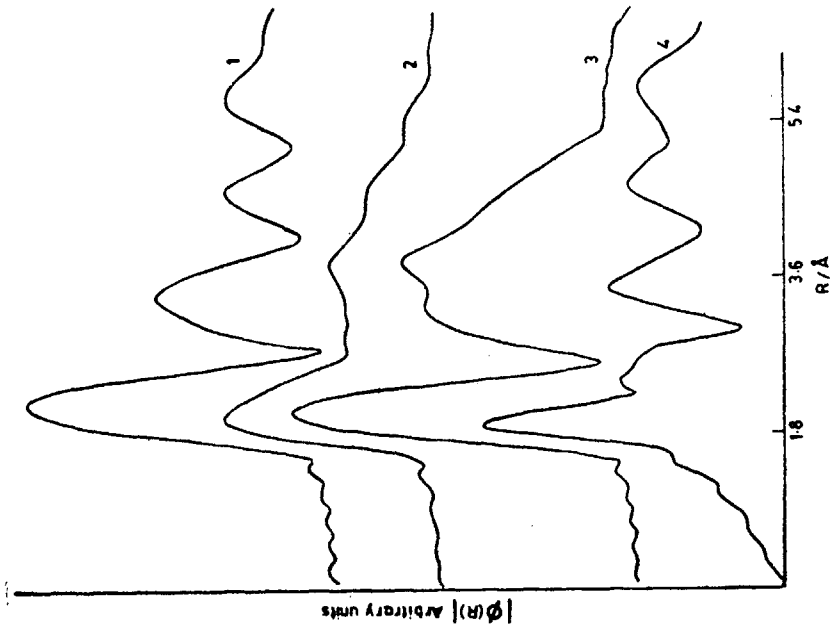


Fig. 8. RSFs of Co-oxide containing glasses. The numbers indicate the molar compositions of individual glasses: (1) $\text{CoSO}_4 \cdot \text{ZnSO}_4 \cdot \text{K}_2\text{SO}_4 \cdot \text{Na}_2\text{SO}_4 :: 25:15:30:30$ (2) $25:25:25:25$ (3) $40:20:20:20$ and (4) $\text{CoO} \cdot \text{B}_2\text{O}_3 :: 20:80$ (Results from I.I.Sc. laboratory).

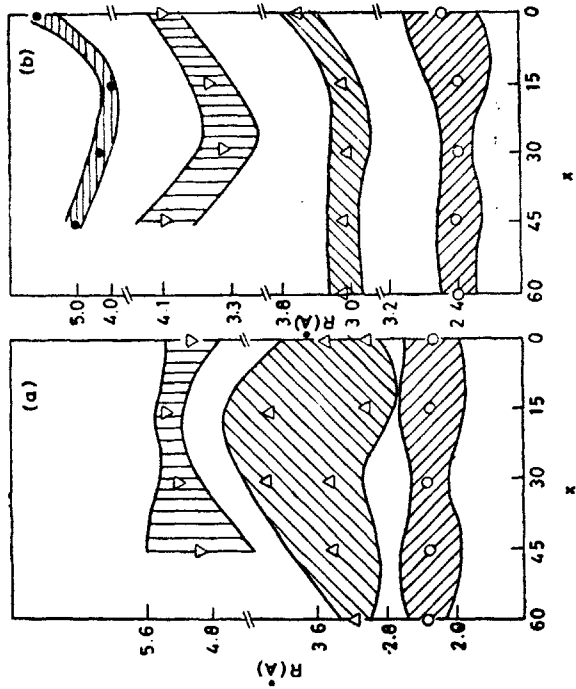


Fig. 7. Distributions of bond lengths about the mean bond length for the various bonds in (a) $\text{As}_3(\text{S}, -\text{Se})$, and (b) $\text{As}_3(\text{Se}, \text{Te})_3$ glasses (after Parthasarathy *et al.*, 1982).

decoupling of both metal ions with their nearest neighbour shells, which is reflected in the variations of the disorder parameter. These workers have also used EXAFS to study the effect of annealing upon the disorder parameter and the effect of phosphorus segregation on mechanical embrittlement. An important problem in metallic glasses that has been resolved using EXAFS studies relates to the elucidation of the metalloid environment. The work by Hayes *et al.* (1978) on $\text{Pd}_{80}\text{Ge}_{20}$ and of Wong (1980) on $\text{Fe}_{80}\text{B}_{10}\text{Ge}_{10}$ has now established that there are no metalloid-metalloid contacts in these glasses as anticipated in Polk's model. The metalloid-metal distance is closer to the sum of the covalent, rather than the atomic, radii. Brown *et al.* (1977) have reported interesting work on amorphous thin films of Nb_3Ge . The decrease in the Nb-Ge distance from 2.87 to 2.66Å in the film which they have noticed has been attributed to the increased covalency of the latter. Such changes in the crystal to glass transformation have been observed to be a general phenomenon by Rao *et al.* (1980) who have studied K-edge chemical shifts in a number of amorphous materials.

EXAFS studies on the crystallisation of chromia gel have been carried out in the I. I. Sc. Laboratory by K.K. Singh and P. Ganguly. Fig. 9 shows the RSF's of different samples heated to different temperatures in different environments. What is interesting is that we see peaks due to Cr—O and other distances in the gel just as in the crystalline material. It is evident that heating causes progressive crystallization as seen from the sharpening of the peaks and the emergence of details in the RSF.

Catalysts

EXAFS studies of catalysts may be expected to indicate appropriate strategies for designing catalysts, particularly those prepared by impregnation of oxide supports with metals (Lytle, 1977). Via *et al.* (1979) have studied metal clusters of Os, Ir and Pt on SiO_2 and Al_2O_3 and have found that the metal atoms have lower coordination numbers with concomitant increase in the average bond-length. A similar study of Cu-Ni clusters on amorphous substrates has revealed that metal-metal distances increase as absorption edge energies decrease (Apai *et al.*, 1979). Sinfelt and co-workers (Sinfelt *et al.*, 1980) have studied Ru-Cu clusters on SiO_2 and have found that Ru atoms are predominantly coordinated to other Ru atoms while Cu shows no such preference. Catalytic impurities (e.g., Ni) in synthetic diamonds exhibit a small lattice dilation and carbide formation is apparently absent (Wong & Lytle, 1980b).

In this laboratory we have been investigating hydro-desulphurization catalysts for some time. EXAFS of a catalyst precursor gives a Co—O distance of 1.96Å. On sulphidation we find a main peak in the RSF at 2.48Å which can only be due to the Co—S distance. Interestingly, samples of MoS_2 containing Co show a Co-S distance of 2.44Å. There appears to be little doubt that Co in these catalysts is in the sulphided form rather than in the metallic form.

Fast Ion Conductors

The atom selectivity of EXAFS has been usefully exploited in the investigation of fast ion conductors (FIC's) (Boyce & Hayes, 1980). Investigation of superionic

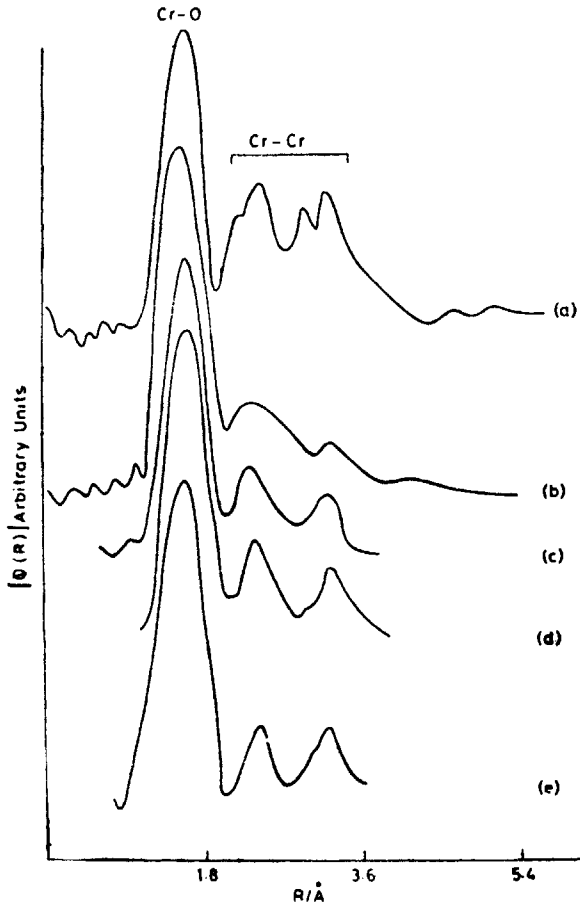


FIG. 9. RSF's of (a) Cr_2O_3 and Chromia gel after heating the latter at (b) 373K in air (c) 623K in hydrogen (d) 723K in hydrogen for 12h in each case. (Unpublished results from this laboratory).

α -AgI and β -AgI (the latter is the insulating phase) using Ag_{K} EXAFS has revealed that Ag ions occupy distorted tetragonal sites in a BCC lattice of iodide ions. Further, Ag ions are displaced in the direction of the most probable path for ion jump (Boyce *et al.*, 1977). Evidence has also been obtained to support the jump-diffusion-conduction model by comparison with theoretically computed EXAFS. A similar investigation of RbAg_4I_5 by Stutius *et al.* (1979) has indicated that Ag^+ ion occupy tetrahedral voids in the iodide lattice and that the $\text{Ag}^+ - \text{Ag}^+$ correlations persist into the superconducting (α) phase. In CuI, however; EXAFS seems to show that Cu^+ ion is present in both tetrahedral and octahedral locations (Boyce *et al.*, 1980). The favoured path of Cu^+ ion motion appears to be along [111] direction. The analysis supports an excluded volume model for the Cu-I pair correlation function. Fig. 10 gives a schematic diagram of the excluded volume model; also shown are the shapes of the first peak of the RSF's at various temperatures for AgI and CuI.

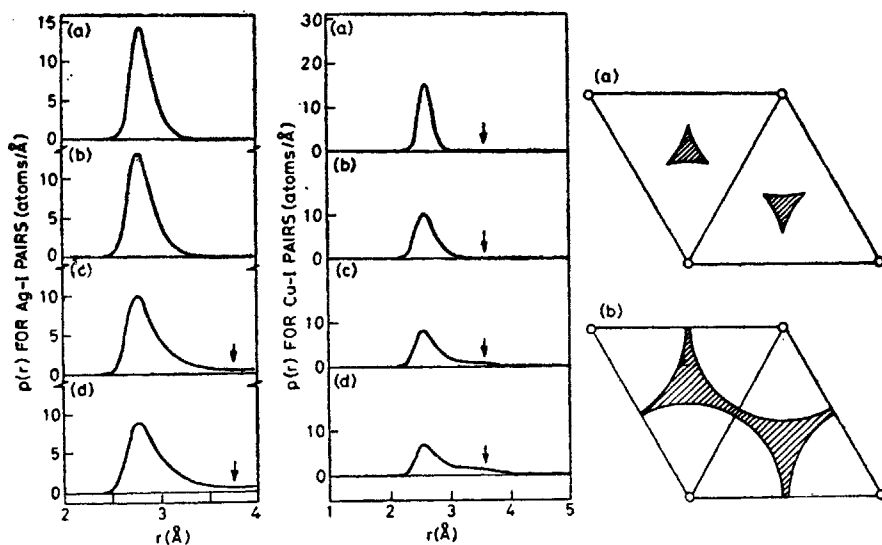


FIG. 10. (i) Radial distribution function of iodide ions about each Ag in AgI in the β -phase at (a) 293K (b) 371K and in the α -phase at (c) 471 and (d) 575K. Each distribution function is normalized to contain 4 iodide ions in the first peak. The arrows in (c) and (d) locate the contribution from a silver ion occupying the centre of a face between adjacent tetrahedra. (ii) Radial distribution function of iodide ions about each Cu in CuI in the γ -phase at (a) 295K (b) 573K (c) 623K and the α -phase at (d) 743K. The arrows indicate the location for Cu ions in the centre of a tetrahedral face, the bridging site between the tetrahedra and octahedra. (iii) A schematic two-dimensional representation of the allowed (shaded) and excluded regions for cation centres in the excluded volume model in the (a) insulating and (b) conducting phases. The anion centres are denoted by small circles. Note the connection between allowed regions in the superionic phase (after Boyce & Hayes, 1979).

Other Studies

Studies of intercalates have also been reported in recent years. In their EXAFS investigation of Br_2 in graphite Heald and Stern (1978) have found that the intercalate retains its molecular structure but the Br-Br distance, however, increases so as to match the periodicity of the graphite lattice. In the series of pseudo stoichiometric alkali metal graphite compounds (KC_n , $n = 2, 3, 4$), EXAFS results suggest that the metal is present as a disordered two-dimensional lattice gas (Caswell *et al.*, 1980). Bourdillon *et al.* (1980) have studied alkali-metal NbSe_2 intercalates and have found an increase in the Nb-Nb distance.

It has been found recently that O^+ ion desorption from oxygen covered surfaces of metals like molybdenum provides information similar to EXAFS (Jaeger *et al.*, 1980). The RSF's of such samples obtained from O^+ desorption data and EXAFS are comparable except for the intensity of the Mo-Mo peak. The lower intensity found in the desorption data is interpreted as due to lower coordination of the metal on the surface as compared to the bulk.

CONCLUDING REMARKS

In summary, we note that the utility of EXAFS arises in large measure from its atom specific nature and its sensitivity to local structure. This makes it especially suitable for the study of materials lacking long range order such as amorphous materials, solutions etc. Information from EXAFS is limited to a one-dimensional structure function since the phenomenon itself is an effect of interference amongst the back scattered waves and the outgoing wave at the absorber site. EXAFS differs from X-ray diffraction in that the small bond length differences manifest themselves variations in oscillation amplitudes ('beats') (Martens *et al.*, 1977; and Rabe *et al.*, 1979). Structural disorder which can be studied as a function of temperature (see equation 4) can be used to separate the static and dynamic components. Further, σ is much more sensitive to temperature than the Debye-Waller factor μ , from X-ray diffraction measurements. Some of the less understood aspects of EXAFS include the focusing effects (Cramer, 1978; and Teo, 1981) in which shells of eclipsed atoms are visible in the RSF as surprisingly large peaks with anomalous phase shifts. Teo (1981), however, shows that amplitudes are more seriously affected than phase shifts by this effect. In any event, phase-shift calculations need further attention if interatomic distances from EXAFS are to be as accurate as those from single crystal X-ray diffraction studies.

Applications of EXAFS to the study of phase transitions are relatively unexplored. It seems that a study of order-disorder (orientational and positional) transitions would be instructive. In transitions involving subtle structural changes (as in SrTiO₃ at 100K where the oxygen octahedra are known to rotate), EXAFS may well provide definitive information. From the point of view of metallurgists, the use of an electron microscope as a source of secondary X-rays should facilitate the study of spatially resolved domains. Pulsed soft X-ray sources will probably permit *in situ* studies of transients in chemical reactions. Lastly, combined L- and K-edge studies in simple systems remain to be exploited; these will, no doubt, help clarify some of the ambiguities present in the EXAFS theory itself.

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