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ABSORPTION SPECTRA USED AS STRUCTURAL PROBE**

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A UNIFIED SCHEME OF INTERPRETATION OF THE X-RAY
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INTRODUCTION:

It is well known that the x-ray absorption spectroscopy (XAS) provides information about to the geometrical arrangement of the environment surrounding the absorbing atom. Up to now only the EXAFS part of the XAS spectrum, which gives the pair correlation function, has been the monopolising object of extended experimental investigation. However, experimental evidence of multiple scattering (MS) effects has been found up to several hundred eV far from the edge. For this reason we think the time is now ripe to begin to look beyond the EXAFS approach and try to exploit all the potentiality of the XAS spectroscopy for obtaining structural information. It is the aim of this paper to go in this direction by presenting a unifying scheme of interpretation of the x-ray absorption spectra valid for the whole energy range based on the multiple scattering theory. This approach calculates the absorbing coefficient in the real space for a small cluster, around the photoabsorber, whose size is determined by the inelastic mean free path of the photoelectron and the core-hole lifetime (see Ref. [1] for a detail discussion of the method). The advantage, in comparison with other method, is that it can be extended to materials where there is not long range order like solutions, liquid and amorphous.

THEORY:

In the MS formalism the polarization averaged coefficient as function of energy ϵ is given by ^{1,2} :

$$\alpha_F(\epsilon) = \alpha_F^{l+1} + \alpha_F^{l-1} = (l+1) \alpha_0^{l+1} X^{l+1} + l \alpha_0^{l-1} X^{l-1} \quad (1)$$

where the $\alpha_0^{l\pm 1}$ is the atomic absorption coefficient of the absorbing atom from a core initial state of angular momentum l ($l=0$ for k-edge) and the quantity X^l contains all the interesting structural information concerning the environment. The expression for these quantities is given by ³ :

$$X^l = 1/[(2l+1) \sin^2 \delta_l^0] \sum_m \text{Im} [(I + T_a G)^{-1} T_a]_{lm, lm}^o \quad (2)$$

where I is the unit matrix, G is the matrix describing the spherical wave propagation of the photoelectron from one site to another, T_a is the diagonal matrix describing the scattering process of the photoelectron by the atom located at some site around the photoabsorber and the δ_l^0 is the phase shift of the photoabsorbing atom (located at site 0) for angular momentum l . In absence of atoms around the photoabsorber $G \equiv 0$ and the absorption coefficient reduces to the atomic absorption. Normally in the XANES calculation⁴ the full MS result of Eq. 2 is compared with the experiment. However it is possible to follow another approach which is more interesting for structural problems. When the condition $\rho(T_a G) < 1$ is verified for all relevant energies of interest, where $\rho(A)$ indicates the spectral radius of the matrix A , one can develop the matrix inverse in Eq. 2 in series, by formally writing:

$$(I + T_a G)^{-1} = \sum_{n=0}^{\infty} (-1)^n (T_a G)^n \quad (3)$$

and thus generating the MS series. In fact insertion of this expression in Eq.1 gives

$$\alpha_F = (l+1) \alpha_0^{l+1} \sum_{n=0}^{\infty} X_n^{l+1} + l \alpha_0^{l-1} \sum_{n=0}^{\infty} X_n^{l-1} \quad (4)$$

where now

$$X_n^l = (-1)^n / [(2l+1) \sin^2 \delta_l^0] \sum_m \text{Im} [(T_a G)^n T_a]_{lm,lm}^o \quad (5)$$

These quantities represent the partial contribution of order n to the absorption coefficient of the cluster coming from all the processes where the photoelectron has been scattered $n-1$ times by the atoms surrounding the photoabsorber before returning to site 0 to exit into free space. Notice that $X_0^l = 1$, $X_1^l = 0$ since there is no propagation from one site to itself and that X_2^l is the usual EXAFS term with spherical wave propagators^{1,2}. Of course the higher order terms are related to the n -particle correlation functions which are the quantities we are interested in. At this point it is really important to notice that this interpretation of the X-ray absorption spectra in terms of MS pathways of the photoelectron is meaningful only if there is numerical equivalence of both sides of the Eq. 3 which is guaranteed only for those energies for which the spectral radius is less than one. Now $\rho(T_a G)$ is a

continuous function of the photoelectron wave vector $k=\sqrt{\epsilon}$, going to zero as k goes to infinity (since the atomic phase shifts tend to zero at high energies) and tending to the infinity as k goes to zero by the fact that spherical wave propagators are singular at $k=0$. As a consequence it must cross at least once the value $\rho = 1$. Moreover the nearest to 1 is its value, the slower is the convergence of the series. The implications of the above considerations are immediate and very important. It is in fact possible to predict on general ground three energy regions in an x-ray photoabsorption spectrum: a full multiple scattering region (FMS) generally at low energy where many or an infinite number of MS paths of high order contribute to the shape of the absorption coefficient (depending whether the series converges or not) followed by an intermediate MS region (IMS) where only few paths of low order are relevant (typically $n=3,4$) which merges continuously into a single scattering (SS) region where only X_2^I is important (EXAFS regime). The energy extent of these regions is obviously system dependent. From the above picture it is clear that n -order correlation function can be extracted mainly from the IMS region where few contributions are important. Typically this region can span as much as 300 eV (typically 100 - 150 eV) and gives information about X_3^I and X_4^I . On mathematical and physical grounds the general functional expression for the quantities X_n^I is given by:

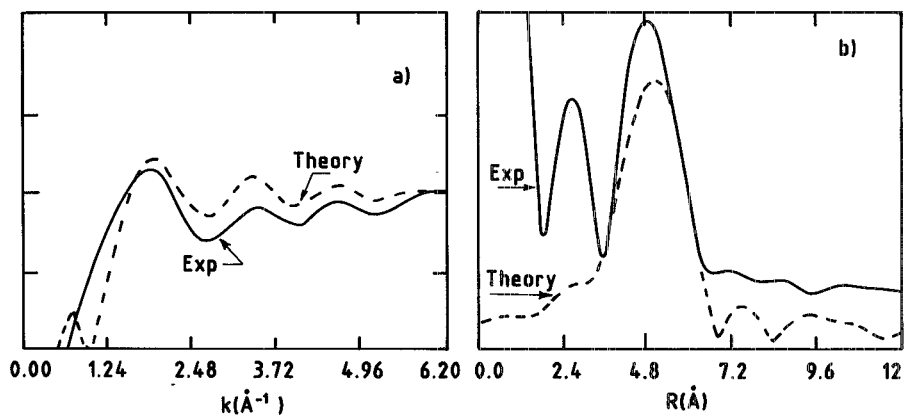
$$X_n^I(\epsilon) = \sum_{p_n} A_n(k, R_{ij}^{p_n}) \sin\{ kR_{tot}^{p_n} + \Phi_n^I(k, R_{ij}^{p_n}) + 2\delta_l^0 \} \quad (6)$$

where \sum_{p_n} indicates the sum over all paths p_n of order n starting from and ending at the central photoabsorbing atom with $n-1$ intermediate steps on the surrounding atoms, $R_{tot}^{p_n}$ indicates the corresponding total path length and the dependence of the amplitude and phase functions is on some rotationally invariant combination of scalar and vector products of vectors joining consecutive site location, the path being symbolically denoted by $R_{ij}^{p_n}$. The theory provides well defined expression for these quantities⁵. The experimental determination of these quantities is clearly of the utmost importance due to the fact that they bear information on the correlation functions of order higher than 2, i.e. on the local geometry around the photoabsorber.

MS DETERMINATION:

To show that this determination it is possible we have used the theory to extract the three particle correlation functions from the absorption spectrum

for $[\text{MnO}_4]^-$ complex in aqueous solution at the K-edge of manganese. To evaluate the atomic phase shifts we have used the usual Mattheiss prescription for the muffin-tin choice and the Z+1 approximation for the potential in the final state. Moreover the exchange-correlation term has been obtained by using the Hedin-Lundqvist energy dependent potential. This complex is a fortunate case. In fact the series converges for all the energies greater than E_c , a point located just below the rising edge and in the energy range 50 - 150 eV the deviation from pure EXAFS behaviour is only due to the $\alpha_3 = \alpha_0 X_3$ term (see Ref [3] for the used procedure and deeper discussion) which therefore can be extracted.



a) Comparison between theoretical X_3 signal (dashed line) and experimental X_3 signal (full line).

b) Fourier transform of theoretical and experimental signal.

Below 50 eV MS contributions of higher order are important while EXAFS (SS regime) extends beyond 150 eV. In the insert (a) of Fig. 1 is shown the X_3 signal obtained by simply subtracting from the experimental spectrum the $\alpha_0(1+X_2)$ contribution compared with the theoretical X_3 . The agreement is striking. This signal is a measure of the three particle correlation function and bears information on the relative positions of the central metal ion with respect to any two oxygens ligand. The associated period is related to the length of the triangular path Mn-O-O-Mn as shown in insert (b) of the same Fig 1, where the Fourier transform of the theoretical and experimental signals are reported. The observed maximum in the Fourier transform is shifted by the amount of the total phase slope which is about -0.85 \AA . Hence we derive for the length of the path a theoretical value of 5.85 \AA and an experimental value of 5.65 \AA as opposed to a real value of 5.87 \AA .

The discrepancy with the experimental value may reflect physical reasons, e.g. effects of vibrational bending modes which we have not taken into account or some inaccuracy of the subtracting procedure. To close this section we note that for optimizing the subtracting procedure it may be enough to consider the Fourier transform of the MS signal and look when the peak intensity corresponding to the residual EXAFS part is minimum.

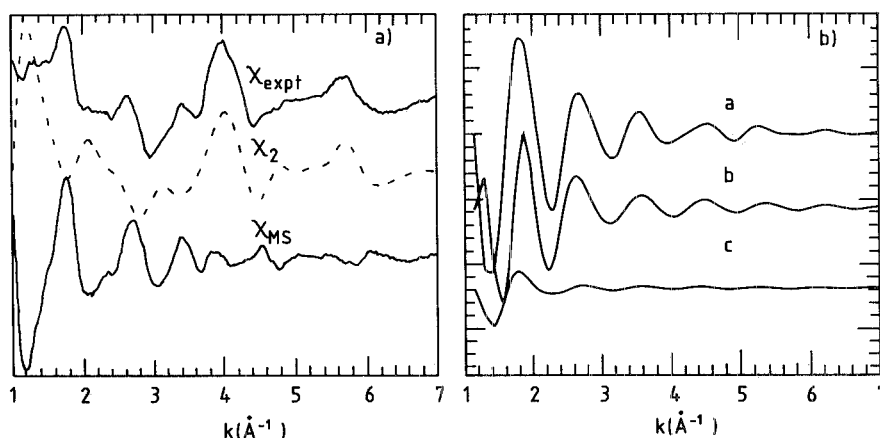
AMORPHOUS PROBLEM:

When an XAS experiment is done what is really measured is the quantity $\langle X^I(\epsilon) \rangle$, where the brackets indicate some configurational average with respect to the distribution of the position R_i of the atoms around the reference center R_0 (photoabsorber), because of the existence of the disorder. This disorder has several sources: the distribution of distance between the photoabsorber and neighbors and relative angles will possess a width which arises from thermal motion (always present), variations within a given site due to the static structure ("structural disorder") and variations between sites throughout the sample ("site disorder")⁶. In other words:

$$\langle X^I(\epsilon) \rangle = 1 + \sum_{n=2}^{\infty} \int \prod_{m=1}^{n-1} d^3R_m g_n(R_1, \dots, R_{n-1}) X_n^I(\epsilon, R_1, \dots, R_{n-1}) \quad (7)$$

where $g_n(R_1, \dots, R_{n-1})$ is the n-th order correlation function. When no disorder at all is present these quantities become combinations of Dirac's delta functions centered at the atomic positions. It is clear that the above expression is meaningful only if it is possible to develop the absorption coefficient in series, but it is also clear that the finite core-hole lifetime, the damping of the photoelectron in the final state and thermal and configurational disorder (if present) reduce the size of the spectral radius of the matrix $T_a \mathbf{G}$ at such point that sometimes only SS signal survives. For example there are experimental indications that in some crystals (Si, Ge) lifetime effects alone makes the series convergent in the whole energy range except the first 10+15 eV above the rising edge⁷. General speaking is possible to identify two types of configurational disorder: the first one concerns the disorder in the interatomic distances which are probed by the pair distribution function, the second type concerns the bond angles which are probed by the higher order correlation functions. Of course some correlations exist between the two types. The XAS spectroscopy can provide information on both types of disorder in condensate systems by switching the focus of data analysis from the EXAFS

part to the XANES part of the absorption spectrum. A lot of job has been made for the EXAFS spectrum using a simplified version of Eq. 7 and cumulant expansion⁶, especially for amorphous semiconductors⁸. On general physical ground we expect that the disorder quenches both EXAFS and XANES signal and in fact is quite evident that the shape of the experimental amorphous spectra is rather structureless. In order to clarify the role of the disorder in the MS signal we present the comparison between amorphous and crystalline silicon at the k-edge. The MS signal in the crystalline silicon, obtained by subtracting the X_2 spherical wave signal in the whole energy range above threshold from the experimental oscillatory part is reported in Fig 2 (panel a).



Panel a: Comparison between exper X_{MS} signal, EXAFS contribution and difference spectrum. A,B,C peaks are mainly due to MS contribution.

Panel b: Total calculated X_3 signal (curve a) very close to the experimental MS contribution, (curve b) X_3 by the total shortest paths with length of 8.54 Å, X_3 contribution due to the paths involving just the first shell (curve c).

In the panel b (curve a) is reported the X_3 calculated signal which arises from the all 756 scattering paths involving two neighbor atoms within the first three shell. In the same figure it is also reported the signal coming from 36 paths with the shortest total length which can be divided into two groups differing in the angles between the outgoing and incoming paths directed at the photoabsorber vertex⁹. The first of these two groups involves 12 paths within the first shell (curve c) while the second one comprises 24 paths involving the atoms of the first and second shell (curve b). From these curves it is evident that the main contribution to the MS signal comes from these 24 paths which involve the first two shell.

The difference between the crystal and amorphous silicon spectra can be written, assuming that the atomic absorption coefficient is the same, as:

$$X_{\text{res}} = (\alpha_{\text{cr}} - \alpha_{\text{am}}) / \alpha_0 = X_{\text{MS,cr}} + [X_{2,\text{cr}} - X_{2,\text{am}}] - X_{\text{MS,am}} \quad (8)$$

with evident notations. The result of this subtraction is reported in Fig.3 where X_{res} is also compared with the total MS signal in the crystall and the MS plus the $X_{2,\text{am}}$ term. Looking at this figure it is possible to say that the disorder suppresses the MS contribution to the absorbing coefficient of the amorphous silicon while a weak $X_{2,\text{am}}$ is still present and can be analyzed¹⁰

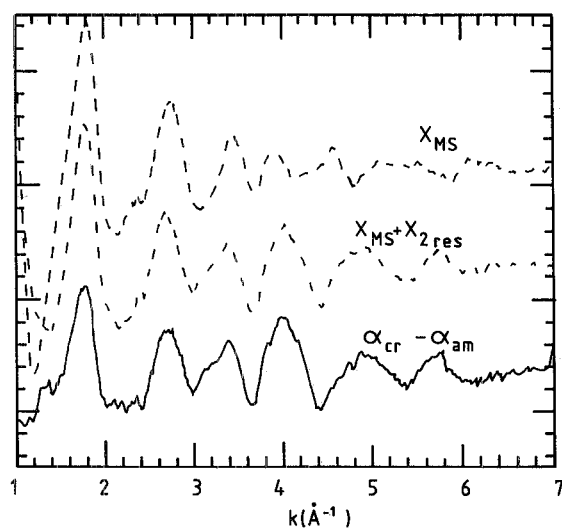


FIGURE 3

Difference spectrum between crystalline and amorphous silicon in comparison with crystalline MS signal (dashed curve) and the sum of MS signal with the single scattering residual by the atoms beyond the first shell (dot-dashed curve).

Of course different "degrees of disorder" suppress in different way the MS signal whose amplitude may hence provide a key to estimate the level of the disorder of an amorphous system. We conclude by noting that up to now no analytical expression exist for Eq. 7 for general case and only Monte Carlo simulations of this equation, made generating different configurations, are available. The preliminar results so obtained confirm the above interpretation¹¹.

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