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**UNIFIED SCHEME OF INTERPRETATION OF THE X-RAY ABSORPTION
SPECTRA BASED ON THE MULTIPLE SCATTERING FORMALISM**

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UNIFIED SCHEME OF INTERPRETATION OF THE X-RAY ABSORPTION SPECTRA
BASED ON THE MULTIPLE SCATTERING FORMALISM

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By studying the convergence of the multiple scattering (MS) series we predict on general grounds three energy regions in an X-ray photoabsorption spectrum from a condensed matter system: a full multiple scattering (FMS) region where many or an infinite number of MS paths of high order contribute to its final shape (depending on whether the MS series converges or not), followed by an intermediate multiple scattering (IMS) region where only few MS paths of low order are relevant (typically of order less or equal to four), this region merging continuously into a single scattering (SS) region where the photoelectron is backscattered only once by the neighboring atoms (EXAFS regime). This picture is supported by following considerations.

In the MS formalism the polarization averaged absorption coefficient is given by (1):

$$\alpha_F = \alpha_F^{\ell+1} + \alpha_F^{\ell-1} = (1+1)\alpha_0^{\ell+1}\chi^{\ell-1} + 1\alpha_0^{\ell-1}\chi^{\ell-1} \quad (1)$$

where $\alpha_0^{\ell+1}$ is the atomic absorption coefficient of the photoabsorber from a core initial state of angular momentum l and the quantity χ^ℓ , containing all the interesting structural information concerning the environment, is given by:

$$\chi^\ell = 1/\left[(2l+1)\sin^2\delta_\ell^0\right] \sum_m \text{Im}\left[(I+T_a G)^{-1} T_a\right]_{\ell m, \ell m}^0 \quad (2)$$

Here δ_ℓ^0 is the l -phase shift of the absorbing atom, assumed to be located at site 0, I is the unit matrix, $G \equiv G_{LL}^{IJ}$ is the matrix describing the free spherical wave (SW) propagation in angular momentum representation of the photoelectron from site l and angular momentum $L \equiv (l, m)$ to site j and angular momentum $L' \equiv (l', m')$ and $T_a \equiv T_{LL'}^{IJ} \equiv \delta_{lj} \delta_{LL'} t_{ll'}$ is the diagonal matrix

of atomic t-matrix elements describing the scattering process of the L spherical wave photoelectron by the atom located at site i.

By formally writing

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

one generates the MS series. In such a case:

$$\chi^\ell = 1 + \sum_{n=2}^{\infty} \chi_n' \quad (4)$$

where

$$\chi_n^\ell = (-1)^n / [(2\ell+1)\sin^2\delta_\ell^0] \sum_m \text{Im} [(T_a G)^n T_a]_{\ell m, \ell m}^0 \quad (5)$$

represents 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 the site 0 to exit into free space. Notice that $\chi_1^\ell=0$ since $G_{ll}^{00}=0$ and that χ_2^ℓ is the usual EXAFS term with spherical wave propagators. However the absolute convergence of the series in eq. (3) and therefore the numerical equivalence of both sides of the equation is guaranteed only for those energies for which $Q(T_a G) < 1$, where $Q(A)$ is the spectral radius of the matrix A, i.e. the maximum modulus of its eigenvalues. Now $Q(T_a G)$ is a continuous function of energy, going to zero as k goes to infinity (due to the fact that the atomic t-matrix goes to zero) and tending to the infinity as k goes to zero (due to the singularity of the SW propagators as k=0). Moreover the nearer to 1 is its value, the slower is the convergence of the series, the point $Q=1$ separating the region of convergence from that of non convergence. These properties immediately entail the existence of the three regions mentioned above. The energy extent of these regions is obviously system dependent.

The experimental determination of the quantities χ_n^ℓ for $n > 2$ 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 geometrical arrangement of the atoms around the photoabsorbing site. To show that this determination indeed possible we have used the theory to analyse the K-edge absorption spectrum of $[\text{MnO}_4]^-$ complex in aqueous solution. For this cluster we have found that MS series converges for all energies greater than E_m , located just below the rising edge. Hence an analysis based on the quantities $\alpha_n = \alpha_0 \chi_n$ is possible and meaningful. Fig. 1 shows the comparison between the calculated and experimental spectrum of $[\text{MnO}_4]^-$ complex. In insert (a) α_F^C is the calculated absorption coefficient obtained by exact inversion of the MS matrix and convoluted by an energy dependent Lorentzian broadening function to take account of the lifetime of the photoelectron in the final state. Inserts (b) and (c) show the breakdown of α_F in terms of the partial contribution α_n for n up to 4. In this case $\alpha_0 + \alpha_2 + \alpha_3$ is enough to get good agreement with

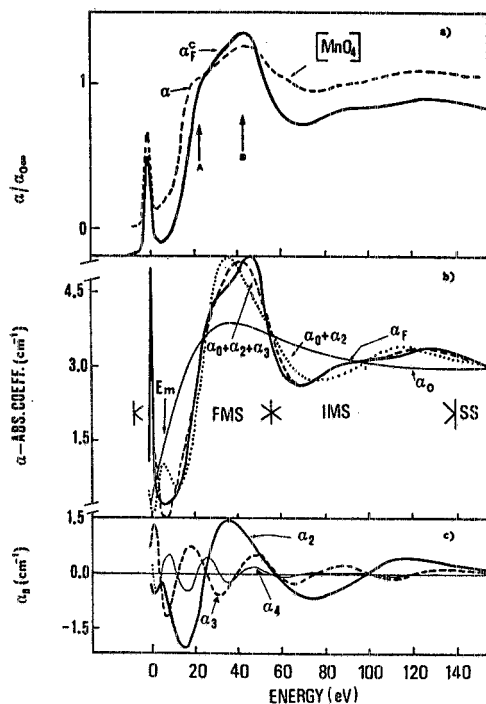


Fig. 1 - (a) Comparison between experimental α_F and calculate α_F^C for $[MnO_4]^-$ complex. (b) Breakdown of the calculated bare spectrum α_F into partial contributions. (c) MS contributions of n-th order to the absorption coefficient.

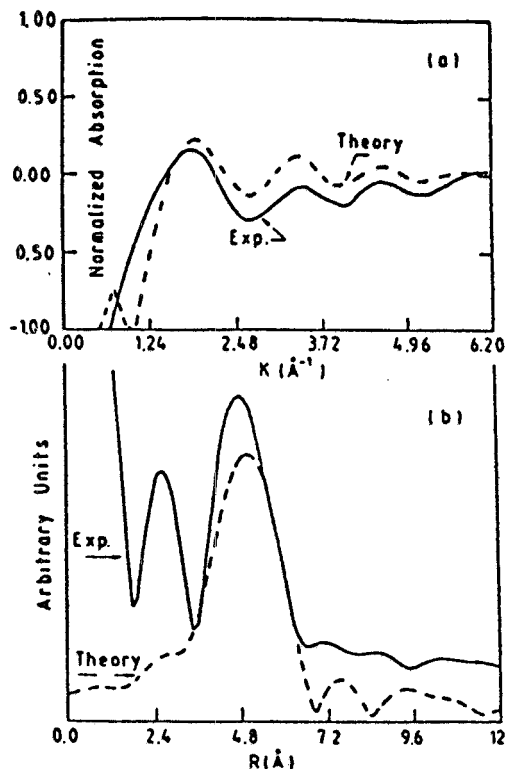


Fig. 2 - (a) Comparison between theoretical χ_3 signal (dashed line) and experimental signal (full line). (b) Comparison of theoretical and experimental Fourier transformed signals.

α_F in the range 50-140 while below 50 eV MS contributions of order higher than 3 are essential to obtain the spectral feature marked A and B in the Fig. 1. Hence the FMS region ranges in this case from 0 to 50 eV, the IMS region from 50 to 150, whereas EXAFS (SS regime) extends beyond 150 eV. This is a rather fortunate case in that it is possible to isolate the α_3 term over a region of 100 eV by simply subtracting⁽²⁾ from the measured spectrum the $\alpha_0 + \alpha_2$ contribution. The signal so obtained, divided by α_0 is shown in Fig. 2, insert (a), where it is compared with the theoretical signal χ_3 . The agreement is striking. This oscillating signal is a measure of 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 obviously related to the perimeter of the triangular path Mn-O-O-Mn as shown in insert (b), where the Fourier transform of the signal is reported. By adding the observed

maximum in the Fourier transform at about 5 Å to the absolute value of the slope of the phase function of the χ_3 signal (about 0.85 Å) as done in EXAFS analysis we obtain 5.85 Å face to a real value of 5.87 Å.

References:

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