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THREE PARTICLE CORRELATION FUNCTION OF METAL IONS IN TETRAHEDRAL
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The three particle correlation function of local atomic distribution at metal ion sites in solutions has been extracted from XANES (X-ray absorption near edge structure) spectra of $[\text{CrO}_4]^{2-}$ and $[\text{MnO}_4]^-$ ions measured by using synchrotron radiation. The absorption cross section for 1s core level excitation is calculated in the real space multiple scattering approach using the Hedin and Lundqvist energy dependent potential. We show that in these systems the expansion of the total absorption cross section in terms of contributions of higher order scattering processes is possible over a large energy range. This gives a unified theory of XANES and EXAFS and allows the third order correlation function to be extracted from experimental data.

ACCORDING TO THE FERMI golden rule for optical transitions the absorption coefficient for excitations from a core level to an unoccupied state at energy E can be calculated in k -space and the measured adsorption coefficient is given by $\alpha(E) = P(E) \cdot D(E)$, where $P(E)$ is the transition matrix element and $D(E)$ the projected particle density of states. As pointed out by Papaconstantopoulos *et al.* [1] the finite lifetime of the excited photoelectron in a high energy conduction band in the range of tens of eV above the Fermi level is an essential physical aspect of core transitions that cannot be neglected.

It has been demonstrated [2, 3] that the absorption cross section for core transition can be solved in *real space* using the Green function approach in the frame of multiple scattering theory. In this approach the limited mean free path of the photoelectron enters directly in the theory determining the finite size of the cluster of neighbouring atoms around the absorbing atom.

The important aspect of the solution of the absorption cross section in the real space is that physical processes determining the unoccupied density of states in

condensed matter appear explicitly. The wavefunction of the excited photoelectron turns out to be determined by the scattering from neighbouring atoms and therefore the spectra probe the geometrical atomic distribution and interatomic distances. Two parts of the spectra have been identified experimentally: the XANES [4] (X-ray absorption near edge structure) and the EXAFS (extended X-ray absorption structure) [5]. At high energies such that the atomic scattering power becomes small (much less than one) a single scattering (SS) regime takes place, where the modulation in the absorption coefficient (EXAFS) is substantially due to the interference effect of the outgoing photoelectron wave from the absorbing atom and the backscattered wave from each surrounding atom. [6]. Hence this latter part of the spectrum provides information about the pair correlation function. By decreasing the photoelectron kinetic energy a gradual turn over occurs from the EXAFS (SS) regime to the XANES full multiple scattering (FMS) regime where all the MS pathways which begin and end at the absorbing atom contribute to the total absorption cross section.

Here we present the results of a study of manganese and chromium K-edge spectra of ions in solution. We show that the absorption coefficient can be expanded in terms of successive multiple scattering events, classified

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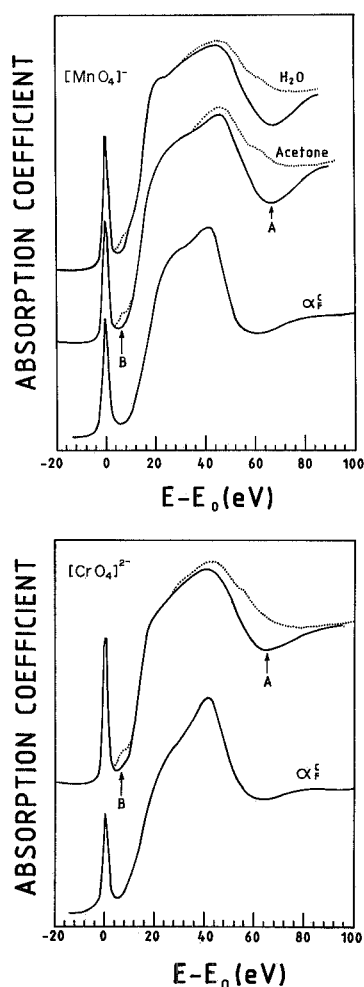


Fig. 1 (a) The K-edge Mn spectrum of MnO_4K solutions compared with the full multiple scattering calculation for the $[\text{MnO}_4]$ tetrahedral cluster. Full-line represents the one-electron absorption coefficient obtained after subtracting multielectron effects from the experimental absorption (dotted line). The threshold energy E_0 has been set at the first absorption peak. (b) The K-edge of Cr spectra of CrO_4K_2 in aqueous solution compared with the full MS calculation for the CrO_4 cluster. Full and dotted lines have the same meaning as in Fig. 1(a).

by the number of atoms involved in the scattering pathways.

The expansion of the absorption coefficient gives a unified picture of EXAFS and XANES. We obtain that there is a transition region where only low order multiple scattering (MS) paths are relevant. Finally the contribution due to multiple scattering pathways including the central and two neighbour atoms is shown to be important over more than 100 eV and can be extracted from the data. We show in this paper the procedure to extract this three particle correlation function in the case of tetrahedral clusters. The exper-

iment has been performed at the Frascati synchrotron radiation facility. The aqueous solutions were prepared at concentrations of 50 mM and a 1 mm thick cell was used for transmission experiments. High resolution was achieved by using a Si(2 2 0) monochromator and an entrance slit of 0.5 mm. The storage ring was operated at 1.5 GeV and ~ 100 mA with a brilliance of about 10^{10} ph/(sec \times mrad 2 \times mm 2 \times (10^{-4} $\Delta E/E$). In the data analysis the pre-edge absorption background is subtracted. We have measured the K-edge absorption spectra of 50 mM of K_2CrO_4 and KMnO_4 solutions reported in Fig. 1. The tetrahedral cluster $[\text{MnO}_4]^-$ and $[\text{CrO}_4]^{2-}$ clusters are known to be quite stable in solution with a distance $d_1 = 1.65$ Å [7] and 1.66 Å [8] respectively. Only the contribution of the first shell is present in the EXAFS spectrum for the photoelectron wave vector k above 5 Å $^{-1}$ in agreement with Rabe *et al.* [7].

We have analyzed the spectra in the framework of MS concepts. In this formalism the polarization averaged absorption coefficient is given by [3, 6]

$$\alpha_F^{l+1} + \alpha_F^{l-1} = A\hbar\omega N_0 [(l+1)M_{l,l+1}^2 \chi_{l+1} + M_{l,l-1}^2 \chi_{l-1}], \quad (1)$$

where l indicates the angular momentum of the core initial state ($l=0$ for K excitations) $M_{l,l\pm 1}^2$ is the atomic dipole transition matrix element relative to the photoabsorbing atom and

$$\chi_l = \frac{1}{2l+1} \text{Im} \chi_{ll} = \frac{1}{2l+1} \frac{1}{\sin^2 \delta_l^0}$$

$$\text{Im} [(I + T_a G)^{-1} T_a]_{lm,lm}^0, \quad (2)$$

where δ_l^0 is the phase shift of the absorbing atom located at site 0, I is the unit matrix, $G = G_{LL'}^{ij}$ ($1 - \delta_{ij}$) is the free amplitude of propagation of the photoelectron in a spherical wave state from site i with angular momentum $L = (l, m)$ to site j with angular momentum $L' = (l', m')$, $T_a = (T_a)_{LL'}^{ij} = \delta_{ij} \delta_{LL'} t_l^i$ is the diagonal matrix describing the scattering process of the spherical wave with angular momentum l by the atom located at site i' through the atomic t -matrix element t_l^i and $T_a G$ implies matrix multiplication [9].

We have used the energy dependent Hedin–Lundqvist [10] potential, which takes account of the energy dependent exchange-correlation interaction between the photoelectron and the electrons of the system. The XANES full multiple scattering calculation for the $[\text{CrO}_4]$ and $[\text{MnO}_4]$ clusters are reported in Fig. 1. The energy positions of the experimental features is well predicted by the present theory. This new result [11] is critically dependent on the use of the H.L. potential [10]. If the energy independent potential $X - \alpha$ is used

the well known disagreement between experimental and one-electron theories [12, 13] appears. The quantity α_F is the calculated absorption coefficient obtained by exact inversion of the MS matrix. The spectra have been convoluted by an energy dependent Lorentzian broadening function with $\Gamma_{\text{tot}}(E) = \Gamma_h + \Gamma_{\text{exp}} + \Gamma_{\text{el}}(E)$, where $\Gamma_h \sim 0.5$ eV is the core hole width, $\Gamma_{\text{exp}} \approx 1$ eV is the experimental resolution and $\Gamma_{\text{el}}(E)$ (of the order of 2 eV) is an energy dependent damping for the electron in the final state, taken from the imaginary part of the complex H.L. potential.

The dashed feature *A* is a two electron excitation involving simultaneously $1s-3d$ and $3p-3d$ electronic transitions. This interpretation is confirmed by the comparison of the energy difference between the $1s-3d$ transition and the two electron feature obtained in the spectrum with the theoretical one-electron levels differences of the $[\text{MnO}_4]$ cluster obtained by Johnson [14]. Due to the fact that the Coulomb repulsion is very similar between molecular orbitals originating from $3p$ or $3d$ Mn atomic states, the one electron level difference should provide a good estimate of the energy of the multielectron transition. A deepest discussion and a full self-consistent calculation of these two electron excitations will be presented in a forthcoming paper. The other shoulder *B*, well resolved both in the case of chromate and permanganate ions, arises from double electron excitation corresponding to a final state with two holes, one the $1s$ core orbital and the other in a valence orbital and with two electrons in the unoccupied T_2 states [2]. Taking account of these results, the one-electron absorption is obtained by subtracting from the spectrum the contribution of the multielectron excitations assumed to have Lorentzian shape. For the $[\text{MnO}_4]$ cluster we report also the measured spectrum for a different solvent to determine the effects due to further shells. Because acetone is less polarizable than water a different disordered distribution around $[\text{MnO}_4]$ cluster is expected. We find that the spectra for different solvents are similar, but in the case of acetone solvent there is a slightly better agreement with the theoretical spectra. As apparent from equation (2) the whole geometrical information of the medium around the photoabsorber is contained in the matrix inverse $(1 + T_a G)^{-1}$. Provided the condition $\rho(T_a G) < 1$ is verified for all relevant energies ($\rho(A)$ is maximum eigenvalue of a matrix *A*) the inverse of the scattering matrix can be expanded as $(1 + T_a G)^{-1} = \sum_{n=0}^{\infty} (-1)^n (T_a G)^n$ where the series on the right is absolutely convergent relative to some matrix norm. Specializing to K-shell excitations, we then have $\alpha_F = \sum_{n=0}^{\infty} \alpha_n$ where $\alpha_0 = A \hbar \omega N_0 M_{01}^2$ is the atomic absorption coefficient and

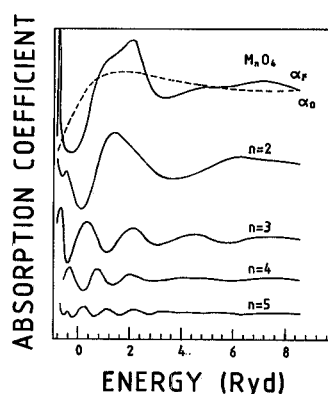


Fig. 2. Theoretical absorption coefficient for a cluster formed by the central Mn and four oxygens. Going from top to bottom we report the total cross section, the atomic contribution (dashed line), the single scattering contribution, $n = 2$ (EXAFS), and the contributions of successive order of multiple scattering pathways of orders $n = 3, 4$ and 5 .

$$\alpha_n = \frac{\alpha_0}{3} \text{Im} \chi_{11}^n = \frac{\alpha_0}{3} \frac{1}{\sin^2 \delta_1^0} (-1)^n$$

$$\sum_m \text{Im} [(T_a H)^n T_a]_{1m, 1m}^0, \quad (3)$$

represents the partial contribution of order n to the absorption coefficient coming from all the processes where the photoelectron has been scattered $n - 1$ times by the surrounding atoms before returning to the absorbing atom at site *O*. Clearly α_n contains information about the n th order correlation function. Notice that α_2/α_0 is the usual EXAFS signal, whereas α_1 is always zero since *G* is off-diagonal in the site indices. For the two clusters under consideration we have indeed found that the condition $\rho(T_a G) < 1$ is verified for all energies greater than a lower bound E_m , which is located just below the rising absorption jump edge. Hence an analysis of the experimental spectra in terms of the quantities α_n is meaningful and the terms $\alpha_0, \alpha_2, \alpha_3, \alpha_4, \alpha_5$ for the $[\text{MnO}_4]$ cluster are reported in Fig. 2, for the $[\text{CrO}_4]$ cluster we obtain similar results. In Fig. 2 it is clear that at high energies only α_2 is important, while decreasing the kinetic energy of the photoelectron the higher order term α_3 becomes relevant below 150 eV and at lower energies also α_4 and α_5 have considerable amplitude. In this case we observe that α_4 and α_5 are nearly in opposition of phase and therefore their sum can be neglected. Considering the $\alpha_0 + \alpha_2 + \alpha_3$ in the range 20–140 eV we obtain a good agreement with the experimental spectra.

We have extracted the experimental three atoms correlation function for MnO_4 and CrO_4 clusters using

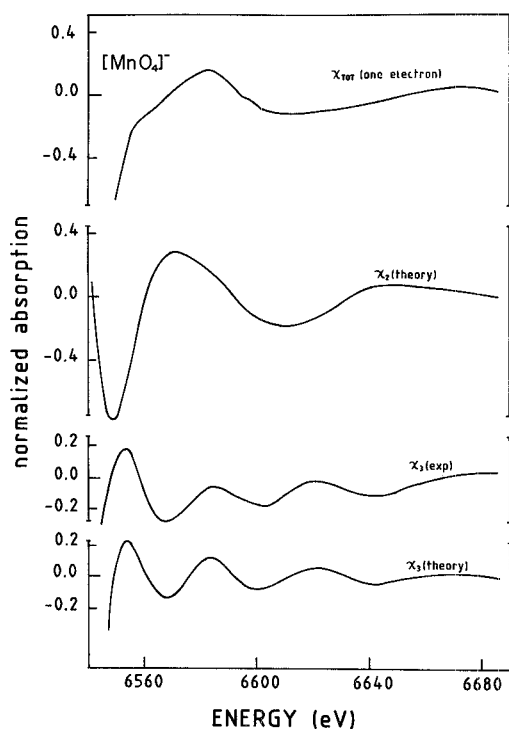


Fig. 3. Experimental signal due to the three particle correlation function for the MnO_4 cluster obtained after subtracting from the data the $n = 2$ contribution as explained in the text. Going from top to bottom we report the experimental one-electron absorption, the χ_2 theoretical contribution, the χ_3 correlation function and the normalized theoretical $\chi_3 = \alpha_3/\alpha_0$ signal.

the following procedure. The experimental modulated part of the absorption coefficient due to photoelectron scattering is obtained as $\chi_{\text{tot}} = (\alpha - \alpha_0)/\alpha_0 = \chi_2 + \chi_3$ neglecting higher order contributions as discussed above, where χ_i are the α_i/α_0 contributions. The extraction of this curve depends on the reliable predictions of α_0 by the theory. To extract χ_3 we have subtracted from χ_{tot} the χ_2 term which has been calculated by the present theory using spherical waves and reliable phase shift up to very low kinetic energy of the photoelectron. The interatomic distances used are extracted by EXAFS [7, 8]. The difference $\chi_{\text{tot}} - \chi_2 = \chi_3$ for the MnO_4 cluster is reported in Fig. 3. In the upper part of this figure we show the one-electron contribution χ_{tot} obtained from the measured spectrum after subtraction of the multielectron excitation as discussed above and the single scattering (χ_2) contribution obtained by theoretical calculation. In the lower part we compare the third order multiple scattering contribution (χ_3) obtained using the procedure described above with the theoretical prediction. The same procedure for extracting the χ_3 contribution has been applied to the experimental data of the chromate. In Fig. 4 we show

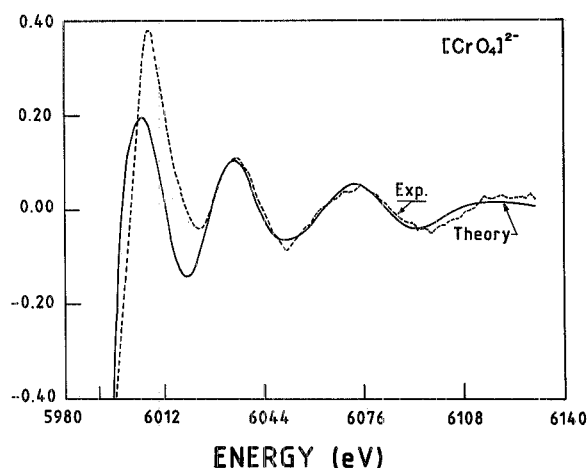


Fig. 4. Comparison of the theoretical (solid line) and experimental (dashed line) χ_3 multiple scattering contribution obtained for the case of the CrO_4 cluster.

the comparison of the experimental and theoretical correlation function (χ_3) for the case of CrO_4 cluster.

We think that this is the first time that an experimentally determined three atom correlation function over a substantial energy range (10--150 eV) is reported. All present methods for structural studies of condensed matter probe only the pair correlation function but direct information on bond angles are contained only in higher order correlation functions. There is a large effort to extract them using different methods based on neutron scattering and X-ray scattering at different pressures, cross correlation light scattering and others [15] but our method seems to be the one which gives directly the three particle distribution function.

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