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(X-RAY ABSORPTION NEAR EDGE STRUCTURE)

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LOCAL ORDER AT MANGANESE SITES IN IONIC SOLUTIONS BY XANES (X-RAY ABSORPTION NEAR EDGE STRUCTURE)

M. Benfatto, C.R. Natoli
INFN - Laboratori Nazionali di Frascati, P.O. Box 13, 00044 Frascati (Italy)

J. Garcia*, A. Bianconi
Dipartimento di Fisica, Università "La Sapienza, 00185 Roma, (Italy)

A. Marcelli, I. Davoli
Dipartimento di Matematica e Fisica, Università di Camerino, 62032 Camerino, (Italy)

ABSTRACT: Geometrical distribution around the metal ion sites in aqueous solutions has been probed by XANES spectroscopy. Multiple scattering theory has been applied to explain the data and we show in these systems the expansion of the total absorption cross section in term of contributions of higher order scattering processes has possible over a large energy range. Therefore higher order distribution functions, beyond the pair one probed by EXAFS, are extracted.

1. INTRODUCTION AND THEORY

The conviction that important geometrical informations about local structure are contained in XANES spectra has stimulated the growing of theoretical and experimental studies in this field⁽¹⁻⁴⁾. The low energy part of the x-ray absorption spectra, in fact, is sensitive to the geometrical arrangement of the environment around the absorbing atom because of strong scattering power of these low energy photoelectrons favoring multiple scattering (MS) processes. Going to the high energy region of the spectra a gradual turn over occurs from the MS regime to the single scattering (SS) regime where the modulation in the absorbing 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^(5,6). Hence, while this latter part of the

* Permanent address: Department of Thermology, Zaragoza, University, Spain.

spectrum provides information about the pair correlation function, the first one contains information about higher order distribution functions by MS pathways which begin and end at the absorbing atom.

By making the expansion of the total cross section, in the energy region where it is possible, it has been shown⁽⁷⁾ that the contributions of successive scattering orders can be identified. To go little deeper into the question, we report the expression for the first three contributions of scattering orders to the total cross section valid for the k-edge. In the framework of the multiple scattering theory we can write for the absorbing coefficient^(7,8)

$$\mu_c = A \pi \omega M_{01}^2 \alpha^{(1)} \quad (1)$$

where M_{01} is the radial atomic dipole element which is smooth with energy whereas the quantity $\alpha^{(1)}$ contains all the geometrical information around the absorbing atom and can be expanded into the contributions due to successive order of scattering pathways as $\alpha^{(1)} = 1 + \sum_{n=2} \chi_n^{(1)}$, where they are classified according with the number of scattering events n , therefore the corresponding number of neighbour atoms participating to the scattering processes are $n-1$.

It can be obtained for $\chi_2^{(1)}$ the expression :

$$\chi_2^{(1)} = \sum_j \text{Im} [f_j(k, \pi) \exp(2i(\delta_1 + kr_j)) / kr_j^2] \quad (2)$$

where δ_1 is the partial phase shift of the absorbing atom, r_j is the distance between the central atom and the neighboring atom j , k is the photoelectron wave number and $f_j(k, \pi)$ is the backscattering amplitude. This is the usual EXAFS term and it contains only information about the pair distribution function. The first MS contribution is the $\chi_3^{(1)}$ term that can be written:

$$\chi_3^{(1)} = \sum_{i \neq j} \text{Im} [P_1(\cos \Phi) f_i(\omega) f_j(\theta) \exp(2i(\delta_1 + k(r_i + r_{ij} + r_j))) / kr_i r_{ij} r_j] \quad (3)$$

where r_{ij} is the distance between the atom i and j , $f_i(\omega)$ and $f_j(\theta)$ are the scattering amplitude which now depend on the angles, by Legendre Polynomials $P_1(x)$, in the triangle which joins the absorbing atom to the ones i and j . In this expression $\cos \Phi = -r_i / r_j$, $\cos \omega = -r_i / r_{ij}$ and $\cos \theta = r_j / r_{ij}$.

All these quantities are obtained neglecting the angular dependence of the Hankel function in the free propagator. Here we report a study of the site geometry of manganese ions by XANES.

2. EXPERIMENTAL AND CALCULATION

The experiment has been performed at the Frascati Synchrotron Radiation Facility. The aqueous solutions at concentration of 50mM have been prepared and 1mm thick cell has been used for transmission experiments. In the data analysis the pre-edge absorption background is subtracted. The MS calculation for the octahedral and tetrahedral clusters formed by central Mn and neighbouring oxygens are made with the usual X- α potential and Mattheiss prescriptions. Hydrogen atoms were neglected.

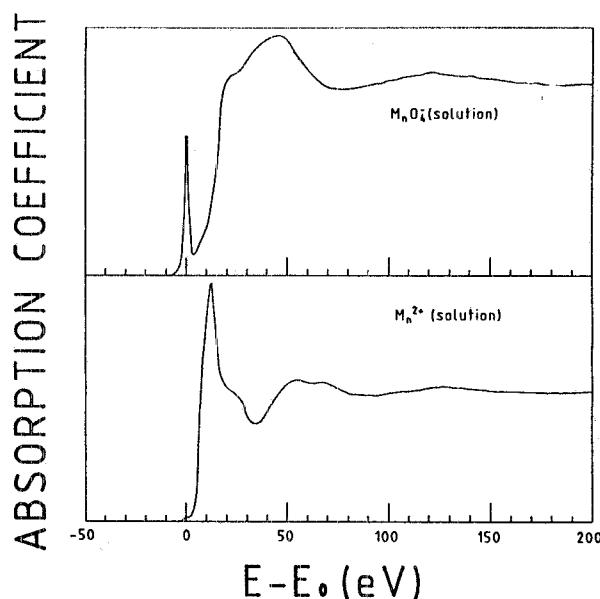


FIGURE 1. X-ray absorption spectra of MnO_4^- (upper panel) and Mn^{2+} (lower panel) in aqueous solution. The zero of the energy scale is fixed at the 1s-3d excitation at the threshold.

3. RESULTS AND DISCUSSION

In fig.1 the x-ray absorption spectrum of Mn ions in solution are reported. The comparison shows the different shape in the energy region between 0 and 160 eV due to the different geometrical structure around manganese atom. Using the multiple scattering theory, briefly described above, we obtained the theoretical spectra for the two clusters. Reported results are in fig.2. The agreement with experimental data is good with respect to the shape of the spectrum but it is less good concerning the location of the high energy maxima due to the energy independence of the X- α potential used. We also reported the breakdown of the total cross section in terms of the partial contributions χ_n classified according with the number of scattering events n. In the octahedral geometry we observe that the MS contributions extend up 150 eV but, because of the destructive interference effect between the n=3 and n=4, the EXAFS signal becomes the main contribution above 40 eV. On the contrary, expansion of the total cross section in tetrahedral geometry shows that the sum $1 + \chi_2 + \chi_3$ is enough to get a good agreement between 50-140 eV and in this range χ_n (n>4) is

negligible. For this reason, we have extracted from the MnO_4^- solution data the experimental χ_3 contribution by subtraction from the total experimental signal, normalized EXAFS-like, the $n=2$ theoretical contribution (see fig.3).

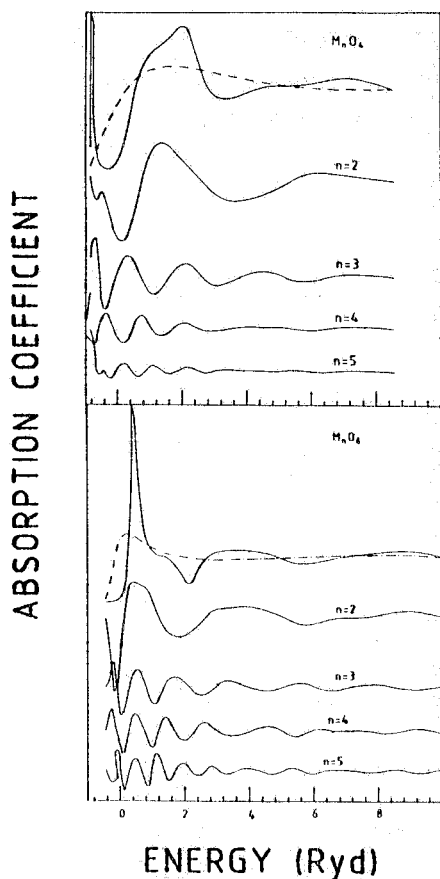


FIGURE 2 Theoretical absorption coefficient for the Mn atom in tetrahedral (upper panel) coordination. In each panel, going from top to the bottom the total cross section, the atomic contribution (dotted dashed line), the single scattering contribution (EXAFS) and the contribution of the successive orders ($n=3,4$ and 5) of MS pathways are shown.

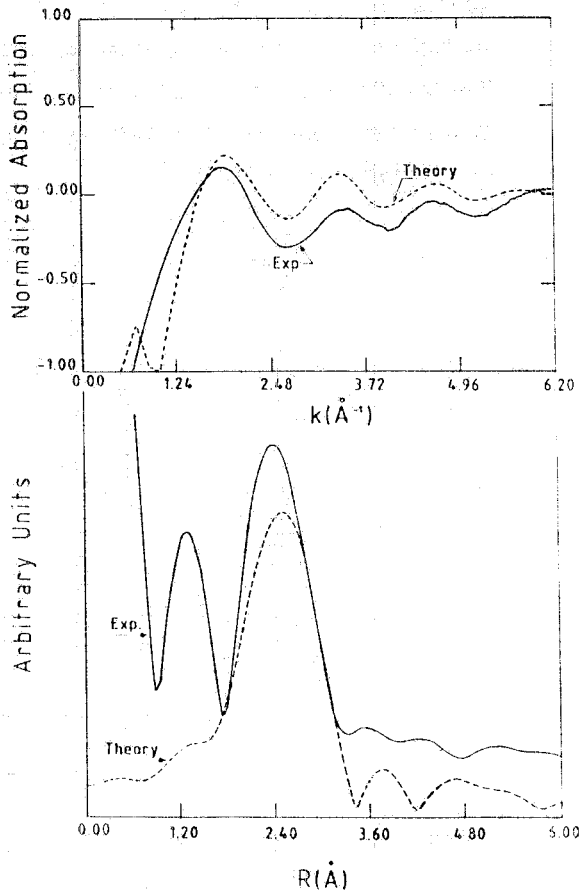


FIGURE 3. Upper panel: comparison between theoretical χ_3 signal (dashed line) and obtained χ_3 experimental contribution (full line) for the MnO_4^- cluster. The threshold energy E_0 is fixed at the first absorption peak. Lower panel: Fourier transform of the theoretical (dashed line) and experimental (full line) of the χ_3 signals.

Good agreement is obtained with the calculated χ_3 and the experimental one. Fourier transform of this two signals shows the same peak centered at 2.4 Å. This value coincide with the optical pathlength for the third order MS pathway for this cluster⁽⁹⁾. In conclusion we have shown that XANES data analysis has reached the level of quantitative agreement with experimental spectra and the way to obtain higher order correlation functions.

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E. Lüscher

Physik-Department
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G. Fritsch

Physikalisches Institut FB BAUV/II
Universität der Bundeswehr München
D-8014 Neubiberg
FRG

G. Jacucci

Dipartimento di Matematica e Fisica
Università degli Studi di Trento
I-38050 Povo
Italy

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