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OCTAHEDRAL WATER COMPLEXES INCLUDING MULTIPLE SCATTERING

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ABSTRACT

The effect of Multiple Scattering in EXAFS region for octahedral transition metal in water solution is analysed. A combined experimental and theoretical study is presented, in which three approximations (Hedin-Lundqvist real and complex, and Xα) of exchange potential are used.

Introduction

EXAFS primarily deals with only single photoelectron scattering (SS) and XANES is a result of both SS and multiple scattering (MS)[1]. The borderline between these two regimes is not well defined and sometimes MS processes appear in EXAFS.

To determine the effect of MS and the energy range where multiple scattering, only involving one shell coordination, is relevant, a theoretical and experimental investigation of octahedral transition metal complexes in water solution has been performed. The samples chosen are suitable because, due to the structural disorder of the higher neighbours shells, the size of the effective absorbing cluster reduces to the metal ion and the first coordination shell. As a previous step, the XANES experimental spectra were reproduced by theoretical calculation, in which only a octahedral cluster of oxygen atoms around the absorbing metal was considered[2].

In this work, theoretical calculations under the exact spherical wave formalism for octahedral clusters of MeO_6 (Me=Mn, Co, Ni and Cu) and for different exchange potentials (real and complex Hedin-Lundqvist and Xα) are carried out . The contribution of multiple scattering terms χ_3 and χ_4, for each different pathway, and their interference effects have been individually analysed. These theoretically obtained signals are used to fit the experimental spectra of the above cited divalent ions in water solution.

Experimental

The metal ion K-edge EXAFS spectra of Mn^{2+}, Co^{2+}, Ni^{2+} and Cu^{2+} ions in $MeCl_2$ 50mM water solutions were recorded at the Frascati Synchrotron Radiation Facility. The spectra are characterized by a main oscillation, which corresponds to the first shell EXAFS term. If, when recording the spectra, a good signal to noise ratio exists, the Fourier Transform reflects the presence of two peaks, the main one, once phase shift corrected, corresponds to the Me-O bond distance. A second peak, 10 times lower, is observed at approximately 3.5 Å and it is assigned to multiple scattering contribution[3], because its filtered oscillatory signal agrees better with the multiple scattering theoretical signal than if a second oxygen coordination shell is considered.

Theory

In the multiple scattering formalism, the absorption coefficient is given by $\alpha = \alpha_0(1 + \Sigma_n \chi_n)$, where a_0 is the atomic absorption and χ_n represents the oscillating signal for all processes in which the ejected photoelectron is scattered (n-1) times by the atoms of the environment, before returning to the absorber atom.
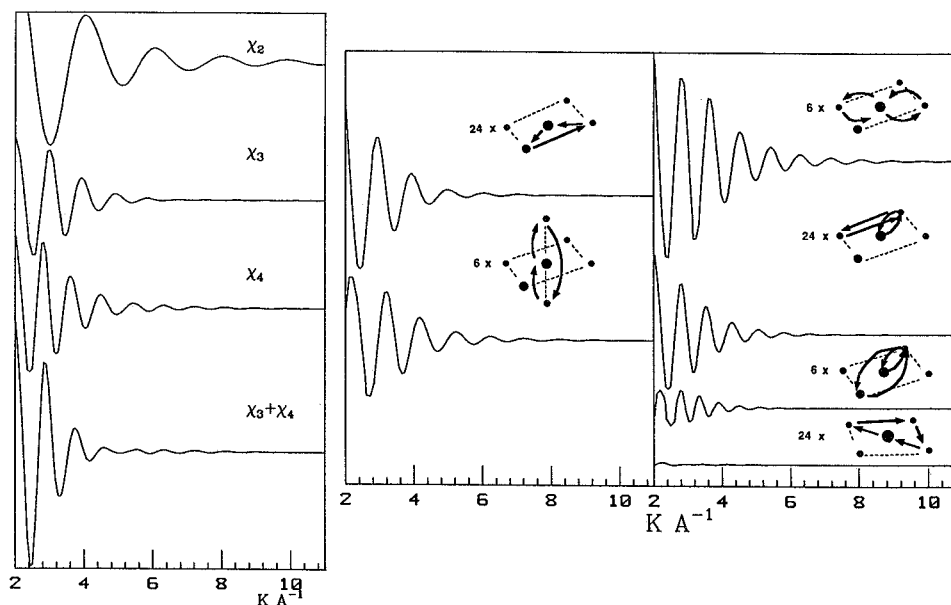

Fig. 1a. Theoretical χ_2, χ_3, χ_4 and $\chi_3 + \chi_4$ signals for the NiO_6 cluster in the $X\alpha$ approximation.No damping has been considered.

Fig. 1b.The χ_3 (panel a) and χ_4 (panel b) terms for individual photoelectron scattering paths.The path-way and its degeneration is drawn near the corresponding curve.
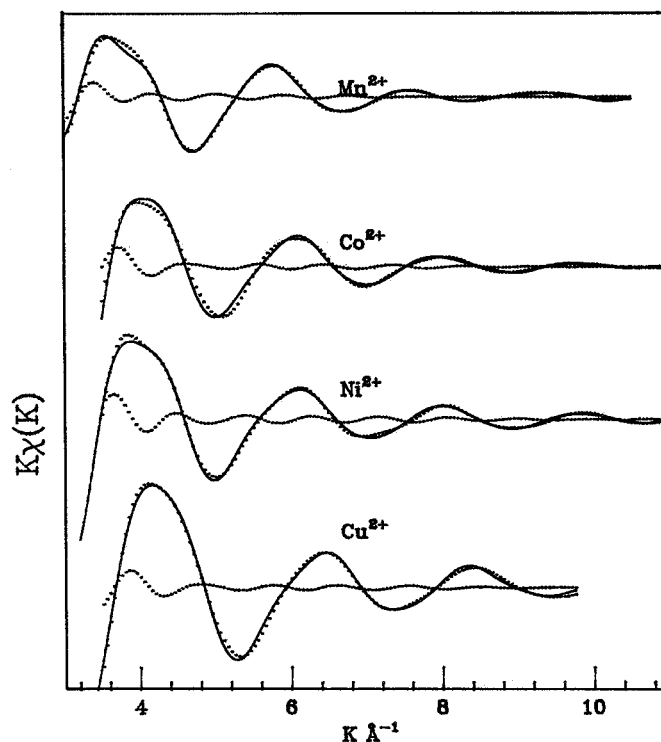
Fig. 2 Experimental filtered EXAFS signals of MeO_6 (solid lines) and their fits to the experimental first shell signals, χ_2, plus the theoretical MS contributions (dotted line). MS signals are also represented.

The χ_2, χ_3 and χ_4 terms for a cluster formed by the metal atom octahedrally coordinated to six oxygen atoms, at the interatomic distances given in literature[4], have been calculated using the spherical wave approximation. Hydrogen atoms were neglected and exchange potential in the $X\alpha$ approximation, as well as the energy dependent Hedin-Lundqvist one, for both the real and complex cases, were used .

In fig. 1a the terms χ_2, χ_3, χ_4 and $\chi_3+\chi_4$, for Ni in the $X\alpha$ approximation, are plotted. From the figure it is clear that the third multiple scattering term vanishes at k=6 $Å^{-1}$, but the fourth order remain important even for k values up to 9 $Å^{-1}$. A quasi-destructive interference reduces the amplitude of $\chi_3+\chi_4$ signal with respect to the individual contributions, and shows a rather constant intensity in the range 5 to 8 $Å^{-1}$. It is worth to notice the importance of the absorbing atom in this interference phenomenon, since if $\chi_3+\chi_4$ for Ni and Co are compared, the signal for Ni is higher, even if the theoretical distances are the same.

With regards to the expansion of the MS terms in their individual paths (see fig. 1b), it is realised that the most important contributions arise from the colinear paths. There are other efficient signals, due to their large degeneracy, but to χ_4 only contribute the paths involving three atoms, in which one atom scatters twice the photoelectron.

Results

For the three different exchange potentials theoretical calculations were performed and the results fitted to the experimental spectra.For every ion, and to avoid indetermination in its value, E_O was fixed using the calculated XANES spectra as reference.With these E_O and parametrizing the χ_2, χ_3 and χ_4 by a function $\chi_n=A(k)$ sin $(2kr+f(k))$, the experimental signal was fitted to the sum of χ_2 and the oscillation $(\chi_3 + \chi_4)$. For the $X\alpha$ and the real Hedin-Lundqvist potentials, the mean free path has been taken as $\lambda = ak$, which is valid up to 500 eV. For the complex potential no damping term has been included, since this potential takes already into account the damping due to the extrinsic energy losses of the photoelectron[5]. The thermal disorder have been introduced, in a crude way, through a term $\exp(-\sigma^2 k^2)$ and no S_O^2 EXAFS amplitude-reduction factor parameter has been used in any fit. The analysis performed with the three potential models gives comparable results, except that the interatomic distances obtained with the $X\alpha$ potential are 5% smaller than the experimental one and that in case of the complex potential the damping term is not included as free parameter. In fig. 2 the experimental Fourier filtered spectra and their fit to the sum of a χ_2 experimental signal, obtained isolating the first shell from the experimental spectra, and of a MS calculated one are plotted.These MS signals are also shown in the same figure, and they represent in all cases about 10 % of the whole signal.

As final conclusion it should be stressed that although the EXAFS spectra of octahedral complexes is mainly described by single scattering, a proper description needs the inclusion of multiple scattering processes. The importance of the MS effect depends on the particular system, because the interference effect between the χ_3 and χ_4 contributions may induce, in many cases, a negligible contribution. Therefore, it seems that the MS corrections should be taken into account when analyzing higher shells in highly coordinated compounds, but, up to now, we have been unable to establish an "a priori rule" to estimate their importance.

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