Laboratori Nazionali di Frascati

LNF-87/35

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Estratto da:
SIF - Conf. Proc. "Synchrotron Radiation at Frascati" Vol. 5, 63 (1986)

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P.O. Box, 13 - 00044 Frascati (Italy)

COORDINATION GEOMETRY OF TRANSITION METAL IONS IN DILUTE SOLUTIONS BY XANES

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An extended investigation on the coordination geometry of transition metal ions in dilute solutions is reported. All experimental techniques for the structure of solutions and disordered systems probe the first order correlation function of atomic distribution. The information on the geometry of atomic distribution are contained beyond the pair correlation function. XANES contains such information. In fact the absorption coefficient can be expanded in a series $\mu(E) = \mu_0(1+\Sigma\varkappa_n)$ where $\varkappa_n$ are partial contributions for scattering pathways involving n atoms going from the EXAFS $\varkappa_2$ term to higher order processes $\varkappa_3,\varkappa_4,\ldots$(1).

In this investigation the role of higher order scattering terms in the XANES spectra of solutions is reported. Acqueous solutions of Cu^{2+}, Ni^{2+}, Fe^{2+}, Mn^{2+}, Cr^{2+} and VO_4^{3-}, CrO_4^{2-}, MnO_4^- at low and high concentrations have been studied. The K-edge of each metal has been measured at the PULS Frascati radiation facility with the highest resolution and in each sample the pH was well controlled. In Fig. 1 we show the good agreement between the experimental and theoretical XANES spectrum of CrO_4 tetrahedral cluster.

The expansion of the total absorption in tetrahedral geometry shows that the successive orders of scattering become negligible with increasing the energy like appear in Fig. 2 where we report the contribution of higher order scattering pathways to the theoretical total absorption coefficient for the CrO_4 cluster. Moreower we show that for fourfold coordinated metal ions the spectra are fitted by $\mu(E)=\mu_0(1+\varkappa_2+\varkappa_3)$ over a range of 150 eV(2) and therefore the triplet distribution function can be measured from the $\varkappa_3$ term in experimental spectra.

The variation of the spectra by changing interatomic distance and central atom and the effect of distorsions from tetrahedral geometry have been studied. The XANES spectra of octahedral clusters are dominated by

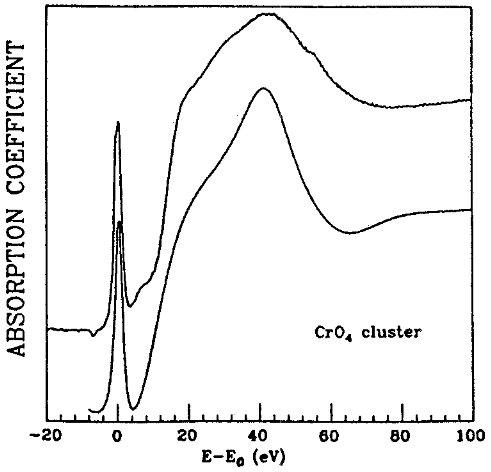

Fig. 1 - Comparison between the experimental K-edge of chromium (upper curve) and theoretical multiple scattering calculation for CrO_4 in solution.

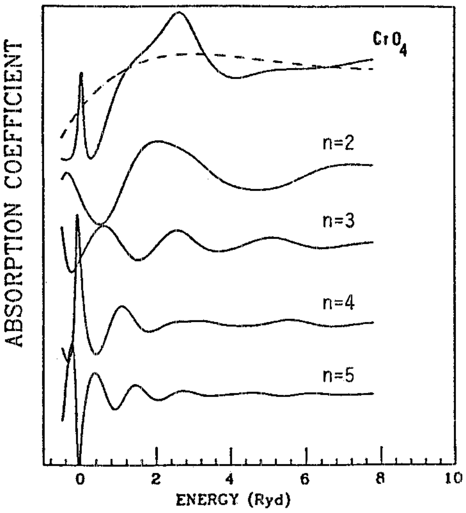

Fig. 2 - Theoretical absorption coefficient for a CrO_4 cluster. Going from top to the bottom the total cross section, the atomic contribution (dashed line), the single scattering contribution (EXAFS) and the contributions of successive order of multiple scattering pathways of orders n=3, 4 and 5 are shown.

a multiple scattering resonance where many orders of scattering contribute. The variation of the lineshape of this resonance with the central atom is studied. For the K-edge XANES of Cu^{2+} solution the effect of tetragonal Jahn-Teller distorsion is discussed.

Two electron transitions have been observed at 7 eV and ~50 eV in tetrahedral complexes.

References

(1) M.Benfatto, C.R.Natoli, J.Garcia, A.Bianconi, A.Marcelli and I.Davoli, Frascati Report LNF-85/26 (1985), to be published in Phys. Rev. B.

(2) J.Garcia, M.Benfatto, C.R.Natoli, A.Bianconi, I.Davoli and A.Marcelli, Solid State Commun., to be published.

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