Unified interpretation of pre-edge x-ray absorption fine structures in 3d transition metal compounds

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Abstract. Here we discuss origin of pre-edge features in the K-edge absorption spectra of transition metal atoms in octahedral coordination, in oxides and sulphides. We provide a unifying interpretation on the basis of multiple scattering simulations performed with different cluster models. We find that the pre-edge features arise due to hybridisation of the orbitals belonging to the central atom with the higher-shell metal orbitals. The results are obtained by performing multiple scattering simulations with cluster of size equal to the cation-cation plus the cation-anion bond lengths in order to ensure that the higher-shell metal atoms remain in the octahedral coordination. Within this framework, we are able to identify the electronic structure of the metal atoms and the ligand-field characters looking at position, shape and intensity of the different features observed in the XANES spectra.

INTRODUCTION

Knowledge of the relation between electronic structure and the atomic environment of 3d transition-metal oxides and sulphides has fundamental importance to understand transport and magnetic properties [1]. Recently, followed by the discovery of the high Tc superconductivity [2], colossal magnetoresistance effects [3] and other correlated phenomena, intense research has been devoted to the investigation of structural and electronic behaviour of these transition metal compounds to address a close interplay between electronic, magnetic and structural properties. Various high energy spectroscopy techniques, such as photoemission, inverse photoemission and x-ray absorption have been applied to investigate the electronic properties of these fascinating and still mysterious materials to find some relation between atomic scale structure related to the single particle excitation properties [4]. However, it is
necessary to interpret these results with a suitable theory in order to clarify the structural environment and symmetry as well the electronic properties of these materials. Such analyses have been extensively carried out in case of photoemission techniques. Although x-ray absorption spectroscopy, as a tool of partial and local empty density of states (DOS), is a powerful method to investigate the electronic structure in these systems,[5] so far, just a few theoretical approaches have been published. In spite of these efforts, interpretation of the X-ray-absorption near edge structure (XANES), and in particular the pre-edge features, still remains an open and controversial problem [6-12]. For example, some weak but sharp pre-peaks appearing several eV below the main absorption edge at the metal K-edge XANES spectra of 3d transition metal oxides, that are dipole forbidden in the octahedral coordination, have been attributed to 1s to 3d or quadrupole transitions.

It is known that properties of transition-metal oxides are correlated to the geometric arrangement around the transition-metal site.[13,14] A quantitative interpretation of the features observed in these spectra is a prerequisite to a complete investigation of the geometrical environment around the photoabsorber as well as the electronic structure of metal-ligand atoms. In this paper we present a detailed theoretical analysis of the XANES spectra at the K edges of the transition metal. For the sake of clarity we summarize some experimental results of the metal K edges in Fig. 1. In left panel are compared the XANES spectra of the Ti K-edge of TiO$_2$ (anatase) and TiS$_2$, the Mn K-edge of MnO$_2$ and the Fe K-edge of Fe$_2$O$_3$. In the right panel, the Mn, Fe, Co, and Ni K-edge spectra for NaCl-type monoxides are shown.

Commercially available high purity powder samples were used for the measurements. X-ray absorption near-edge structure (XANES) spectra were recorded using the synchrotron radiation source of the BEPC storage rings of the Beijing Synchrotron Radiation Facility (BSRF), working at the typical energy of 2.2 GeV with an electron current of about 120 mA. The Ti, Mn, Fe, Co and Ni K edges were recorded in transmission mode using a Si(111) double crystal monochromator at the beam line 4W1B with 1.0 eV resolution.

The spectra reported in Fig. 1 display pre-edge features that were previously attributed to 1s to 3d or quadrupole transitions. However, in these compounds, the metal ions are coordinated with six ligand ions and the 1s to 3d transition is not allowed. We may than concentrate on the possible alternative interpretation of the near-edge structures in these systems using the multiple scattering (MS) theory, which is capable to interpret the modulations of the XAS spectra in a variety of systems.[19] In order to clarify the type of the transition involved and to identify the origin of the spectral features, we report several theoretical simulations, taking TiS$_2$ (d$^6$) and α-Fe$_2$O$_3$ (d$^5$) compounds as model examples, based on one-electron full multiple scattering theory.[20-26] We have used the Mattheiss prescription [27] to construct the cluster density and obtain the Coulomb part of the potential by superposition of neutral atomic charge densities using the Clementi and Roetti basis set tables.[28] For practical reasons we use the energy independent X$_a$ exchange potential followed by a Lorentzian convolution to account for inelastic losses of the photoelectron in the final state and the core hole width. The total width of the Lorentzian is given by
Figure 1. XANES spectra at the metal K edges. Left panel: Ti in rutile and anatase (TiO$_2$, and TiS$_2$); Mn in MnO$_2$ and Fe in α-Fe$_2$O$_3$. Right panel: K edge of monoxides.

$\Gamma_{\mu\nu}(E) = 2I_{\mu\nu} \Sigma(E)$ where $\Sigma(E)$ is a volume averaged value over the unit cell of the compound of self-energy $\Sigma(r, E)$ as suggested by Penn.[29] The use of the $X_a$ exchange-correlation potential is not a limitation, since at low energies (around 30 eV above the onset of the absorption, the energy region we are interested to interpret) this potential and the real part of the Hedin-Lundqvist (H-L) one roughly coincide if the constant $\Sigma$ is appropriately chosen. In order to simulate the charge relaxation around the core hole, in a photoabsorber of atomic number $Z$, we used the well screened $Z+1$ approximation (final state rule).[26] This method start considering the orbitals of the $Z+1$ atom and consequently truncating the charge density by using the excited electronic configuration of the photoabsorber with the core electron promoted to an empty orbital. We have chosen the muffin-tin radii according to the criterion of Norman [20] and allowed a 10% overlap between contiguous spheres to simulate the atomic bond.

TiS$_2$ is described in the 1T-CdI$_2$ type structure [31] and the sulphur atoms form a perfect octahedron around Ti. In the Fig. 2, we report the MS calculations at the Ti K edge of TiS$_2$ by using different atomic clusters containing increasing numbers of atoms, from 7 to 81, until convergence was achieved. The cluster has D$_{3d}$ symmetry with respect to the central titanium atom. For a minimal cluster composed of a Ti atom
Figure 2. Theoretical XANES spectra as a function of the cluster size at the Ti K edge in TiS₂.

(emitter) surrounded by six sulphur (forming a perfect octahedron), the calculated absorption spectrum only gives rise to the peak A which corresponds, as expected, to transitions to Ti p-like states. Only after adding the second Ti shell, the pre-peak P appears. The presence of this feature has to be associated with the existence of unoccupied states due to the hybridisation of the central Ti p states with higher-neighbour Ti d orbitals. The increase from 13- to 51-atom cluster calculations is very clear: at the pre-edge two peaks arise. In fact, the 51-atom cluster includes an enough amount of outer-shell sulphur atoms (the cluster size is about Ti-Ti plus Ti-S bond lengths) to form an octahedral geometry around the Ti atoms surrounding the central atom in order to build t₂g⁻ and e_g-like molecular orbitals. These d orbitals can recombine symmetry-adapted, transforming them as the same irreducible representations of the photoabsorber,[32,33] and mixing with the p-states of the central atom (contribution P1 and P2). All the features observed in the experimental spectrum, in particular in the pre-edge region, are very well defined in the 81-atom cluster calculation indicating that the cluster size is sufficient to describe the bulk properties
Figure 3. The last model used in Fig. 2 (81-atom cluster) with different potentials; full relaxed final state (Z+1) and ground state (GS) potentials. The inset gives the theoretical TB-LMTO Ti p-like density of states (DOS) (lower curve) multiplied by 100 and d-DOS (upper curve).

while the pre-peaks reflect the density of states associated with the medium-range order of solid.

It is appropriate to compare the near-edge data, such as the pre-edge structures with the unoccupied conduction-band density of states (DOS) of the compound [34]. In Fig. 3 we report experimental data and the MS XANES spectrum calculated using a 81-atom model compared with the calculated DOS just above the Fermi level $E_F$, as derived from tight-binding linear muffin-tin orbital (TB-LMTO) band-structure calculations which has been widely used for this type of systems, e.g., on 3d TM monoxides [35] and more recently extended to the investigation of high-$T_c$ cuprates.[36].

There are two peaks in the Ti p-projected DOS, corresponding exactly to the P1 and P2 feature observed in the experimental data and in the MS calculation. From the corresponding d-projected DOS one can easily conclude that features P1 and P2 are due to dipole transitions to Ti 4p states hybridised with the crystal-field split of Ti 3d orbitals on neighbouring Ti atoms, i.e. $t_{2g}$ and $e_g$ band-like states. The energy separation between them is about 2.0(1) eV, nearly the same as the crystal-field d
orbitals splitting and agrees well with Fischer [37] and other studies. [7,38,39,40] We present also ground state (GS) potential calculations, which ignores core hole relaxation effects (lower curve in Fig. 3) and that, in the pre-edge region, is almost identical. This result is not surprising since the pre-edge features reflect the density of states associated with the medium-range order of the solid, as illustrated above. They should be rather insensitive to the details of the potential on the central Ti atom.

MS calculations of iron K-edge spectra of α-Fe₂O₃ (corundum) with different cluster models (7, 30, 51, and 90 atoms) are shown in the right panel of Fig. 4. In this compound, oxygen atoms are close packed and Fe³⁺ cations occupy nearly perfect octahedral sites. As in the case of TiS₂, the first model calculation does not give the pre-edge peaks. They appear only when cluster includes the next-nearest iron atoms (30-atom cluster calculation). All features observed in the experimental data are well reproduced in the 90-atom cluster calculation. As one may see in Fig. 4 when the cluster contains 51 and 90 atoms (i.e., the second Fe shell are in octahedral coordination with oxygen), the crystal-field splitting in the calculated spectra is not well defined like the behaviour at the O K-edge spectra because 13 iron atoms in the outer coordination shell, one at 2.88 Å, three at 2.95 Å and 3.35 Å, and six at 3.68 Å. Each of them is associated with its own t₂g-e_g-like splitting. The energy position will be
modified by the overlap of these octahedral orbitals and by the interaction with the oxygen orbitals. The overall absorption consists of a mixing of several components leading to a loss of resolution.

The pre-edge features in other compounds have the same origin as illustrated by TiS$_2$ and α-Fe$_2$O$_3$. For example, in the monoxide MnO, the pre-edge peak is reproduced only using large atomic clusters (including 57 and 123 atoms) as shown in Fig. 5. The intensity of these features decreases going from TiO$_2$ (rutile) to monoxides NiO and reflects the decreased number of unoccupied 3d states available for mixing with the central atom p-states and the increased cation-cation distance. This trend has been observed in the O and metal K edge in TM compounds by Colliex et al. [41], Kurata et al. [42], de Groot et al. [39] and Wu et al. [17].

Above results should not be confused with the results of metal in a tetrahedral site. The K-edge XANES of some transition atoms in tetrahedral coordination are characteristic roughly of a tetrahedral MO$_4$ (M=transition metal). The pre-edge peak in these systems with acentric tetrahedral symmetry is very intense and comparable to the transition to p states in the continuum above the absorption jump. It is now very well known that it is the result of a transition from 1s to the d part of final states T$_2$.
(irreducible representation of the T₆ point group) which includes not only the p but also the d base of the orbitals, is a dipolar transition partially allowed due to the mixing of the p and d orbitals. In Fig. 6 we report the calculated Ti K-edge spectrum (curve (b)) of a TiO₄ cluster (a perfect tetrahedron) compared with the experimental result (curve (a)) of Ti in glass from Ref. 12. A reasonable agreement has been obtained. Curve (c) is the calculation, suppressing the complete d base set in the final states of the photobase, the preedge structure disappears as indicated above.

Figure 6. Comparison of experimental data (curve a) at the Ti K-edge from Ref. 12. MS calculations in tetrahedral coordination (curve b). Curve (c) is the calculation without d base set in the final states (see text for more details).

In conclusion, by comparison the ab initio full MS computations and the experimental data at the metal K edge, all the transition features in the pre-edge region of TM compounds in octahedral coordination can be explained as due to the mixing of p orbitals of the absorbing atom with 3d orbitals of the higher-neighbouring metal octahedra. A good agreement between experimental data and theoretical ones has been achieved in the framework of the dipole approximation only. The core hole potential does not have a significant influence on the pre-edge peaks because they are dominated by higher-neighbouring metal orbitals.

We wish to emphasize that our comparison is precise and may be able to identify the higher-shell structural arrangement due to the position, shape and intensity of
different features in the spectra and relates them with the electronic structures and ligand-field characters. The interaction of different higher-neighbouring octahedral configuration-dependent hybridisation mechanism can be involved to explain why the relative pre-edge intensity and energy separation are different in all 3d TM compounds. In fact, the amplitude for the p character of the central atom wave function varies for changing values of the M-M distances and configuration of interactions.\cite{43,44} We discovered a theoretical and simple formula that shows how the pre-edge features and their splitting depend on the medium-range order of solid and consequently the cluster size should be equal to metal-metal plus metal-anion bond lengths. Our results can be also extended with success to other transition-metal compounds and to more complex biomaterials.

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