Interpretation of the pre-edge X-ray absorption fine structures in MnO

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Abstract The weak pre-edge features in the Mn *K*-edge X-ray absorption near-edge structure (XANES) spectrum of manganese monoxide (MnO) were investigated by comparing experimental data with dipolar and quadrupolar cross-section calculations in the framework of multiple-scattering theory. We assign the first pre-edge feature to a direct quadrupolar transition from 1s core state to 3d molecular orbitals of the central atom, e.g., the lowest in energy, due to the more effective attraction of the core hole. The second peak in this region arises unambiguously from the hybridization between *p*-orbitals of the central atom with higher-shell metal octahedral orbitals.

KeywordsX-ray absorption fine structures, X-ray absorption near-edge structure, MnOCLC numbersO657.62, O766

X-ray absorption fine structure (XAFS) is a unique probe to determine local atomic structure as well as electronic information in many systems related to biology, chemistry, geophysics, metallurgy, materials science, etc.^[1,2] Over the past three decades this technique has made great progress by providing high precision information. In fact, the success of the XAFS technique must be attributed, in large part, to the advance of the theory, which allows a reliable quantitative structural information. So far systematic theoretical analyses of X-ray absorption spectroscopies in 3d transition metal (TM) compounds have not been conclusive and most of the interpretations and general understanding of the X-ray-absorption near edge structure (XANES), in particular at the pre-edge, remains an open and controversial problem.^[3-9]

It is well known that various properties of these transition-metal oxides are correlated to the geometrical structure around the transition-metal sites.^[10,11] Therefore a quantitative understanding of the transition features in spectra is a prerequisite to a full investigation of the atomic environment around the photoabsorber as well as the electronic structure of metal-ligand atoms. In this work we present a detailed

theoretical analysis of experimental XANES data at the K edge of Mn for the MnO system.

An XANES spectrum at the Mn *K* edge was measured in transmission mode using a Si(111) double crystal monochromator by using synchrotron radiation at the X-ray absorption station (beam line 4W1B) of the Beijing Synchrotron Radiation Facility (BSRF). The storage ring was working at a typical energy of 2.2 GeV with an electron current of about 100 mA. To suppress higher harmonics, a detuning of 30% was performed between the monochromator crystals. The spectrum was taken at the step of 0.5 eV and at the energy resolution of ~1.5 eV. MnO samples of fine powder were obtained by spreading powder on two pieces of Kapton tape.

The calculations were carried out by using the one-electron full multiple-scattering theory^[12-14] and the Mattheiss prescription^[15] to construct the cluster electronic density and the Coulomb part of the potential (by superposition of neutral atomic charge densities obtained from the Clementi-Roetti tables^[16]), and the screened Z+1 approximation (final state rule)^[17] for simulating the charge relaxation around the core hole. The energy-dependent real Hedin-Lundqvist exchange potentials was used, followed by a Lor-

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entzian convolution (~2.5 eV consistent with the core hole life time and the experimental resolution) to account for inelastic losses of photoelectrons in the final state and the core hole width. We have chosen the muffin-tin radii allowing a 10% overlap between contiguous spheres to simulate the atomic bonds.^[18,19]

The manganese *K*-edge experimental XANES spectrum of MnO is shown in Fig.1 (curve *a*). It displays several main features (marked with A_i , *B* and *C*) in good agreement with other published work.^[9] Actually, we may divide the spectrum into three regions:



Fig.1 The experimental spectrum (a) and the multiple scattering calculation (b) of the XANES spectra at the Mn K edge in the MnO system.

(I) the first region (marked with *A*) named the "pre-edge" region. For MnO, in this region there appears to be two components, A_1 and A_2 of approximately equal intensity, separated by about 1.1 eV;

(II) the second region, around the maximum of the cross section, presenting a strong feature marked with *B*.

(III) the third region, extending up to about 20 eV from the edge (e.g., from about 6560 to 6580 eV), that contains the broad peak marked with C.

The comparison in Fig.1 reveals a good agreement between the calculated (curve b) and the experimental (curve a) Mn K-edge XANES spectra for MnO. The calculation took into account all multiple-scattering paths in a rather big cluster (123 atoms) but did not allow us to assign a particular shell of neighbors to each feature. To clarify this point, we have to perform MS calculations adding consecutive Mn and O shells around the emitter atom.

MnO has a cubic structure with a lattice constants $a_0 = 0.4446$ nm.^[20] The coordinating oxygen octahedron around the manganese atom is perfect with the Mn-O bond length of 0.2223 nm. In Fig.2, we present computations of the Mn K-edge XANES spectra for MnO by using a fully relaxed final state potential obtained within the Z+1 approximation^[17] for different cluster sizes (7, 57 and 123 atoms) up to the convergence. The first one contains all atoms within 0.7 nm from the photoabsorber (i.e. Mn) taken as the center of the cluster. For a minimal cluster composed just of a Mn as the central atom (emitter) and six nearest neighbors (O atoms), the calculated absorption spectrum shows the main peak B and a broad peak C which correspond to the transition to Mn p-like final states. In MS calculations, from the point of view of scattering, the second shell (six O atoms) is necessary to reproduce the quite strong peak B as well as the broad peak C. So, these features arise from the scattering within the first oxygen atomic shell. This behavior is the demonstration of relatively strong backscattering of O²⁺ ions.^[21]



Fig.2 Theoretical dipolar XANES spectra at the Mn *K* edge in MnO, as a function of the cluster size (7, 57 and 123 atoms).

Increasing the cluster, up to the fourth shell of Mn and O atoms, the pre-peak A_2 appears. The reason for this is rather clear. Higher coordination neighbors (the next-nearest Mn shell plus surrounding O atoms) are necessary to construct the appropriately hybridized 3d-like molecular orbitals around each Mn atom in the cluster which are made up of 3d metal orbitals and 2p oxygen orbitals. The 57-atom cluster in fact already includes enough O around Mn to form octahedra whose orbitals mix with the 4p states of the central atom. Furthermore, these neighboring octahedra strongly interact with each other and cause molecular orbitals to overlap, forming extended energy bands and modifying their energy position.

All features observed in the experimental spectrum, except the pre-edge A_1 , are reasonably well reproduced in the calculation of the largest cluster (123 atoms), not only in terms of relative intensities but also in energy separations. This indicates that a 123-atom cluster is sufficient to describe bulk properties and that the pre-peak is, at the same time, very sensitive to the "medium-range" order of the solid. It might therefore be used to extract information on this range. Furthermore, the peak A_2 comes from dipole transition based on theoretical MS simulation of absorption cross sections.

Since in transition-metal compounds the empty 3d-derived states normally lie at lower energies than the empty 4p-like states, significant quadrupole transitions are mostly to occur mainly in the pre-edge region. In order to shed light on the type of transition involved and identify the origin of spectral feature A_1 , we present a theoretical simulation, based on one-electron full multiple scattering theory, of the unpolarized quadrupole absorption cross sections by using the following equation:

$$\sigma^{Q}(\omega) = 4\pi^{2} (\alpha \hbar \omega)^{3} \cdot \frac{1}{240} \cdot \frac{(2l_{0} + 1)}{(2l + 1)} \cdot \frac{\sum_{lm} \operatorname{Im} \tau^{00}_{lm,lm} (M^{q}_{l_{0}l})^{2} (l_{0} 020 \mid l0)^{2}}{2}$$

where $\tau_{lm,lm}^{00}$, as usual in MS theory, is the scattering path operator calculated at the photoabsorbing site for angular momentum *lm*, the imaginary part of which is proportional to the site and *lm* projected density of

state of the system; M_{lol}^{q} is the radial matrix element of the quadrupole operator between the core state and the *l* component of the final state wavefunction; l_0 is angular momentum of the initial core state, and $(l_0 0 l_t 0 | l 0)$ is a Clebsch-Gordan coefficient. We use atomic units (u) for length and Rydberg units for energy so that the cross section is expressed in u². In Fig.3 the contribution of the allowed quadrupole absorption is presented by the solid line and compared with the allowed dipole absorption (dot line) for the 123-atom cluster before the convolution. As can be recognized, the quadrupolar spectrum is almost featureless except for a pronounced pre-edge peak A_1 lying at the energy about 1.0 eV lower than the allowed dipole pre-edge structure A_2 with similar intensity. The agreement between the experiment and theoretical simulations is much better by taking into account both contributions of dipole and quadrupole as shown in curves (b) and (c) of Fig.3, indicating that the first prepeak in the Mn K-edge XANES spectrum of MnO is a pure quadrupole one.



Fig.3 The curves (*a*) are the multiple scattering quadrupolar (solid line) and dipolar (dot line) calculations of the XANES spectra at the Mn *K* edge in MnO, using a 123-atom cluster. Curve (*b*) is the convoluted sum of the dipolar and quadrupolar contributions while the experimental data are the curve (*c*).

In conclusion, we have studied experimentally and theoretically for the first time the pre-edge features in the X-ray absorption spectrum of MnO at the

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Mn *K* edge in octahedral centrosymmetric coordination. By comparing the dipolar and quadrupolar cross sections calculated in the framework of *ab initio* full MS computations theory we claim that the lowest feature in energy is mainly quadrupolar in character followed by dipolar transition due to the medium range order of the system (a mixing of p orbitals of absorbing atom with 3*d* orbitals of higher-neighbouring metal octahedra). A good agreement between experimental and theoretical data has been achieved, indicating a pure quadrupole nature of the pre-edge.

We stress here that the comparison is precise and may be extended to other 3d TM compounds and more complex systems.

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