Symmetry role on the preedge X-ray absorption fine structure at the metal K edge

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The preedge features in a system with “even” symmetry, apart from quadrupolar transition contribution, are mainly dipolar in character, associated with the existence of unoccupied states made up of mixed cation-4p with higher-neighboring cation-3d orbitals, and reflect the density of states due to the medium-range order of the system. In "odd" symmetry materials these preedge features are the result of a transition from the 1s to a final density of states of p symmetry due to an unsymmetrical mixing of the ligand wave functions with the central cation 3d orbitals, similar to atetrahedral configuration. These results are validated for Fe as a photoabsorber by comparing XAS spectra of Fe_2SiO_4 (fayalite) to ab initio full multiple scattering calculations at the Fe K edge, but pertain to all systems containing sixfold-coordinated cations.

Keywords: XANES, Symmetry, Electronic properties.

1. Introduction

It is well known that the various properties of transition metal oxides are often crucially connected with the geometric structure around transition-metal sites (Sarma et al. 1995; Satpathy et al. 1987). A quantitative understanding of the features in the spectra is a prerequisite to a full investigation of atomic environment around the photoabsorber as well as the electronic structure of metal-ligand atoms. Despite of significant progress over the past years in the quantitative evaluation of the edge itself, there is an obvious lack of understanding as to the origin of features in the preedge region. The preedge peaks are mostly attributed to distortion-induced 1s to nd transitions in the sixfold-coordinated cation systems (Waychunas, 1987). In this paper we present a detailed interpretation of the characteristic features of the cation K-edge spectra in the light of ab initio full multiple scattering calculations. We use the Fe K edge as an example and concentrate on the model compound fayalite(Fe_2SiO_4) in which the iron ions have typical distorted sixfold coordination by oxygen, but with different symmetry parity.

2.Methods

XANES spectra at Fe K edge were measured in transmission mode by using synchrotron radiation with a Si (111) double crystal monochromater at the EXAFS station (Beam line 4W1B) of Beijing Synchrotron Radiation Facility. The storage ring was run at typical energy 2.2 GeV with the electron current about 90 mA. To suppress the unwanted harmonics, the angle between the monochromater crystal faces was adjusted to mistune the incident beam by 30%. The incident and output beam intensities were monitored and recorded using a nitrogen gas and a 50% argon-doped nitrogen flowing ionization chamber. The spectra were scanned in the range of 7.0-7.2 KeV, which cover the Fe K-edge absorption. Energy resolution was 1.5eV for the near edge structure. The fayalite sample has been synthesized at high temperature and pressure using a pyston cylinder apparatus and a mixture of oxides in stochiometric proportions as starting materials.

XANES spectra have been simulated via the full multiple-scattering (MS) theory(Bianconi 1988; Durham et al. 1981, 1982; Lee and Pendry 1975; Natoli and Benfatto 1986). In dealing with the x-ray absorption process one is faced with two fundamental problems, namely: a) the reduction of the inherent many-body problem to the more tractable problem of one electron moving in an effective optical potential and b) the full description of all orders of the multiple scattering (MS) events that the excited photoelectron undergoes in its way in the system, since the perturbation expansion of the MS problem might not converge. A possible solution to these problems has been indicated (Tyson et al. 1992) both with respect to the choice of the optical potential and the treatment of MS to all orders of perturbation theory (full MS). Actually the striking success of that approach in dealing with the amplitude and phase problem of fine structure oscillations in absorption spectra (Rehr et al. 1992) makes one reasonably confident that this approach can work well for more complicated materials (Wu et al. 1998). The construction of the charge density and potential follow the same patterns as in Ref.[Tyson et al. 1992].The calculated spectra are further convoluted with a Lorentzian shaped function with a full width Γ_h=1.2 eV (Fuggle et al. 1992) to account for the core hole lifetime and Γ_{exp}=0.8 eV, the experimental resolution.

3.Results

Fayalite, Fe_2SiO_4-Pbnm (Fulino et al. 1981) has two independent cation iron sites: M1 and M2. Both of them are occupied by Fe+2 and display large distortions with different symmetries: M1 has S2 with central symmetry and M has Cs without a symmetry center.

We first calculate the XANES spectra for the individual M1 and M2 sites via atomic clusters containing an increasing number of atoms, from 7 to 83, up to cluster size convergence. The convergent cluster is within 6 Å from the Fe atom, taken as the center of the cluster. The calculated spectra for the Fe-M1 and Fe-M2 clusters are reported in Fig. 1a and 1b. For a minimum cluster composed of a single Fe atom (emitter) surrounded by six oxygen atoms (forming so-called "distorted octahedra"), the two calculated absorption spectra give rise to the same peaks a and c which correspond to transitions to Fe p-like states as expected. However, they show definite differences in the preedge region as a result of the point symmetries of the cluster center, reflecting the different electronic structure just near the Fermi level. The M1 cluster, as mentioned above, has a strongly distorted sixfold coordination but with an "even-parity" symmetry center under the

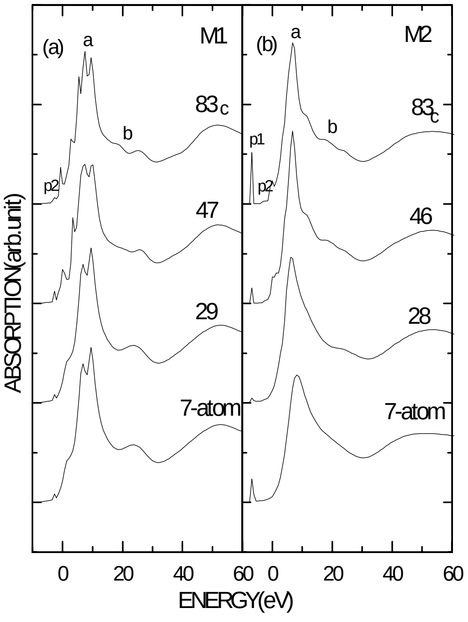

Figure 1

Fe K-edge XANES calculations for fayalite Fe_2SiO_4 for the M1-site cluster (a), and the M2-site cluster (b). Curves refer to cluster calculations with increasing number of atoms: 7, 29, 47, and 83, respectively, around the central photoabsorbing Fe.

inversion operation (S2). It therefore does not show any feature in the preedge region (dipole forbidden);the M2 cluster, having a slightly less distorted sixfold coordination but with "odd-parity" symmetry Cs, gives a preedge peak p1 already in the first small cluster model which can be attributed to the dipole-allowed transition from 1s to the d part of final states A' and A" (irreducible representation of the Cs point group), the same as in an acentric tetrahedral system.

After adding the higher-neighbor iron and oxygen shells, a weak prepeak p2 in the M1-cluster appears, as well as in the M2-cluster (Fig. 1). The presence of this feature has to be associated with the existence of unoccupied states arising from the hybridization of the central Fe p orbitals with higher-neighboring

Fe d orbitals, contrary to the traditional assignment of a 1s to 3d transition (Waychunas, 1987). In fact, the 47-atom cluster includes enough outer-shell oxygen atoms (the cluster radius of about 5 Å being ≥ the sum of Fe-Fe and Fe-O bond lengths) around the second neighbor Fe atoms so that molecular orbitals are constructed. This is at variance with the 28-atom case. These d orbitals can recombine in a symmetry-adapted way to transform according to the dipole-allowed irreducible representations (Ballhausen 1962; Kettle 1985) and mix with the 4p-states of the central atom, giving rise to the features p2. Increasing the cluster size further, we observe that in the 83-atom calculation the cluster size (7 Å radius) is sufficient to reproduce all features present in the first 60 eV of the experimental spectrum. Calculations using clusters with greater radii produce spectra not substantially different from the latter cluster. Therefore these features, and in particular the pre-edge structure p2 and b, reflect the density of states associated with the medium-range order of the solid.

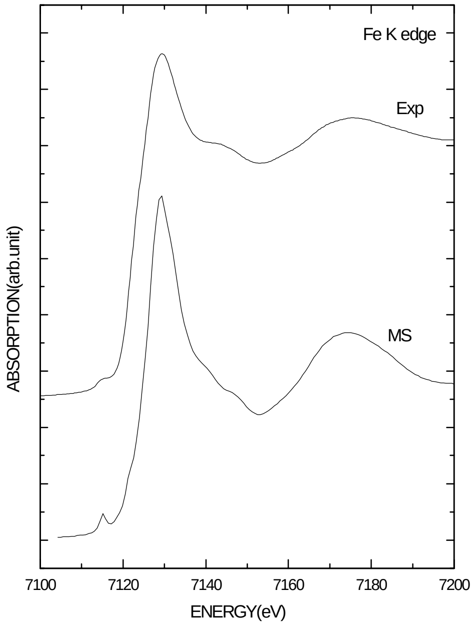

Figure 2

Comparison of the experimental spectrum with combination of two-site contributions obtained by using 83-atom cluster MS calculations with convolution at Fe K edge.

The experimental Fe K edge XANES spectrum of fayalite consists of the superimposed contributions of all Fe atoms (combination in the 1:1 proportion of M1 and M2) present in the structures, i.e. of all clusters. In Fig. 2 we report the combined calculated spectra with convolution by using 83-atom cluster, along with the experimental XANES spectrum. Excellent agreement is obtained, not only for the peak positions but also the intensities in MS region as well as the preedge part. For fayalite, in summary, the less distorted M2 site produced higher preedge intensity due to its "odd" parity symmetry compared to the strongly distorted M1 site with "even" parity symmetry. Predictions that stronger polyhedral distortion should induce higher preedge intensities (Waychunas, 1987) are therefore only true for a comparison of structures with the same point group symmetry.

As complement to the above results, we present briefly a result of the metal in 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 preedge peak in these systems with acentric tetrahedral symmetry is very strong and usually comparable to that of the transition to p states in the continuum above the absorption jump. It is now very well known to be the result of a transition from 1s to d part of final states T2 (irreducibal representation of Td point group) which includes not

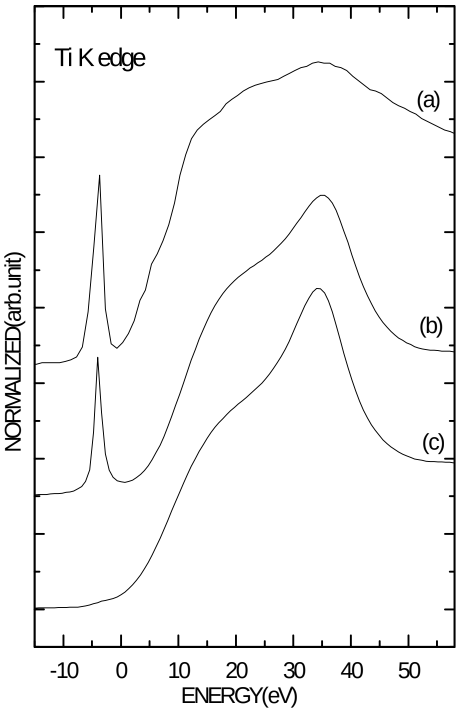

Figure 3
Comparison of the experimental data (Lytle et al. 1988) with MS calculation at Ti K edge in tetrahedral coordination.

only the p but also the d base of orbitals. It is a dipolar transition partially allowed due to the mixing of the p and d orbitals.

In Fig. 3 we report the calculated Ti K-edge spectrum (curve (b)) of TiO_4 cluster (a perfect tetrahedron) compared with the experimental result (curve (a)) of Ti in glass (Lytle et al. 1988). A reasonable agreement has been obtained. Curve (c) is the calculation by suppressing the d base components in the final states of photoabsorber, the preedge structure disappeared as expected.

4.Conclusion

From the present investigation of Fe K-edge XANES experiments and full MS theoretical computations in the model compound Fe_2SiO_4 as well as from general considerations, we have clarified the effect of the "distorted octahedral" configuration on XANES spectra and solved a long-time puzzle by pointing out that in sixfold coordination systems the symmetry point group ("odd-parity" versus "even-parity" properties) is critical. In centrosymmetric systems combinations of higher-shell cation d orbitals can give rise to u character (possessing odd-parity). The preedge features are to be associated with the existence of unoccupied states made up of mixed cation-4p orbitals with these combined d parts. In contrast, the direct transition from 1s core state to 3d molecular orbitals of the central atom is dipole allowed in the "odd-parity" systems.

The symmetry point group related to the photoabsorbing atom is crucial for the existence of prepeaks and their intensity, whereas traditional descriptions of octahedral distortion via bond length and/or bond angle variation are inappropriate. This result can be applied to more complex systems, especially for 3d transition metal compounds, minerals and unknown structure materials.

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