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J. Phys.: Condens. Matter 7 (1995) 4975–4981. Printed in the UK

Electronic structure of $SmFeO_3$: x-ray absorption fine structure analysis

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Received 21 November 1994, in final form 17 March 1995

Abstract. Oxygen K edge and iron $L_{2,3}$ edge x-ray absorption spectra of $SmFeO_3$ have been measured and theoretical analysis of these data on the basis of full multiple-scattering formalism in real space has been made. Combined oxygen K edge and Fe L_3 edge XANES is shown to be a useful tool for the study of RE orthoferrite electronic structure. The full multiple-scattering approach is found to be successful in analysing experimental oxygen K edge XANES in $SmFeO_3$, while the single-scattering approximation is not valid in this case. Unoccupied oxygen p states interact with Fe 3d in a specific resonance manner.

1. Introduction

The electronic structure of perovskite-type rare-earth (RE) orthoferrites is of interest primarily due to the anomalous changes of their electrical and magnetic properties as a function of temperature [1]. In recent years the important role of oxygen atoms in the formation of specific properties of oxides has initiated measurements of x-ray absorption above oxygen K edge. Up to now most such studies have been performed for simple transition metal and RE oxides (for a review see [2]). Recently oxygen XANES have been measured in $LaNiO_3$, $PrNiO_3$, $NdNiO_3$ [3], $LaCoO_3$ [4], $LaNi_{1-x}Me_xO_3$ (Me = Mn, Fe and Co) systems [5]. Theoretical interpretation of experimental oxygen EELS and XANES data in various oxides has been done in the framework of various approaches: the tight-binding method [6], energy band calculation [7] and a very suitable multiple-scattering (MS) calculation in real space [8–11].

Information on unoccupied oxygen p states in RE orthoferrites like $SmFeO_3$ is of great importance due to the possible O p–RE 4f–Fe 3d interaction in such rather complex compounds where it can give a large enough contribution to the chemical bond. In spite of the localized character of Fe 3d and RE 4f states there are some indications for the hybridization of oxygen 2p states with these states both in the valence band and in the unoccupied region of the conduction band [12] in orthoferrites in analogy with sulphur 3p state–RE 4f state mixing in RE sulphides [13] and Ni 3d–O p hybridization in $LnNiO_3$ (Ln = RE) compounds [3].

Here we have measured oxygen K edge and Fe $L_{2,3}$ edge XANES of $SmFeO_3$ and the Fe $L_{2,3}$ edge of $EuFeO_3$ to study the fine structure of unoccupied electronic states. We have also applied the multiple-scattering approach in real space to analyse these data in comparison with XANES of $EuFeO_3$ [2].

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2. Experimental details

XANES above the oxygen K edge and Fe $L_{2,3}$ edges have been measured on the laboratory x-ray monochromator with the total electron yield technique. A spherical quartz grating of 6 m radius was covered with a thin layer of pure gold to increase the reflectivity and eliminate the peculiarities of background radiation originating from the oxygen of the grating material. Spectra for each sample were measured six times and then averaged. The spectra from different scans were matched to the same energy scale by using the channel pair method. (In the second channel of the spectrometer we measured the O XANES of an Fe_2O_3 sample and its very sharp maximum served as a matching point.)

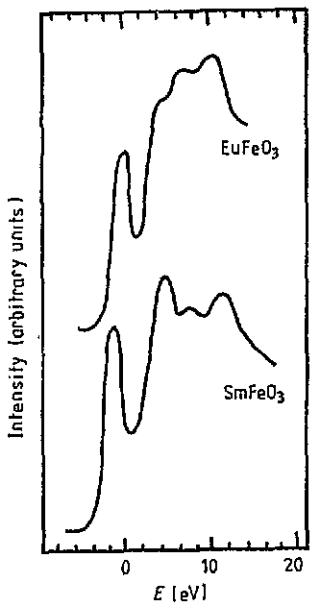

Figure 1. Experimental oxygen K edge XANES of $SmFeO_3$ in comparison with data taken from [2] for $EuFeO_3$.

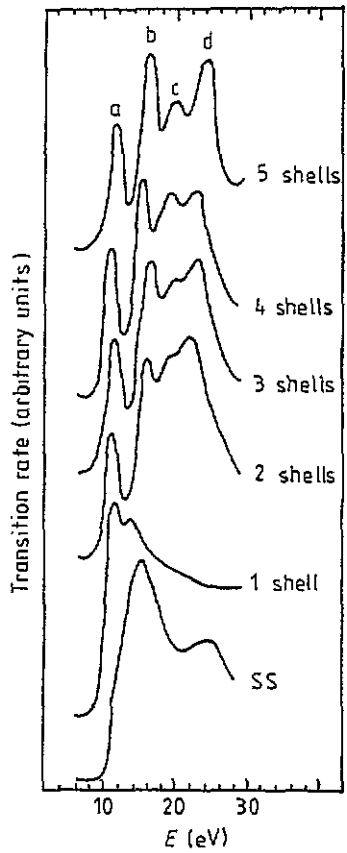

Figure 2. Theoretical x-ray absorption coefficients for O K edge of $SmFeO_3$ calculated within clusters of different size. All spectra have been calculated taking into account the broadening factors and Fermi distribution (see text). The zero of the energy scale is chosen at the average interstitial potential (i.e. muffin tin zero) V_0 of the O atom. All spectra (except the lowest one) are obtained within the full multiple-scattering formalism; the spectrum marked SS is calculated in the single-scattering approximation for five shells cluster.

3. Calculation

The algorithm of the the full multiple-scattering method used in this study has been described earlier [14–16]. For calculation we use the perovskite type of crystal structure with lattice constant equal to 3.836 Å for $SmFeO_3$ [17] (in a real crystal this perovskite structure is only slightly distorted due to the small size of the RE atoms). The cluster of neighbour atoms around the central O is divided into shells as reported in table 1. For phase shift calculation we have obtained the crystal muffin tin (MT) potential with touching MT spheres.The muffin tin radii and the muffin tin constants that we have obtained according to our procedure of muffin tin potential construction [15] are reported in table 2. We use the muffin tin approximation according to Mattheiss prescription with exchange parameter equal to 1.0 while constructing the crystal potential. Atomic charge densities were obtained with the help of the self-consistent Dirac–Slater method. In our calculation we included phase shifts with orbital momentum up to four for all types of atom. To compare theoretical spectra obtained from the projected density of states and the dipole transition matrix element with experimental XANES one must take into account the Fermi distribution function and all main factors that cause the broadening of the spectra (i.e. the final lifetime of the core hole [18], the mean free path of the photoelectron function [19] and experimental resolution). We treated all these factors contributing to the imaginary part of the complex potential we had used.

Table 1. Structure of the five-shell cluster for $SmFeO_3$.

Shell number	Atom	Number of atoms in shell	Sphere radii (Å)
1	Fe	2	1 9225
2	O	8	2.7188
2	Sm	4	2.7188
3	O	6	3.8950
4	Fe	8	4.2988
5	O	16	4.7091
5	Sm	8	4.7091

Table 2. The muffin tin radii R_{mt} of the atoms included and the muffin tin constants V_0 (if the origin of the energy scale is at vacuum level).

Atom	R_{mt} (Å)	V_0 (eV)
O	0.8915	−24.098
Fe	0.9168	−24.604
Sm	1.0040	−24.238

4. Discussion

In figure 1 we compare the experimental XANES above the oxygen K edge of $SmFeO_3$ with the same spectrum of $EuFeO_3$ from [2]. The lattice parameter changes only by 0.009 Å and one additional localized 4f electron appears while going from $SmFeO_3$ to $EuFeO_3$. But as one can see the XANES spectra reflecting the density of unoccupied oxygen p states

changes significantly. So, oxygen K edge XANES is found to be very sensitive to the fine peculiarities of the electron density of unoccupied states in orthoferrites like $SmFeO_3$ and $EuFeO_3$ that are very useful objects for study because they let us see the changes of the electronic fine structure features versus RE atomic number and almost negligible changes of local structure. In the $LaNiO_3$–$PrNiO_3$–$NdNiO_3$ series very small changes in relative intensity and first ('prepeak') maximum energy shifts in oxygen XANES have been found [3]. This first low-energy peak 'a' in orthoferrites changes its relative energy position by a larger value (the energy shift is about 1.1 eV in comparison with the 0.2 eV shift for the $LaNiO_3$–$PrNiO_3$ pair and 0.4 eV for $LaNiO_3$–$NdNiO_3$ [3]) and peak 'b' changes its relative intensity.

In order to study the nature of these changes we performed full multiple-scattering analysis of the experimental XANES. The first step in the multiple-scattering analysis of XANES data is the determination of the minimum size of the cluster of neighbour atoms around the absorbing O atom, within which the scattering of the photoelectron can reproduce all the fine structure of XANES (and of cause the corresponding density of unoccupied states). In figure 2 we report the results of O K edge XANES calculation for $SmFeO_3$ by considering clusters of different size. In the case of a one-shell cluster, where only two Fe atoms surround the central oxygen atom, XANES consists of only one broad maximum with a very small low-energy detail and its shape is far from the experimental XANES. On adding the *second shell of neighbour atoms including Sm and O atoms the structure of the spectrum* becomes closer to the experimental one: there is a well separated low-energy maximum 'a' and higher-energy subbands in the energy interval 16–24 eV. The further increasing of cluster size leads to a more correct relative intensity for 'b', 'c' and 'd' peaks and the structure of the theoretical XANES comes into agreement with the experimental one. On the other hand the single-scattering approach that is widely used for x-ray absorption analysis is shown to be unsatisfactory in the case of O K edge XANES of $SmFeO_3$ even for a large enough cluster of 53 atoms (see the curve labelled 'SS' in figure 2). Large values of *the mean free path of the low-energy photoelectron and the high symmetry of the crystal* lattice seem to be the main reasons for the breakdown of the single-scattering approach here. Therefore we may conclude that O K edge XANES in $SmFeO_3$ is a result of multiple scattering of the excited photoelectron within a cluster of large enough size (not less then 21 *atoms in total, including all types of atom i.e., O, Fe, Sm). In the language of quantum* solid state chemistry one can say that the wave function of the electron in the conduction band is formed with some degree of covalency, or in other words there is a hybridization of O p , Fe 3d and Sm 4f states. In figure 3 we report the normalized absorption coefficient (i.e. the absorption coefficient in the relative units of atomic absorption α_0 at high energy). So, if one needs to obtain absolute values of absorption coefficient it is possible to do so by multiplying these normalized data by corresponding value of atomic absorption. As one can see we succeed in obtaining good agreement of the full multiple-scattering theoretical *results with experimental data for* $SmFeO_3$

In figure 4 we present the experimental Fe $L_{2,3}$ edge XANES of $SmFeO_3$ and $EuFeO_3$. For $EuFeO_3$ there is a pronounced difference in L_3 (located at about 700 eV) and L_2 (located at about 712 eV) edge shapes. This indicates a breakdown of the one-electron approach for their description, as was found for $L_{2,3}$ x-ray absorption edges of other transition elements with partially occupied d levels where significant multielectron interactions lead to the multiplet splitting of $L_{2,3}$ edge XANES [20]. Only in the case of a fully occupied (unoccupied) *n*d electronic energy band one can succeed in obtaining good enough results in the framework of the one-electron multiple-scattering calculation (see for example [21, 22]). Even though for $SmFeO_3$ the structures of L_3 and L_2 edges are closer to each other

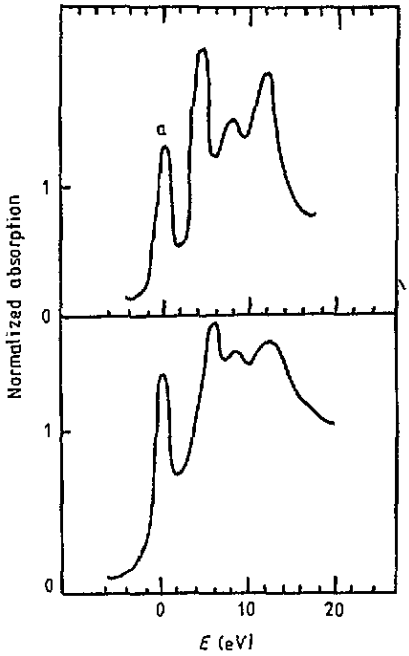

Figure 3. Comparison of theoretical full multiple-scattering O K edge XANES of $SmFeO_3$ with experimental spectrum. The absorption coefficient has been normalized to the value of the atomic absorption at high energies α_0. The experimental spectrum is matched to the same energy scale by the position of the first low-energy maximum 'a'.

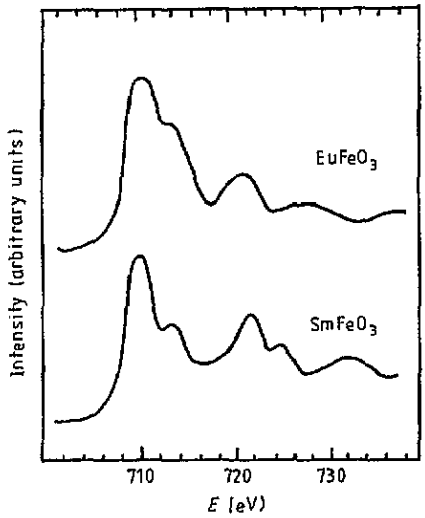

Figure 4. Experimental Fe $L_{2,3}$ edge XANES of $SmFeO_3$ and $EuFeO_3$.

we prefer not to compare the results of our one-electron full multiple-scattering calculation with experimental data but use them to analyse the peculiarities of the $SmFeO_3$ ground state electronic structure in the region of unoccupied states. In figure 5 we show the the results of theoretical full multiple-scattering calculation of Fe L_2 edge XANES for a three-shell cluster(p $\rightarrow$ s transition—curve 1, p $\rightarrow$ d transition—curve 2) and oxygen K edge XANES (s $\rightarrow$ p transition—curve 3) for a five shell cluster. If one neglects the energy dependence of the transition matrix element (which influences only the relative amplitude of XANES that is not so important in our case; however we present curves in an arbitrary unit scale for the y axis) the curves reflect the distribution of Fe s (curve 1), Fe d (curve 2) and O p unoccupied states in the conduction band of $SmFeO_3$. To make fine details in the high-energy interval visible the right-hand part of curve 2 is scaled 50 times. In order to obtain the precise energy matching of iron and oxygen spectra calculated with slightly different values of the constant parts of the muffin tin potential (see table 2) oxygen spectrum was shifted by the value of 0.5 eV. Thus we put the spectra in a unique energy scale corresponding to the same values of vacuum level energy. The detailed analysis of the data in figure 5 leads to the conclusion that the interaction of oxygen unoccupied p states with iron d states does not have a simple admixture character when both densities of states must have their maxima at the same energy. On the contrary the energy positions of Fe d state maxima correspond mostly to the minima of O p states and vice versa. So, one may conclude that the electronic

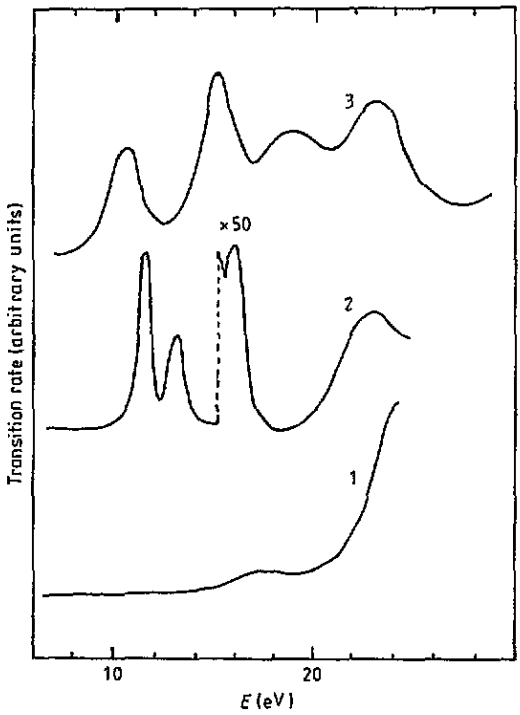

Figure 5. The results of the theoretical full multiple-scattering calculation of Fe L_2 edge XANES for 3 shells cluster (p → s transition—curve 1, p → d transition—curve 2) and oxygen K edge XANES (s → p transition—curve 3) for a five shells cluster. Neglecting the energy dependence of the transition matrix element the curves reflect the distribution of Fe s (curve 1), Fe d (curve 2) and O p unoccupied states in the conduction band of $SmFeO_3$. The high-energy part of curve 2 is scaled 50 times to make visible fine details in this energy interval. The origin of the energy scale corresponds to the muffin tin constant of the Fe atom; the oxygen spectrum is shifted according to its muffin tin constant deviation (see table 2). Thus all spectra are presented in a unique energy scale corresponding to the same energy of the vacuum level.

states with O p symmetry are pushed out of the energy interval from 11 to 14 eV, where Fe d states are localized. For the unoccupied states such a type of resonant interaction between electronic states has been found previously in rare earth sulphides [13] and CeO_2 [23]. The detailed description of this resonance mechanism for occupied states in the valence bands of some transition elements compounds can be found in [24] and [25].

5. Conclusions

We have shown oxygen K edge XANES to be very sensitive to the fine peculiarities of the electron density of unoccupied states and thus it is a useful tool for the study of complex oxide (like RE orthoferrite) electronic structure. The full multiple-scattering approach is found to be very successful to analyse experimental oxygen K edge XANES in $SmFeO_3$, while the single-scattering approximation is not valid in this case. We suggest unoccupied oxygen p states to be hybridized with both Fe 3d and RE 4f states in the conduction band of $SmFeO_3$. There are some indications that unoccupied oxygen p states interact with Fe 3d not in simple manner of state admixture but in a specific resonance manner when localized d states push oxygen p states out of the energy interval where these d states are localized.

Acknowledgments

This research was partially supported by NATO grant CRG 930305, RBRF grant 94-02-03038 and a grant from the Committee for Higher Education of Russia.

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