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High-energy-spectroscopy studies of a charge-transfer insulator: X-ray spectra of α-Fe_2O_3

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X-ray emission and absorption spectra of α-Fe_2O_3 have been arranged on a common binding-energy scale and compared with results of multiplet theory and cluster calculations. In the case of the Fe $L\alpha$ emission and the Fe K absorption, the information content of x-ray spectroscopy has been further increased by measuring and analyzing linearly polarized spectra. The results of the x-ray spectroscopic investigations and their comparison with the theory complement the findings of other types of high-energy spectroscopy and seems to provide good support for the validity of certain cluster theories. Especially, x-ray spectra reflect the strong influence of correlation and charge-transfer effects on the electronic structure of α-Fe_2O_3 and support the suggestion that this compound should belong to the class of charge-transfer insulators.

INTRODUCTION

α-Fe_2O_3 (hematite) is an antiferromagnetic insulator with some peculiar properties. Between a certain transition temperature ($T_t = 260$ K) and the Néel temperature of 956 K, it shows weak ferromagnetism[1-3] and its conductivity is activated at high temperatures with a thermal gap of about 2 eV.[4] α-Fe_2O_3 belongs to the transition-metal sesquioxides α-M_2O_3 ($M =$Ti, V, Cr, or Fe) which have the α-Al_2O_3 corundum structure. This gives the possibility to study and compare electronic properties in a series of transition-metal oxides which all possess the same structure but with a diversity of their physical properties. These interesting phenomena have given rise to a still growing number of theoretical and experimental, especially spectroscopic, investigations of the α-M_2O_3 oxides and therefore also of α-Fe_2O_3.

In the present investigation, special interest will be dedicated to the MS $X\alpha$ calculations of Nagel[5] for an $[Fe_2O_9]$ cluster consisting of two distorted $[FeO_6]$ octahedrals and being representative for the Fe_2O_3 crystal structure. Furthermore, results of the configuration-interaction theory obtained by Fujimori *et al.*[6] are considered and a recent photoemission study of the valence-band electronic structure of α-Fe_2O_3 by Lad and Henrich.[7]

In the present investigations, some results of the mentioned theoretical electronic structure calculations are discussed in the light of the experiments with respect to the question if the α-Fe_2O_3 compound can be considered as a Mott-Hubbard insulator or must be classified as a charge-transfer insulator. Furthermore, the investigation will show the abilities of x-ray spectra to provide answers to such questions.

EXPERIMENTAL DETAILS

Photoelectron and x-ray spectra of our own measurements and those taken from the literature were aligned on a common binding-energy scale by means of experimental Fe and O XPS (x-ray photoemission spectroscopy) core-level energies (Fig. 1). XPS core line spectra of α-Fe_2O_3 were obtained by us from a commercial Fe_2O_3 powder sample using an ESCA (electron spectroscopy for chemical analysis) spectrometer. After a careful analysis of our results in a comparison with values taken from the literature,[6-9] the corresponding core line binding energies could be used for transforming the photon-energy scale of the emission and absorption spectra into the binding-energy scale within an uncertainty of about ±0.2 eV.

The Fe $K\alpha$, line of α-Fe_2O_3, necessary for the determination of the Fe $1s$ binding energy $[E_B(1s) = E_B(2p_{3/2}) + E(K\alpha_1)]$ and the Fe $K\beta_{2,5}$ emission were measured by using the same commercial Fe_2O_3 powder material using a two-crystal x-ray spectrometer with highly perfect Si(111) analyzing crystals in the first-order reflection and with a W tube for fluorescence excitation.[10]

The polarized Fe $L\alpha$ emission from a natural hematite single crystal was registered by a fluorescence excitation with a Cu anode[10] using a SARF x-ray spectrometer with a KAP analyzing crystal and an appropriate geometry as described, in principle, in Ref. 11. The spectra have been taken for two different positions of the emitting sample but with the same outer geometry relative to the reflection plane of the spectrometer crystal. Because of the Bragg angle of about 41.3° and the used sample geometry, the measured Fe $L\alpha$ spectra are nearly linearly polarized parallel ($\mathbf{e}\| c$) and perpendicular ($\mathbf{e}\perp c$) to the c axis.

Self-absorption effects and satellite emission[10] distorting the high-energy tail of the Fe $L\alpha$ emission cannot be taken into consideration quantitatively. Therefore, this part of the spectrum has not been used for any interpretation in the present work. The polarization dependent Fe K preedge absorption spectra [Fe K x-ray absorption spectroscopy (XAS) in Fig. 1] were measured with linear-

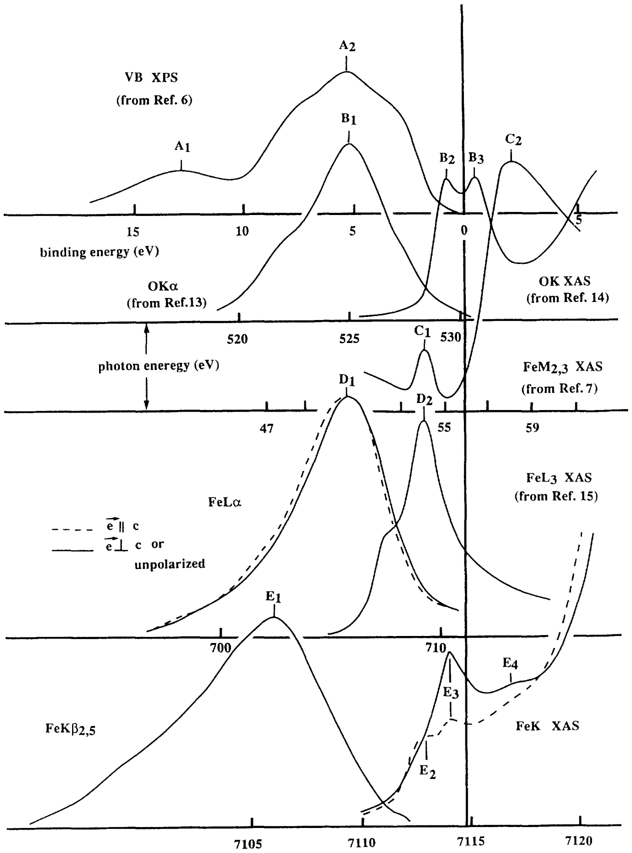

FIG. 1. Alignment of the experimental α-Fe_2O_3 spectra with reference to the binding-energy scale of the valence-band photoelectron spectrum (VBXPS). For detailed explanations, see the text.

ly polarized synchrotron radiation at HASYLAB at DESY, Hamburg. The single-crystal absorbers were also prepared from natural hematite crystals.[12] The samples were uniform and thin enough to avoid the well-known "thickness effect."

All the other spectra aligned in Fig. 1 were taken from the literature. The valence-band x-ray photoemission spectrum (VBXPS) measured with $h\nu = 1253.6$ eV from Ref. 6, the oxygen valence-band emission (O $K\alpha$) of α-Fe_2O_3 from Ref. 13, the oxygen absorption edge (O K XAS) recorded in the total-electron-yield mode at natural mineral Fe_2O_3 from Ref. 14, the iron $3p$ absorption edge (Fe $M_{2,3}$ XAS) taken also in the total-electron-yield mode at a synthetic α-Fe_2O_3 crystal from Ref. 7, and the iron $2p_{3/2}$ absorption (Fe L_3 XAS) from Ref. 15.

RESULTS

A comparison of experimental data with the results of some theoretical investigations of the electronic structure of α-Fe_2O_3 is shown in Fig. 2. In the middle of Fig. 2 the energetic positions of the spectral features are marked, using the same notation as in Fig. 1. These experimental data will be discussed and compared with a MS $X\alpha$ cluster calculation of Nagel[5] (upper part of Fig. 2), with results of the configuration interaction theory of Fujimori *et al.*[6] and with those of an atomic multiplet theory, published by de Groot *et al.*[16] (lower part of Fig. 2).

All experimental and theoretical data are aligned on a common binding-energy scale. The upper part of Fig. 2 shows theoretical spectra, calculated from results of a multiple-scattering $X\alpha$ (MS $X\alpha$) cluster calculation of Nagel.[5]

The MS $X\alpha$ calculation performed for an Fe_2O_9 cluster uses a muffin-tin potential with a local statistical exchange. A spin-polarized version was applied and the atom-centered orbitals are single-center projections of the total one-electron wave functions. The overall picture of chemical bonding in α-Fe_2O_3 as obtained from the results indicates important deviations from a simple ionic model. Due to substantial interaction between iron d and p orbitals and oxygen p orbitals, the calculated ground-state electronic structure is strongly influenced by covalency and charge transfer from oxygen to iron.

To compare spectral features of the Fe K and Fe L spectra with the results of the MS $X\alpha$ cluster theory according to Ref. 5, quantities were calculated which resemble the local, partial (l,m)-resolved density of states (DOS).[11] These quantities, in the following called "cluster DOS,"[17] were calculated by convoluting the individual cluster levels with Lorentzians having a constant full width at half maximum (FWHM). The peak height of the Lorentzians was chosen to be proportional to the percentage of the corresponding Fe (l,m)-orbital character. The polarization dependence of the spectra was taken into account by using the selection rules for polarized x-ray transitions as given in Refs. 11, 18, and 19.

The Fe K spectra were reproduced by calculating the Fe $4p$ cluster DOS using Lorentzians with a FWHM of 1.6 eV for the unpolarized Fe K emission and with a

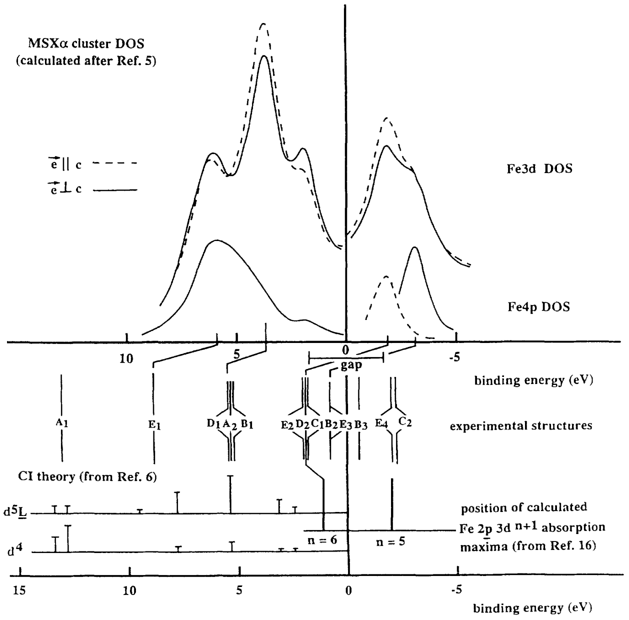

FIG. 2. Comparison of the position of experimental spectral structures in the binding-energy scale (middle part) with the results of a one-electron MS $X\alpha$ cluster calculation (upper part) and with those of many-body calculations (lower part).

FWHM of 1.2 eV for the polarized Fe K absorption. The Fe L spectra were calculated considering only the Fe $3d$ orbital character and Lorentzians with a FWHM of 1.6 eV. The Fe $3s$ cluster DOS was not taken into account for the Fe L spectra because of its small contribution[5] and the comparatively low transition probability.[20]

In the lower part of Fig. 2 the emission spectra from the Fe_2O_3 valence-band states can be compared with results of a configuration-interaction theory based on an FeO_6 cluster model by Fujimori *et al.*[6] These theoretical results together with photoemission and Auger-electron spectra of Ref. 6 indicate that α-Fe_2O_3 cannot be considered as a Mott-Hubbard insulator but must be classified as a charge-transfer-type insulator according to the theory of Zaanen, Sawatzky, and Allen.[21] These findings are supported by the present investigations of the x-ray spectra. The paper of Fujimori *et al.*[6] on Fe_2O_3 was initiated by previous theoretical and experimental studies on NiO which have given additional insight into the electronic structure of this type of compounds. It has been found that the hybridization between the nearly localized, strongly correlated Ni $3d$ levels and the bandlike O $2p$ levels is essential and that charge transfer between these levels screens d electrons and holes created in high-energy spectroscopies as in photoemission, for instance. By considering configuration interactions (CI), including charge transfer, the main lines of the valence-band photoemission which had earlier been interpreted as d^7 final-state multiplet lines within the framework of the ligand-field (LF) theory were found to be $d^8\underline{L}$ final states ($\underline{L}$ is the ligand hold) resulting from $\underline{L} \rightarrow d$ charge-transfer screening of d holes. On the other hand, the high binding-energy satellite was found to be unscreened d^7 final states.[22] Therefore, it was concluded that the band gap is not a Mott-Hubbard (d-d) type, where the magnitude is determined only by the on-site d-d Coulomb correlation energy U. Instead, the gap is interpreted as to be of charge-transfer type, determined by the $L \rightarrow d$ charge-transfer energy rather than only by U. In this context, Zaanen *et al.*[21] have postulated that Ti and V compounds are in the Mott-Hubbard regime, while Cu, Ni, and Co compounds are in the charge-transfer regime.

The ground-state configuration of Fe in α-Fe_2O_3 is a high-spin d^5 state, i.e., ^6S. LF theory as well as band theory predict only two peaks in the Fe $3d$–derived photoemission spectrum, the two multiplet lines, $^5T_{2g}$ and ^5E_g, or the t_{2g} and e_g bands, respectively, separated by the crystal-field splitting. In Ref. 6, however, it has been shown that the main band is due to the $d^5\underline{L}$ final states which are screened via $L \rightarrow d$ charge transfer while the satellite is originated by unscreened (or poorly screened) d^4 final states.

In the lower part of Fig. 2 the cluster level energies and their spectral weights are shown for the two main final configurations $d^5\underline{L}$ and d^4. These results were obtained in Ref. 6 as the best fit to the XP valence-band spectrum (VBXPS in Fig. 1) by using adjustable energy differences between different configurations. This adjustment provides the best values for the correlation energy and the charge-transfer energy in the ground state as to be 8±2 and 3±1 eV, respectively,[6] and extends the charge-transfer regime from the Cu, Ni, and Co compounds to Fe compounds. For further comparison between experiment and theory, in the lower right-hand part of Fig. 2 the positions of calculated Fe $\underline{2p}\, 3d^{n+1}$ final states resulting from Fe $3d^n \rightarrow$ Fe $\underline{2p}\, 3d^{n+1}$ x-ray absorption transitions are marked. The $\underline{2p}$ x-ray absorption spectra were calculated by de Groot *et al.*[16] using multiplet theory with inclusion of the cubic crystal field. In this case transitions to the $4s$ states were neglected too, but the $3d$-$3d$ as well as the $2p$-$3d$ two-particle interactions were found to be of fundamental importance for the description of the $L_{2,3}$ XAS spectrum. In Fig. 2 the position of the Fe $\underline{2p}_{3/2}\, 3d^6$ and $3d^7$ final states are shown, proceeding from the $3d^5$ and $3d^6$ ground-state configurations of the Fe^{3+} and Fe^{2+} ions, respectively.

DISCUSSION AND CONCLUSIONS

In Refs. 6 and 7 the occupied valence states of α-Fe_2O_3 have been studied preferentially by x-ray photoemission, resonant ultraviolet photoemission, and constant-initial-state (CIS) spectra. Photoemission spectra reproduce the weighted mean of the local partial DOS where resonant excitation across the Fe $3p$ threshold can be used to distinguish the Fe $3d$–derived valence states from the overlapping unhybridized O $2p$ states. CIS spectra measured across the $3p$ excitation are able to identify hybridized cation-ligand states in the valence band.

Both methods provide a lot of information about the electronic valence-band structure, but they are not able to give a direct and selective picture of the local partial DOS. Therefore, in the experimental investigations of Refs. 6, 7, and 23, the question concerning the exact location of the O $2p$ region still remains, for instance.

Hence, the x-ray emission spectra (XES) can give additional information. The location of the core orbitals and the strong validity of dipole selection rules indicate the highly selective character of XES in reproducing a direct picture of the local partial DOS. Therefore, the arrangement of various kinds of XE spectra on a common binding-energy scale by means of the appropriate XPS core lines, as done in Fig. 1, allows one to analyze the character of the valence-band states more in detail. From the aligned XES in Fig. 1 and from the shape and position of the O $K\alpha$ emission in the binding-energy scale, one can see that the O $2p$ valence-band states are distributed over the whole width of the upper valence bands below the gap between 1 and 10 eV. The maximum of O $K\alpha$ at about 5 eV coincides very well with that of the VBXPS (structure A_2) and the Fe $L\alpha$ emission (D_1) indicating strongly hybridized Fe $3d$–O $2p$ states at this energy. Moreover, it can be assumed from the experimental O $K\alpha$ and Fe$L\alpha$ spectra that Fe $3d$–O $2p$ hybridization takes place over the whole valence band. Unfortunately, no interpretation can be given for the range of the Fe $L\alpha$ high-energy tail because of the spectra distortions mentioned above. There (at about 2–3 eV below the zero level) could exist nonbonding O $2p$ states only as can be concluded from the small hump in O $K\alpha$ at about 2.5 eV. The x-ray spectra also suggest that the O $2p$ DOS contributes to the VBXPS maximum A_2. This is assumed also by Fujimori *et al.* in Ref. 23, utilizing their 35-eV spectrum.

The coincidence of the Fe $K\beta_{2,5}$ (Fe $4p \rightarrow 1s$ transition) peak with the low-energy shoulder of O $K\alpha$ between 8 and 9 eV shows the Fe $4p$–O $2p$ bonding states as suggested by Fujimori *et al.*[6] The main band (A_2) and the satellite (A_1) of the VBXPS reflect the existence of the $3d^6\underline{L}$ and the $3d^5$ configuration in the ground state and are to be seen as the $d^5\underline{L}$ and the d^4 final-state configurations, respectively, for the VBXPS.

From these two configurations the Fe $L\alpha$ emission reflects mainly the $3d^6\underline{L}$ ground state, or the $3d^5\underline{L}$ final-state configuration. This suggestion appears to be in a very good agreement with CI theory as can be seen from the cluster level distribution in the lower part of Fig. 2 and from the Fe $L\alpha$ maximum D_1 as well as from the shape of the Fe $L\alpha$ spectrum in Fig. 1.

No Fe $L\alpha$ structure, however, appears at the energetic position of A_1 and therefore no contribution of the d^4 satellite seems to be present in the final-state configuration. The possible reason is the valence-state relaxation of excited x-ray states as proposed previously in Ref. 24. Then, due to the assumed two-step process where the relaxation and screening process $\underline{2p}d^5 \rightarrow \underline{2p}d^6\underline{L}$ is completed before the $\underline{2p}d^6\underline{L} \rightarrow d^5\underline{L}$ transition for the Fe $L\alpha$ emission takes place, we have the same final-state configuration as for the O $K\alpha$ spectrum where we observe only the O $\underline{1s}$ Fe $d^5 \rightarrow d^5\underline{L}$ transition.

The cluster states for the $d^5\underline{L}$ final-state configuration after the CI theory very well reproduce the features of the Fe $L\alpha$ emission as can be seen from their comparison in the lower part of Fig. 2. This behavior of the x-ray emission spectra was also found for the copper-oxide-based high-temperature superconducting compound $YBa_2Cu_3O_{7-\delta}$.[24] It seems to be characteristic of such materials where charge-transfer effects play an important role. For the first time in the Cu $K\alpha$ core line emission of CuO an anomalous narrowing of the x-ray emission lines was observed by comparing them with the corresponding very broad Cu $2p$ XPS lines.[25] The FWHM of $K\alpha_1$ which should be the sum of the FWHM of the $1s$ and $2p$ XPS core lines is much smaller than expected from this relation, whereas the sum relation holds very well for the Cu metal and also for Cu_2O. An explanation was given by calculations of Kawai *et al.*[26] who attributed these phenomena to the relaxation of the excited x-ray core-level states caused by charge-transfer effects.

A similar line narrowing was also observed for the Fe $K\alpha_1$ line of α-Fe_2O_3. In this case the FWHM of Fe $K\alpha_1$ was measured as to be about 3.7 eV. On the other hand, from our own and another measurement,[8] the FWHM of the Fe $2p_{3/2}$ XPS core line of α-Fe_2O_3 was found to be about 3.5–4 eV. Together with a semiempirical value of the Fe $1s$ FWHM of 1.25 eV,[27] the Fe $K\alpha_1$ FWHM should not be smaller than 4.75–5.25 eV opposite to the measured value of 3.7 eV.

Returning to the valence-band spectra of α-Fe_2O_3, we compare the experimental results with the MS $X\alpha$ cluster DOS calculated by using results of Ref. 5 (upper part of Fig. 2). At first we see that the calculated Fe $3d$ and Fe $4p$ DOS reproduce, the main features of the Fe $L\alpha$ and Fe $K\beta_{2,5}$ emission, respectively. The same holds for the polarization dependence of the Fe $L\alpha$ emission measured from a single-crystal sample. On the other hand, to get coincidence between theoretical and experimental peak positions of Fe $L\alpha$ and Fe $K\beta_{2,5}$, the calculated spectra must be shifted to higher binding energy by about 1.7 and 2.9 eV, respectively. Similar shifts were observed for the $YBa_2Cu_3O_{7-\delta}$ spectra in Ref. 24 where they were called "correlation shifts." Even, in the case of α-Fe_2O_3, the shifts seem to be caused by correlation and charge-transfer effects and refer to an at least partial invalidity of one-electron calculations for interpreting the high-energy spectra of systems in which correlation and charge-transfer effects play an important role.

The main features of the Fe K preedge absorption (Fe K XAS in Fig. 1) can be explained by the Fe $4p$ cluster DOS. These p-like states of the iron atoms arise from the noncentrosymmetric ligand field of the oxygen atoms and are admixed to the dominating Fe $3d$ states in the lowest part of the conduction band. The coincidence of the Fe $4p$- and $3d$-like states can be seen from the position of the experimental Fe K, Fe L_3, and Fe $M_{2,3}$ XAS on the common binding-energy scale in Fig. 1. Moreover, the existence of unoccupied $3d$-like states at that energy could also be proved directly by the appearance of $1s \rightarrow 3d$ quadrupole transitions in the K XAS.[12]

The polarization dependence of the so-called preedge Fe K absorption results from an anisotropic admixture of the p_z- and $p_{x,y}$-like states to the $3d$ states.[12] This experimental finding is well reproduced by the corresponding Fe $4p_z$- and Fe $4p_{x,y}$-like cluster DOS.

The difference of about 3.5 eV in the position of the experimental and calculated Fe K XAS comes beside other things from the effect of the screening of the $1s$ core hole. One should notice also an anisotropic shift of the Fe K main absorption edge $[E_K(\mathbf{e}\|c)-E_K(\mathbf{e}\perp c)\approx -0.7 \text{ eV}]$. In general, for iron compounds this edge shifts towards higher energy with increasing oxidation state of the iron atom. Therefore, the conclusion can formally be drawn that the oxidation state of the iron atom in α-Fe_2O_3 is lower in the direction parallel to the c axis than perpendicular to it according to the experimental Fe K-edge shift.

In the middle and lower part of the right-hand side of Fig. 2, the position of the Fe L_3 XAS peak D_2 is compared with the energy of the transitions Fe $3d^n \rightarrow$ Fe $\underline{2p}$ $3d^{n+1}$ after the calculations of de Groot *et al.*[16] The best energetic coincidence has been found for $n=6$ according to a ground-state configuration $3d^6$ of an Fe^{2+} ion and not for the $3d^5$ (Fe^{3+}) as one would expect for α-Fe_2O_3. The same holds for the shape of the absorption structure, where the best agreement has been observed for the $3d^6$ ground-state configuration with cubic crystal-field parameters $10\,Dq=1.5$ eV (see Figs. 11 and 12 of Ref. 16).

This shows that crystal field, hybridization, and charge transfer will influence very strongly the electronic structure of α-Fe_2O_3. Especially, it means that besides the $3d^5$ configuration (formally a Fe^{3+} ion state) the $3d^6\underline{L}$

configuration (according formally to a Fe^{2+} ion state), too, will take an important part of the ground state in this compound.

The peak D_2 of the Fe L_3 XAS coincides very well with peak C_1 of the Fe $M_{2,3}$ XAS (Fig. 1). According to Ref. 7 this structure can be attributed to the ^6D state of the $3p^5 3d^6$ final configuration, whereas the C_2 structure of the $M_{2,3}$ XAS is associated with the ^6P multiplet. The difference between the $M_{2,3}$ and L_3 spectra is, to a considerable extent, the result of the change of the coupling from the *LS* to the *jj* type if one goes from shallow to deeper core holes.[15]

The position of the oxygen 1*s* x-ray absorption edge (O *K* XAS in Fig. 1) on the binding-energy scale and its appropriate alignment with the Fe L_3 and Fe $M_{2,3}$ spectra support the interpretation of de Groot *et al.*[14] that the double-peaked structures B_2 and B_3 near threshold can be related to O 2*p* character hybridized with the sharp structured Fe 3*d* states. From the coincidence of the B_2 structure in the O *K* XAS with the E_3 structure of the Fe *K* XAS, one can deduce also some O 2*p*–Fe 4*p* mixing in that region and complete the conclusions which were drawn above in connection with the discussion of the preedge Fe *K* absorption.

The rise of the O *K* absorption to higher binding energy and a broader structure between 4 and 15 eV (outside of Fig. 1) coincides very well with the onset of the Fe *K* main absorption edge, i.e., with the appearance of strong Fe 4*p* character. This also confirms the assignment of the broader structure to O 2*p*–Fe 4*sp* mixed states in this part of the conduction band.[14]

As a general conclusion we have shown the fundamental and powerful capability of x-ray spectroscopy in giving additional information for deciding on special problems of the electronic structure of matter. The investigation of α-Fe_2O_3 clearly demonstrates that, in spite of its comparatively low-energy resolution, x-ray spectroscopy exhibits several advantages over other methods of high-energy spectroscopy in identifying the orbital character of electronic states. The experimental findings with respect to the symmetry of states and their discussion on the basis of theoretical results support the suggestion that α-Fe_2O_3 is rather a charge-transfer- than a Mott-Hubbard-type insulator.

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