High-resolution EELS investigation of the electronic structure of ilmenites

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The electronic structure of a series of compounds belonging to the ilmenite family is investigated using high resolution electron energy loss spectroscopy (EELS). The energy loss near edge structure (ELNES) of the O-K, Ti-L23, and transition metal L23 edges have been recorded in MnTiO3, FeTiO3, CoTiO3, and NiTiO3 with an energy resolution of 0.20–0.25 eV. The formal valency and spin-state of the transition metal are determined unambiguously from the analysis of the L23 edges with theoretical ligand field multiplet calculations. The results confirm the evolution of the interatomic distances observed along this series. The O-K edge is analyzed by comparison to the experimental signatures observed in the structurally related Ti2O3 compound and using theoretical molecular orbital results.

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I. INTRODUCTION

The ternary oxides of chemical formula MTiO3 with M=Mn, Fe, Co, and Ni form a series of compounds with similar crystallographic structure and magnetic properties.1–11 At room temperature and under normal pressure, they adopt an ordered corundum structure1–4 of space group R̅̅̅3, the ilmenite structure, in which M2+ and Ti4+ form alternating layers along the rhombohedral axis of the crystal, with oxygen layers between them. This structure, displayed in Fig. 1, can be alternatively described in terms of octahedra arrangement. Each cation octahedron shares three edges with the same cation octahedra inside the layer, a face with an octahedron of the second type of cation in the adjacent layer and the opposite face with an empty octahedral site. In such a structure, Ti and M atoms are forming pairs separated by a vacant site along the rhombohedral axis. As a consequence, a metal-metal interaction is allowed between the d orbitals (of t2g symmetry) extending their lobes through the face shared by the two octahedra. A number of interesting properties observed in the compounds adopting the corundum structure are directly related to this metal-metal interaction.12 For example, the temperature induced metal-insulator transition of Ti2O3 has been first explained by Van Zandt, Honig, and Goodenough13 through a theory based on a molecular orbital description of the Ti3+/Ti4+ interaction. Similarly, the Fe3+/Ti4+→Fe3+/Ti3+ intervalent charge transfer in natural FeTiO3 is also explained by an enhanced atomic orbital overlap between Ti and Fe under pressure.14–16 This charge transfer, also named hopping small polaron, is considered as the dominant conduction mechanism in FeTiO3. The understanding of the electronic structure of these compounds thus appears as a key parameter to explain their electrical properties.

Although the structural and magnetic properties of ilmenites have been widely investigated, only little information on their electronic structure is available. From a theoretical point of view, the complex crystallographic structure and magnetic order observed in these compounds as well as the difficulty to account correctly for electron correlations17 in these systems partly explain this scarcity of published results. Experimentally, x-ray absorption spectra acquired in natural ilmenite18 or synthetic crystals19 on the M-L23 and Ti-L23 edges can be found in the literature. However, no systematic or detailed analysis of the near edge fine structures and thus of the electronic structure are presented. In addition, the presence of hematite (Fe2O3) in ilmenite samples has led to the recording of “artificially” mixed valence signatures.18–20 This is an important issue, for example in the context of the determination of the formal valencies in FeTiO3 as the presence of Fe3+ has been previously debated.21,22 In this paper, we therefore present a study of the electronic structure of ilmenites through the analysis of the M-L23, Ti-L23 and O-K edges recorded in MnTiO3, FeTiO3, CoTiO3, and NiTiO3. The use of monochromated electron energy loss spectroscopy in a transmission electron microscope is of key importance in this work since this technique combines the advantage of an excellent spatial (few tens of nanometers) and energy (0.2 eV) resolutions and is essentially bulk sensitive. Artifacts due to surface effects or inh-

FIG. 1. Crystal structure of ilmenites showing the MO6 (light grey) and TiO6 (dark grey) octahedra. The ilmenite structure is an ordered corundum structure with alternating M and Ti along the rhombohedral axis.
mogeneous samples can thus be easily avoided as samples can be characterized in situ during the experiments. In order to investigate the electronic structure, we first assessed the formal coordination, valency, and spin state of the transition metal atoms in the series. From the comparison between experimental and theoretical L\(_{23}\) edges, modeled using ligand-field multiplet calculations,\(^\text{23,24}\) we established unambiguously the presence of tetravalent Ti and divalent transition metal in the high-spin state along the series and confirmed in particular the Fe\(^{2+}\) formal valency in FeTiO\(_3\). These results are consistent with the monotonic decrease of the M-O interatomic distance observed experimentally in these compounds when increasing the atomic number of the transition metal. In addition, the fine structure of the O-K edge, providing information on the unoccupied states at the oxygen site, has been discussed by comparison to the simpler and structurally related Ti\(_2\)O\(_3\), for which band structure calculations are available in the literature. The analysis of this edge along the series led to a precise assignment of the energy levels in the conduction band. In particular, the pre-edge structure observed in the O-K edge of MnTiO\(_3\) is directly related to the 3\(d\) states of manganese.

II. EXPERIMENTS

The experimental spectra have been recorded on a FEI Tecnai 200 FEG microscope equipped with a monochromator and a high-resolution energy loss spectrometer. This system enables the recording of EELS spectra with an energy resolution of 0.10–0.20 eV (measured at full width at half-maximum (FWHM) of the zero loss peak), as described elsewhere.\(^\text{25}\) In these experiments, the probe size was a few tens of nm and the energy resolution was about 0.20–0.25 eV. The spectra were acquired in diffraction mode with a large collection angle (>10 mrad) and a dispersion of 0.05 eV/channel. For each edge shown hereafter, a series of spectra recorded with relatively short acquisition times (between 5 and 30 s) were added yielding a total acquisition time varying between 50 and 300 s. The background, modeled with a power law, was fitted on the pre-edge region, extrapolated and finally extracted from the edge using standard power law procedures. We ensured that the samples were thin enough to consider multiple inelastic scattering contributions as negligible. The TEM samples were prepared by crushing commercial powders\(^\text{26,27}\) of MnTiO\(_3\), FeTiO\(_3\), and CoTiO\(_3\) pure at 99.9% and NiTiO\(_3\) pure at 99.5% in ethanol and by dispersing the suspensions on a holey carbon-covered Cu grid. During the EELS measurements, special care has been taken to record the spectra on particles characteristics of the compound under investigation as impurities are readily identifiable by the edges in the energy loss spectrum or by dispersive x-ray microanalysis.

III. RESULTS

A. Ti-L\(_{23}\) edge

The Ti-L\(_{23}\) edges recorded in the four compounds of the series are compared with a ligand-field multiplet calculation for Ti\(^{4+}\) in octahedral symmetry in Fig. 2. The four main lines dominating the multiplet structure and arising from the \(2p^6 3d^0 \rightarrow 2p^5 3d^1\) electronic transition for a tetravalent Ti ion in octahedral site can be simply interpreted in a one electron picture. The core-hole spin-orbit coupling gives rise to two main lines, the \(L_3\) and \(L_2\) edges, further split under the effect of the octahedral crystal field on the 3\(d\) states. The parameters used in the calculation are the same as those used in Ref. 28 to calculate the Ti-L\(_{23}\) in FeTiO\(_3\). Except for small intensity variations, visible on the first prominent peak (at 458 eV), the experimental spectra are very similar and characteristic of Ti\(^{4+}\) in an octahedral symmetry. The excellent agreement obtained with this calculation leads to the conclusion that no effect of the trigonal (\(D_3d\)) distortion can be detected in the fine structure of this edge. The lack of sensitivity of the spectral shape to the trigonal distortion of the oxygen octahedron is indeed predicted theoretically when the lower symmetry of the atomic site is explicitly taken into account in the ligand-field multiplet calculation, as shown by De Groot et al. in Ref. 29. The Ti-L\(_{23}\) edge recorded in Ti\(_2\)O\(_3\) is given in the same figure to underline the clear experimental evidence for the Ti formal valency change in ilmenites. The energy positions and the relative intensities of the different peaks being similar in the four compounds, the same value of the crystal field parameter 10 \(D_q\) (1.80 eV) is needed to reproduce the experimental spectra. We can therefore conclude that the local environment around the Ti atoms is identical along the series, in terms of both symmetry and metal-ligand interaction.

FIG. 2. Comparison between experimental Ti-L\(_{23}\) edge recorded in MnTiO\(_3\), FeTiO\(_3\), CoTiO\(_3\), NiTiO\(_3\) (circles) and the ligand field multiplet calculation for Ti\(^{4+}\) in octahedral crystal field (solid line). The reference spectrum of Ti\(^{3+}\)-L\(_{23}\) edge recorded in Ti\(_2\)O\(_3\) is also given at the top of the figure.
In this section, the experimental L23 edges of the $M^{2+}$ ions are presented successively and compared to theoretical ligand-field multiplet calculations in Figs. 3–6. As in the case of the Ti-L23 edge, the crystal field has been approximated using the perfect cubic symmetry ($O_h$ point group) since all the fine structures observed within our experimental resolution are well reproduced and the agreement between experimental and theoretical spectra is not substantially improved by the introduction of a trigonal distortion ($D_{3d}$). The free ion values for the Slater integrals describing $p$-$d$ and $d$-$d$ Coulomb and exchange interactions have been used. A Gaussian broadening of 0.2 eV was applied to correct the spectra for the instrumental resolution. Additional Lorentzian broadenings of 0.1–0.2 eV for L3 and 0.3–0.4 eV for L2 edges were applied to account for the finite lifetime of the final state, this difference being essentially due to the additional Coster-Kronig decay channel for the L2 edge.

The first spectrum of this series is the Mn-L23 edge recorded in MnTiO$_3$ (Fig. 3). The experimental spectrum is in excellent agreement with theoretical spectrum calculated for Mn$^{2+}$ with a relatively low value of the crystal field parameter (10 $D_q$=0.75 eV). In a weak field of octahedral symmetry, the $6S$ atomic ground state of Mn$^{2+}$ does not split and is only projected into the $6A_1$ cubic symmetry, corresponding to the high-spin configuration. Because its ground state corresponds to the fully symmetric irreducible representation, the spectral shape of high-spin Mn$^{2+}$ is not sensitive to symmetry distortions and 3$d$ spin-orbit coupling.

The Fe-L23 edge recorded in FeTiO$_3$ is compared with theoretical spectra calculated for Fe$^{2+}$ in octahedral field (10 $D_q$=0.75 eV) in Fig. 4. Here again, the best agreement is achieved for the high-spin ground state of $5T_2$ symmetry. The $T$ symmetry is particularly sensitive to the 3$d$ spin-orbit coupling. Its main effect is to lift the degeneracy of the ground state and split it further in states separated by energies of order of few kT. It is thus important to take the contributions of the thermally populated excited states into account when calculating the spectrum at room temperature. Here, the spectrum including the 3$d$ spin-orbit coupling (Fig. 4(a)) is compared to the one calculated with the 3$d$ spin-orbit coupling set to zero (Fig. 4(b)). If the shape of the L3 edge is not dramatically affected by this parameter change, the agreement between theoretical and experimental L2 edges is clearly improved. The peaks at 719 and 721 eV, absent in spectrum (a) appear under these conditions and are thus explained by a quenching of the 3$d$ spin-orbit coupling at room temperature. This quenching has been observed recently for the same ion in Fe$_2$SiO$_4$ in Ref. 32 and may be attributed to...
dispersion effects or distortion of the cubic symmetry. The good agreement obtained between the experimental and the theoretical spectra confirms clearly the presence of a high-spin Fe$^{2+}$ in FeTiO$_3$, coherent with the presence of tetravalent Ti discussed in the preceding section. This unambiguous result contrasts with the mixed valence signatures presented previously.$^{18,19}$

The Co-L$_{23}$ edge recorded in CoTiO$_3$ is in good agreement with the theoretical spectrum calculated for high-spin Co$^{2+}$ in octahedral field with 10 D$q=0.9$ eV. These structures are therefore very similar to those observed in CoO and discussed in details in Ref. 33. As in the previous case of Fe$^{2+}$, its 4$^3T_1$ symmetry is sensitive to the 3d spin-orbit coupling but the situation is however very different in this case. Spectrum (a) is calculated with the 3d spin-orbit coupling set to zero. Spectrum (b) corresponds to a calculation including the 3d spin-orbit coupling at 300 K. Contrary to the case of Fe$^{2+}$, the 3d spin-orbit coupling clearly improves the agreement with the observed spectral shape in CoTiO$_3$.

At the end of this series, the Ni-L$_{23}$ edge recorded in NiTiO$_3$ is displayed in Fig. 6. The fine structure observed in this compound is characteristic of the high-spin Ni$^{2+}$ with the corresponding 3$^3A_2$ symmetry.$^{34,35}$ The theoretical spectrum displayed in the same figure confirms this conclusion. The doublet structure observed at both L$_1$ and L$_2$ edges are well reproduced using a crystal field parameter 10 D$q$ of 0.9 eV.

A number of interesting conclusions can be drawn from the analysis of these edges. First of all, we clearly established that Mn, Fe, Co, and Ni are all divalent in this series of compounds, consistent with the tetravalent signature observed in the Ti-L$_{23}$ edge. Second, under the influence of the crystal field, approximated in the calculations by a perfect cubic symmetry, they all adopt the high-spin configuration originating from Hund’s rule ground state. In terms of occupation number of the crystal field orbitals, this implies that when increasing the atomic number from Mn to Ni, the $t_{2g}$ orbitals are progressively filled from 3 to 6 electrons while the occupation of $e_g$ orbitals remains constant. We finally demonstrated that the Fe-L$_{23}$ edge can only be explained by a quenching of the 3d spin-orbit coupling in contrast with the Co-L$_{23}$ where its effect is clearly visible.

C. O-K edge

The O-K edge recorded in the different compounds of the series are given in Fig. 7 and compared with the reference spectrum of Ti$_2$O$_3$. In contrast to transition metal L$_{23}$ edges, the multiplets effects are not visible on K edges$^{24}$ and their spectral features are usually well explained using single-particle models.$^{36}$ Owing to the dipole selection rules and the $s$ ($l=0$) symmetry of the initial state, the O-K edge can be understood in first approximation (by neglecting the weak energy dependence of the dipole matrix element) as proportional to the O-p ($l=1$) projected density of states. The spectral shape in MnTiO$_3$, FeTiO$_3$, CoTiO$_3$, and NiTiO$_3$ show very strong similarities and can be divided in two main energy regions. The first one, between 530 and 535 eV, is dominated by two strong peaks labeled (A) and (B) separated by 2.5 eV. In Ti$_2$O$_3$, this double structure is already present but the splitting is reduced to 2.25 eV. The second part extends over 10 eV, from 536 to about 546 eV and is constituted by three broad structures labeled (C), (D), and (E) on the figure at 538, 541.5, and 544 eV, respectively. These features are present at the same energies in Ti$_2$O$_3$. Only minor differences in the relative intensities and widths of peaks (A) and (B) occur along the series except in the case of MnTiO$_3$ where a low intensity shoulder is clearly visible at 529 eV, just below the edge onset.

This general shape is characteristic of the O-K edge of transition metal oxides.$^{37}$ The first part of the spectrum corresponds to the energy region of the narrow transition metal 3d bands. The 4$sp$ states are found at higher energies and can be assigned to the broad energy band located between 536 and 546 eV. In the different polotypes of TiO$_2$, these structures are very sensitive to the crystallographic structure and constitute an excellent fingerprint used to differentiate the rutile, brookite or anatase structure.$^{38,39}$ In our case, the invariance of the experimental features in this energy range is coherent with the fact that they all share the same corundum structure.

IV. DISCUSSION

A. Relation with the interatomic distances

As mentioned in the preceding section, the L$_{23}$ edges can be used as a direct probe of the formal valency and the spin state of the transition metal atoms. The analysis of the experimental results indicates the presence of M$^{3+}$/Ti$^{4+}$ pairs in these compounds and clearly excludes, for example, the possibility of Fe$^{3+}$/Ti$^{3+}$ in FeTiO$_3$. In addition, the relatively low value of the crystal field leads to a systematic stabiliza-
FIG. 8. Comparison between the interatomic distances for M-O and Ti-O bonds predicted from ionic radii tables (solid line) and from the experimental data (dashed line) for MnTiO3, FeTiO3, CoTiO3, NiTiO3, and for Ti2O3. The electronic configuration of the ions is represented schematically in each case.

tion of the high-spin configuration for $M^{2+}$. At this point of our analysis, it is very interesting to correlate these results with the structural properties of these compounds. As mentioned in the introduction, they adopt the same corundum crystal structure. The variation of the lattice parameters along the series is directly related to the variation of the $M$-O interatomic distance when changing the transition metal. The averaged experimental $M$-O and Ti-O distances extracted from Refs. 2–4 are displayed in Fig. 8. Although the Ti-O distance remains constant along the series, a trend of the average $M$-O bond length to decrease with the increasing atomic number of the transition metal is clearly observed. This variation reflects the contraction of the atomic 3$d$ orbitals due to the partial shielding of the extra nuclear charge by the extra electron for the divalent transition metals. This contraction of the $M$-O distance is further enhanced by the fact that, in the high-spin configuration, the extra d electrons are progressively filling the $t_{2g}$ orbitals and thus leads to an increase of the crystal field energy stabilization when moving from Mn to Ni. With this precise knowledge of the coordination number, the formal valency and the spin-state of the transition metal determined from the spectra, as well as the coordination number of the O$^{2-}$ atom, we calculated the mean interatomic $M$-O and Ti-O distances in this series of compounds using the ionic radii tabulated by Shannon and Prewitt.40 These interatomic distances in ilmenites are displayed in Fig. 8 along with the Ti-O distance41 in Ti2O3. The excellent agreement obtained with the experimental data (within 1%) cannot be reached using a different spin state or a different formal valency and demonstrates the consistency of our conclusions on the electronic structure of the transition metal atoms with the structural parameters of these compounds. The constant length of the Ti-O bond in these compounds is also coherent with the constant $t_{2g}-e_g$ splittings observed in the Ti-L3 (2.25 eV), L3 (2.25 eV), and O-K (2.5 eV) edges along the series. This point will be discussed in detail later in this section.

B. The unoccupied states of Ti2O3

We can now turn to the discussion of the experimental results on the O-K edge starting with the simpler case of Ti2O3 for which a number of theoretical investigations are available.13,42,43 An early molecular orbital description of the electronic structure of Ti2O3 has been given by Van Zandt, Honig, and Goodenough13 to explain the temperature-induced metal-insulator transition observed in this compound and is summarized in Fig. 9. The coordination octahedron of oxygen surrounding the Ti ions splits the 3$d$ states in two sets of orbitals of $t_{2g}$ and $e_g$ symmetries, extending their lobes, respectively, between and towards the ligand atoms. Due to a small trigonal distorsion, the $t_{2g}$ states are further split into low lying $a_{1g}$ and $e_g^*$ levels. As the $a_{1g}$ orbitals (or $d_{z^2}$ orbitals) are oriented along the rhombohedral axis, i.e., through the face shared by two Ti coordination octahedra, a direct $dd\sigma$ interaction between the metal atoms is expected to occur. The hybridization between the two $a_{1g}$ orbitals of neighboring Ti atoms is strong enough to form bonding $a_{1g}$ and antibonding $a_{1g}^*$ molecular orbitals. The remaining $e_g$ orbitals are pointing in the direction of the three Ti neighbors within the layer. The interaction is much weaker in this case and does not create a separate $e_g^*$ band. These states are thus contained between $a_{1g}$ bonding and antibonding bands. These $t_{2g}$ orbitals only experience a weak $\pi$ hybridization with the oxygen $2p$ orbitals. The remaining $e_g$ orbitals interact strongly with the oxygen and contribute mainly to a $\sigma^*$ band at higher energy. In this schematic picture, the Fermi level falls between the $a_{1g}$ and $e_g^*$ bands corresponding to the filling of the two doubly degenerated $a_{1g}$ bands in the solid state (the rhombohedral unit cell contains two Ti2O3 molecular units) or to one electron per Ti atom. The energy separation between these states was originally used to explain the low temperature semiconducing nature of Ti2O3. However, LDA calculations showed that such a gap does not occur using the actual Ti2O3 lattice parameters and pointed out the importance of electron correlation effects.42,43 In this band picture, structures (A) and (B) observed near the O-K edge onset in Ti2O3 can be simply attributed to the $e_g^*$ and $e_g$ bands, respectively. The difference in the energy width between these two peaks [1.1 eV for (A) and 2.2 eV for (B) measured in our spectra as the full width at half-maximum of the peaks] is directly related to the weaker Ti-O $pd\pi$ inter-
action for the first case compared to the stronger pdσ interaction in the latter case. The smaller splitting between peaks (A) and (B) found in this compound with respect to solids containing tetravalent Ti in Ti2O3. If the a1g band is clearly identified just below the Fermi level in photoemission spectra, its antibonding counterpart a1g* band is not resolved in the O-K edge, first because of its dominant metal 3d character and second because of the proximity of the strong signal coming from the neighboring peaks (A) and (B). We can now consider the O-K edge in ilmenites for which the same corundum structure is observed, but this time with alternating M and Ti planes, i.e., with M2+/Ti3+ instead of Ti3+/Ti4+ pairs along the rhombohedral axis.

C. The unoccupied states of ilmenites

As mentioned earlier, the high-lying structures of the O-K edge in ilmenites are similar to those observed in Ti2O3 and are associated with M and Ti 4sp bands. The main spectral differences observed with respect to Ti2O3 are found in the first 5 eV after the edge onset: (1) the (A)-(B) splitting is slightly increased from 2.25 in Ti2O3 to 2.50 eV in ilmenites and remains constant in the series; (2) changes are observed in the energy width and intensity of peak (A); (3) in MnTiO3, a pre-edge shoulder of low intensity (indicated by the arrow in Fig. 7) is visible at 529 eV. We will discuss these three points starting with the results of Sherman’s molecular orbital calculations. These calculations have been performed in a (FeTiO10)14+ cluster constituted by edge shared FeO6 and TiO6 octahedra. This geometry is not the same as in the corundum structure where the octahedra share a face but the results of these calculations give a strong insight into the electronic structure of ilmenites and can be used as a useful guideline to interpret the experimental spectra. The resulting electronic structure, given in Fig. 10, is basically the superposition of the electronic states of (FeO6)10− and (TiO6)8− clusters. The valence band is dominated by the O-2p states separated by approximately 4 eV from the empty Ti 3d states. These states are split by about 2.5 eV in low-lying t2g states and higher eg orbitals by the octahedral ligand field. The Fe α-spin states are found in the upper part of the valence band and are split from the β-spin states by the intra-atomic exchange energy. These latter states fall just in the energy region of the Ti t2g states. As the exchange energy is larger than the ligand field splitting, the Fe2+ ion adopts a high-spin configuration, the highest occupied molecular orbital being the lowest of the β-spin t2g orbitals. This overall picture is in qualitative agreement with the recent ab initio calculations performed on FeTiO3 by Wilson et al. in Ref. 17.

It is now possible to interpret the constant (A)-(B) splitting observed along the series: peak (A) corresponds to the energy range containing Ti t2g and transition metal β-spin t2g and eg states whereas peak (B) is essentially associated with Ti eg states. In first approximation, the (A)-(B) splitting thus reflects mostly the Ti t2g – eg splitting. Its amplitude is indeed coherent with the splitting observed in the O-K edge of other compounds containing tetravalent titanium. This splitting is 2.6 eV in rutile and anatase where the Ti-O distance are, respectively, 1.959 and 1.960 Å (Ref. 46) and 2.8 eV in SrTiO3 where the Ti-O distance is 1.953 Å. The presence of the transition metal β-spin d states in the same energy range as the Ti t2g states also explains the variations observed in the energy width and the intensity of peak (A).

In order to understand the origin of the pre-edge feature only observed in the case MnTiO3, we first need to determine the relative energy position of the Ti and M unoccupied 3d states. This energy difference can be obtained in first approximation by a comparison of the absolute energy of the O-K edge recorded in monoxides (MnO, FeO, CoO, and NiO) and in TiO2. Measurements of the energy position of the first prominent peak of the O-K edge calibrated in x-ray absorption37,47 indicate that pre-edge features are to be expected only in MnTiO3 and FeTiO3. Indeed, the edge onset in CoO and NiO falls at higher energies than in TiO2 whereas it falls at 1.1 and 0.9 eV below the edge onset of TiO2 for MnO and FeO, respectively. This prediction is in good agreement with the experimental O-K edge recorded in MnTiO3 where the pre-edge feature is observed at around 1.5 eV below the main feature (A). This shoulder can thus be directly attributed to the 3d states of manganese, hybridized with oxygen 2p states. Surprisingly, this feature is not observed in FeTiO3. The absence of this shoulder in the experimental spectrum can be explained by the very low intensity of these transitions with respect to the strong features related to transitions to the Ti 3d states. This effect is already visible in the case of MnTiO3 where the pre-edge intensity is only 20% of the intensity of peaks (A) and (B). In addition, the O-K edge recorded in FeO in energy loss48 or x-ray absorption49 spectroscopies already show a low intensity of these 3d features with respect to the higher lying 4sp structures.

V. CONCLUSION

The electronic structure of four compounds belonging to the ilmenite family has been studied using high energy resolution EEL spectroscopy. The combination of the excellent energy resolution obtained for the L23 edges and the use of theoretical multiplet calculations allowed a direct and unam-

FIG. 10. Simplified energy diagram of FeTiO3 based on Sherman’s molecular orbital calculations (Ref. 16) performed in a (FeTiO10)14+ cluster.
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