

Soft x-ray absorption spectra of ilmenite family

Akane Agui^{a*}, Masaichiro Mizumaki^b, Yuji Saitoh^a, Tomohiro Matsushita^b, Takashi Nakatani^b, Atsuko Fukaya^c and Eiko Torikai^d

^aSynchrotron Radiation Research Center, Japan Atomic Energy Research Institute, 1-1-1 Kouto, Mikazuki, Sayo, Hyogo 679-5148, Japan

^bJapan Synchrotron Radiation Research Institute, 1-1-1 Kouto, Mikazuki, Sayo, Hyogo 679-5198, Japan

^cRIKEN, 2-1, Hirosawa, Wako, Saitama, 351-0198, Japan

^dFaculty of Engineering, Yamanashi University, 4-4-37, Takeda Kofu, Yamanashi, 400-8510, Japan
E-mail: agui@spring8.or.jp

We have carried out soft x-ray absorption spectroscopy to study the electronic structure of ilmenite family, such as $MnTiO_3$, $FeTiO_3$, and $CoTiO_3$ at the soft x-ray beamline, BL23SU, at the SPring-8. The Ti and M $L_{2,3}$ absorption spectra of $MTiO_3$ ($M=Mn$, Fe , and Co) show spectra of Ti^{4+} and M^{2+} electron configurations, respectively. Except the Fe $L_{2,3}$ spectrum, those spectra were understood within the O_h symmetry around the transition metal ions. The Fe L_3 -edge spectrum clearly shows a doublet peak at the L_3 edge, which is attributed to Fe^{3+} state, moreover the very high-resolution the L -edge spectra of transition metals show fine structures. The spectra of those ilmenites are compared.

Key words: soft x-ray, absorption, ilmenite

1. Introduction

A series of ternary oxides $MTiO_3$ ($M=Mn$, Fe , Co , and Ni) has the ilmenite structure. This is an ordered corundum structure in which ions of M and Ti occupy the basal cation planes alternatively in which M is divalent and Ti is tetravalent. Figure

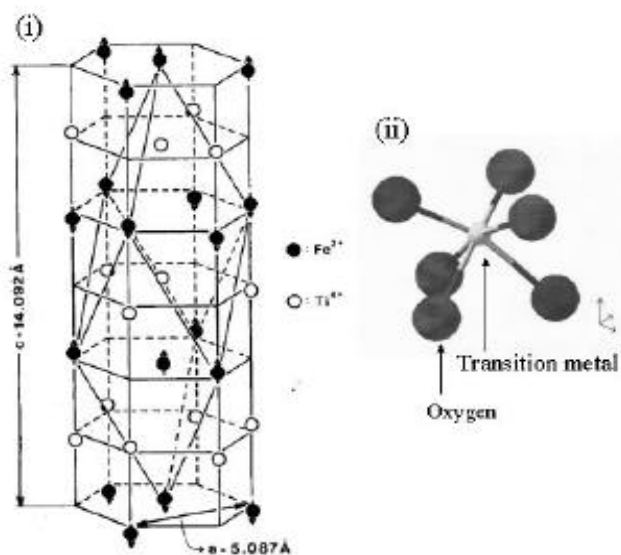


Figure 1

(i) Crystal and magnetic structure of $FeTiO_3$, in which oxygen ions are omitted (Kato *et al.* 1982). (ii) Local surroundings around transition metal.

1 (i) shows the crystal and magnetic structure of $FeTiO_3$, in which oxygen ions are omitted. Arrows denote the magnetic moment directions of Fe^{2+} ions. The ilmenites are antiferromagnets below Neel temperature. M^{2+} magnetic moments are ferromagnetically coupled within a c -plane and are antiparallel between adjacent c -planes in $FeTiO_3$ and $CoTiO_3$. On the other hand, the magnetic moments are antiparallel within a c -plane in $MnTiO_3$. The moment direction is perpendicular to the layer plane, *i.e.*, along the c -axis ($c=14.283$ Å ($MnTiO_3$), 14.073 Å ($FeTiO_3$), and 13.920 Å ($CoTiO_3$)) (Syono *et al.*, 1979; Ishikawa *et al.*, 1957; Newnham *et al.*, 1964; Newnham *et al.*, 1963).

In many cases, the M ion in an ionic crystal has a degenerate ground state when it is surrounded by anions octahedrally with trigonal distortion. In this case, the orbital angular momentum is not quenched. Consequently, the spin magnetic moment is tightly bound to the trigonal axis *via* spin-orbit coupling. Many authors have investigated magnetic properties of ilmenites (Kato *et al.*, 1982), however, basic information of electronic states is very few.

As a result of experimental progress in the field of synchrotron radiation in the last decade, the energy resolution power ($E/\Delta E$) of soft x-ray absorption spectroscopy has reached up to 10000. For the $L_{2,3}$ x-ray absorption, the dipole-allowed transitions are mainly $2p \rightarrow 3d$. In this paper, the high-energy resolution $L_{2,3}$ soft x-ray absorption spectra of ilmenite family, such as $MnTiO_3$, $FeTiO_3$, and $CoTiO_3$, are presented to study the electronic state of the $3d$ conduction band.

Using the group-theory formalism, it is possible to project the atomic spectrum (spherical symmetry) onto a specific symmetry. Local symmetry around transition metal ions (both M and Ti) of $MTiO_3$ can be treated within O_h symmetry with a simplification. It accounts for both six fold (octahedral) and eightfold (simple-cubic) surroundings and considered with distorted crystal-field. Figure 1 (ii) shows local surroundings around transition metal ions, which is in the distorted O_h symmetry.

2. Experimental

The absorption measurements were carried out at the variable polarizing undulator beamline BL23SU at SPring-8. This is Japan Atomic Energy Research Institute beamline, for soft x-ray spectroscopy studies in a wide variety of applications (Yokoya *et al.*, 1998; Nakatani *et al.*, 1998). A double-array variable undulator of APPL-2 (advanced planar polarized light emitter) type (Sasaki *et al.*, 1994) had been installed as a light source in the storage ring at BL23IN. It provides a lineally-, an elliptically-, and a circularly- polarized radiation. For instance, a magnetic circular dichroism measurement system is being developed by our group.

BL23SU has a varied line-spacing plane grating monochromator and post-focusing mirrors (Saitoh *et al.*, 2000). The monochromator covers the energy region from 0.5 to 2 keV (Yoshigoe *et al.*, 2000). The $E/\Delta E$ of the monochromator was estimated over 7000 during the measurements. The photon flux is expected to be greater than 10^{11} photons/sec on a few-square-millimeter sample in an experimental station. For the present measurements the 600 l/mm groove-density grating was used. The drain current of post-focusing mirror was recorded as an incident photon intensity monitor.

Single crystals of $MTiO_3$ were grown by means of a floating-zone method. These single crystals were powdered and pasted on a sample holder using conductive carbon tapes. The absorption spectra were recorded at room temperature in the total electron yield mode. Circularly polarized soft x-rays were used for the absorption measurements. The photon energy scale of spectra was calibrated by referring the nickel and titanium $L_{2,3}$

absorption spectra of NiO and TiO₂.

3. Results and Discussion

Figure 2 shows the Ti $L_{2,3}$ absorption spectra of MnTiO₃, FeTiO₃, and CoTiO₃. The Ti $L_{2,3}$ absorption spectrum of FeTiO₃ has been reported by several groups (de Groot *et al.* 1990; Droubay *et al.* 1997; Butorin *et al.* 1997). The Ti $L_{2,3}$ spectrum of FeTiO₃ is only consistent with Ti⁴⁺, not with Ti³⁺ (Goodenough, 1972). Within ligand-field model, the main four peaks of the Ti $L_{2,3}$ absorption spectrum are ascribed to the $2p^63d^0 \rightarrow 2p^53d^1$ transitions of Ti⁴⁺ ion to the states of t_{2g} (peaks A and C) and e_g (peaks B and D) symmetry (de Groot *et al.*, 1990), regardless of the distortion of the octahedral crystal-field symmetry in FeTiO₃ (see Fig. 1 (ii)). The weak high-energy satellites (humps E and F) are assigned to the charge-transfer satellites, which are anti-bonding combinations between $2p^53d^1$ and $2p^53d^2L^{-1}$ (L^{-1} stands for a hole in the ligand $2p$ band) configurations (Okada *et al.*, 1995).

The Ti $L_{2,3}$ absorption spectrum of MnTiO₃ and CoTiO₃ are compared with that of FeTiO₃. Not only the main peaks of A, B, C, and D, but also the satellites E and F are essentially attributed to the same origin with those of FeTiO₃. That means the valency of Ti remains quaternary even though changes atomic number of M . That the peak energies shift to lower energy and the peaks broaden with increasing atomic number of transition metal (M). It is known that a small ion radius of transition metal (M) makes the final state broadening to be larger. As increasing atomic number of transition metal (M), the ion radii become small. That causes the $M3d-O2p$ hybridization to be small and the $Ti3d-O2p$ hybridization to be large. Thus this makes the broadening trend for the Ti $L_{2,3}$ spectra of $MTiO_3$ to be $CoTiO_3 > FeTiO_3 > MnTiO_3$.

Leaving the Ti $L_{2,3}$ spectra, we turn to the $M L_{2,3}$ spectra. Figure 3 shows the Mn $L_{2,3}$ spectrum of MnTiO₃ and its detail at

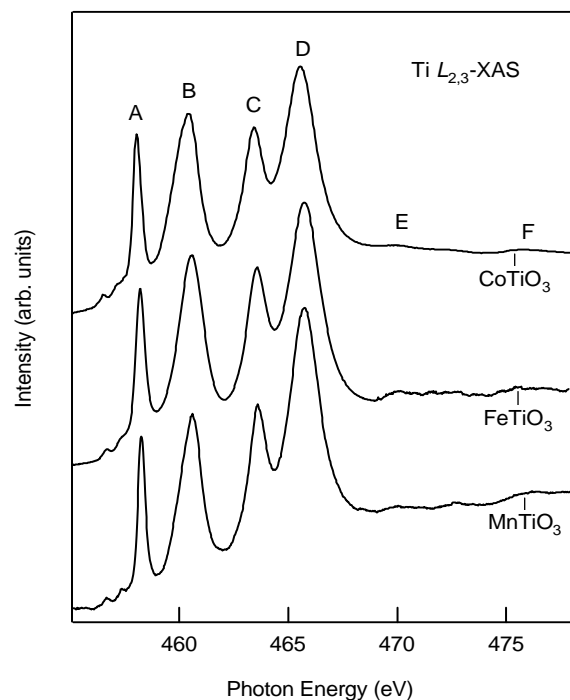


Figure 2
The Ti $L_{2,3}$ soft x-ray absorption spectra of MnTiO₃, FeTiO₃, and CoTiO₃ measured by total electron yield detection.

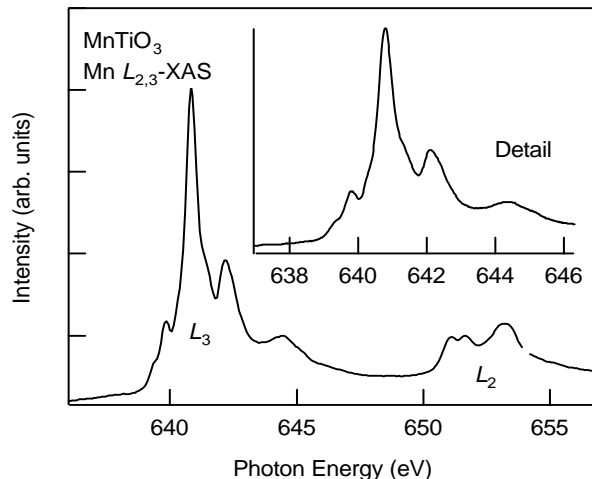


Figure 3
The Mn $L_{2,3}$ soft x-ray absorption spectrum of MnTiO₃ and its detail measured by total electron yield detection.

the L_3 edge. The Ti $L_{2,3}$ spectrum is understood by taking into account only Ti⁴⁺ charge state so that the spectrum is ascribed to $2p^63d^0 \rightarrow 2p^53d^1$ transitions of Mn²⁺ ion. Theoretically calculated $L_{2,3}$ absorption of $3d$ transition metal compounds using atomic multiplet theory with inclusion of cubic crystal field had been reported (de Groot *et al.* 1990). The present experimental spectrum is well-reproduced by the calculated spectra within O_h with the crystal-field parameter ($10Dq$) around 1, even though the local symmetry around Mn²⁺ is distorted O_h . We assume that the distortion of the ground state of the $3d$ electron configuration is not significant.

Figure 4 shows the Co $L_{2,3}$ spectrum of CoTiO₃ and its detail at the L_3 edge. The L_3 spectrum of CoTiO₃ has finer structures than those of MnTiO₃. In the same way as MnTiO₃, Co of CoTiO₃ is divalent because Ti is quaternary. The Co $L_{2,3}$ spectrum is ascribed to $2p^63d^7 \rightarrow 2p^53d^8$ transitions of Co²⁺ ion to the states. The present spectrum is roughly reproduced by the calculated spectra (de Groot *et al.* 1990) within O_h with the $10Dq$ over 1. The ion radius of Co is smaller than that of Mn and that means the $Co3d-O2p$ hybridization is smaller, so that it makes the crystal field parameter larger. It seems that the effect of the O_h symmetry distortion of the ground state of $3d$ electrons is larger than that of MnTiO₃.

Figure 5 shows the Fe $L_{2,3}$ spectrum of FeTiO₃ and its detail at the L_3 edge. Two large peaks and shoulder structures at the lower energy side characterize the L_3 spectrum. The Fe $L_{2,3}$ spectrum of mineral ilmenite was reported (Droubay *et al.* 1997). They took into account the contributions of the Fe²⁺ and Fe³⁺ charge states to understand the two large peaks because a mineral ilmenite contains hematite. However, for the present measurements FeTiO₃ powder of a single crystal was used so that the Fe $L_{2,3}$ spectrum must be understood by taking into account Fe²⁺ charge state only. The Fe $L_{2,3}$ absorption peaks should be ascribed to the $2p^63d^6 \rightarrow 2p^53d^7$ transitions of Fe²⁺ ion. In the case of FeTiO₃, the Fe $L_{2,3}$ spectrum is not reproduced by the calculated spectra by de Groot *et al.* (1990). The environment around Fe²⁺ ion changes the $3d$ electron ground state configuration from the O_h symmetry.

Owing to the very high spectral resolution, a small valley is observed at the top of the lower L_3 peak. It suggests that the local symmetry of Fe²⁺ is heavily distorted from the O_h symmetry. The

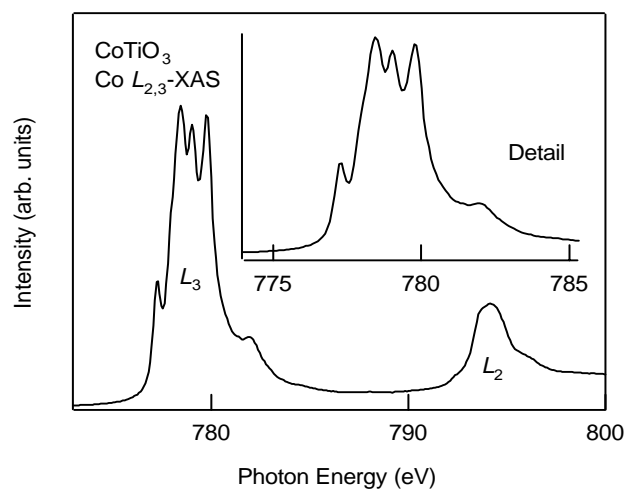


Figure 4
The Co $L_{2,3}$ soft x-ray absorption spectrum of CoTiO_3 and its detail measured by total electron yield detection.

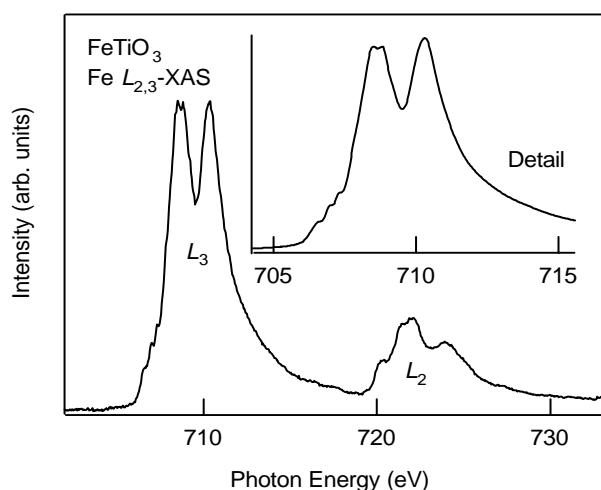


Figure 5
The Fe $L_{2,3}$ soft x-ray absorption spectrum of FeTiO_3 and its detail measured by total electron yield detection. The L_3 edge has doublet peaks and further the top of lower energy peak shows doublet peak owing to the very high-energy resolution.

valley and shoulders are attributed due to the crystal field effect.

Let us compare $M L_{2,3}$ spectra of ilmenites. In MTiO_3 , the valency of M are divalent, such as Mn^{2+} , Fe^{2+} , and Co^{2+} , have different number of $3d$ electrons *e.g.* $3d^5$, $3d^6$, and $3d^7$, respectively. Increasing the number of $3d$ electrons, the number of distinct peaks increases. The calculated $L_{2,3}$ absorption spectra of transition metals by de Groot *et al.* (1990) are basically in agreement with the present experimental spectra. The $3d$ electron numbers symmetry in MnTiO_3 and CoTiO_3 are similar in terms of the electron configurations. On the other hands, the electron configuration of Fe^{2+} in FeTiO_3 has different symmetry. The deviation of local symmetry might change the energy level of Fe^{2+} state, and thus it makes the doublet peak at the L_3 -edge. Of course, the crystal field effects should be considered as well. Recently the $L_{2,3}$ spectra of ilmenites have been calculated (Nakazawa *et al.*, 2000) and were well reproduced by taking into account the crystal field effect. In order to study the absorption

spectra of ilmenites and its magnetic property in detail, theoretical calculation and magnetic circular dichroism measurements will be carried out in the future.

4. Summary

We have measured soft x-ray absorption spectra of ilmenite family, such as MnTiO_3 , FeTiO_3 , and CoTiO_3 , at the soft x-ray beamline BL23SU to study its electronic structure. The Ti $L_{2,3}$ spectra of MTiO_3 show quaterovalent spectra. The $M L_{2,3}$ spectra are attributed to M^{2+} charge state. Still more very high-resolution L -edges spectra of transition metals show finer structures. The small valley was found at the top of doublet peak of Fe $L_{2,3}$ spectra of FeTiO_3 . The spectra gave basic information on the ilmenite family.

We are grateful to Professor S. Suga for his helpful assistance in designing the monochromator. Thanks to Mr. T. Shimada and Dr. Y. Miyahara for developing the undulator. The beamline operation is supported by JAERI soft x-ray science staff, including Drs. A. Yokoya, A. Yoshigoe, and Y. Teraoka. Support from the SPring-8 staff is also acknowledged. We also wish to thank Drs. M. Nakazawa and N. Ikeda for useful discussions.

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