



Polarization-dependent Ti K X-ray absorption and emission studies of Ti₂O₃ single crystal

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ABSTRACT

Polarization-dependent Ti K X-ray absorption and Ti K_α X-ray emission spectroscopy (XAS and XES) experiments have been carried out for single-crystalline Ti₂O₃ with metal-insulator transition (MIT) around 450 K. Both the XAS and XES spectra exhibit remarkable polarization dependences between *E*//*c* and *E*⊥*c* conditions, where the *c*-axis is parallel to the Ti ion pair direction and *E* represents a polarization vector of incident photons. The main peak of the *E*//*c*-XAS spectrum is 3 eV lower in energy than the *E*⊥*c*-spectrum at 300 K, reflecting the highly anisotropic unoccupied Ti 4p states, and the energy separation of the main peaks decreases to 2 eV at 520 K, in consistent with the reduced anisotropy of electronic structure followed by MIT. The broad features of the Ti K_α XES spectra taken far below the Ti K absorption edge are similar to the XAS features including the polarization dependence, suggesting that the 2p4p monopole excitation causes the broad XES features, where 2p denotes a 2p core hole.

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1. Introduction

The titanium oxide Ti₂O₃ undergoes a gradual metal-insulator transition (MIT) around 450 K from a non-magnetic semiconductor in the low temperature phase to a paramagnetic metal in the high temperature phase [1,2]. The crystal structure is α-Al₂O₃ corundum-type and a Ti ion with a honeycomb lattice in the *ab* plane forms a pair together with a Ti ion on the next layer along the *c*-axis. Each of the Ti ions is octahedrally surrounded by six O ions, leading to a crystal field splitting of the 3d levels into t_{2g} and e_g^σ levels. Due to a trigonal distortion, the t_{2g} levels further split into a_{1g} and e_g^π levels. Two a_{1g} orbitals in a Ti pair along the *c*-axis strongly hybridize and form bonding (a_{1g}) and antibonding (a_{1g}^{*}) states. The e_g^π and e_g^{π*} bands locate between them. At the low temperature, there exists an energy gap between the a_{1g} and e_g^π bands [3,4].

Recently, we have investigated the Ti 3d electronic structure of Ti₂O₃ by means of the polarization-dependent Ti 2p–3d soft X-ray absorption spectroscopy (XAS) [3]. The Ti 2p (L) XAS spec-

tra exhibit remarkable linear dichroism (LD) between the *E*//*c* and *E*⊥*c* conditions, reflecting the anisotropy of the 3d electronic structure. Here *E* represents a polarization vector of incident photons. The LD intensity is reduced in the high temperature phase, indicating the change of the 3d configuration within the Ti ion pair from (a_{1g}↑; a_{1g}↓) to (a_{1g}↑; e_g^π↑) across MIT. Such a large configuration change has been predicted by Tanaka with a new MIT model for Ti₂O₃ from a view of electron correlation [4], and is not explained by the one-electron band theory [5,6] and the dynamical mean field theory [7].

In this paper, we report the results of the polarization-dependent Ti K XAS and Ti K_α X-ray emission spectroscopy (XES) experiments for Ti₂O₃ single crystal. The Ti K XAS spectra exhibit remarkable polarization dependence as the Ti L XAS spectra, indicating the highly anisotropic unoccupied Ti 4p states, and the dependence is reduced at 520 K. The Ti K_α XES spectra also exhibit several fine structures with the polarization dependence. The broad structure observed in the XES spectra taken far below the Ti K absorption edge has similar feature to the Ti K XAS spectra including the polarization dependence, suggesting that the broad structure originates from the 2p4p monopole excitation. To our knowledge, this paper is the first report of the Ti K_α XES spectra of 3d¹ electron systems.

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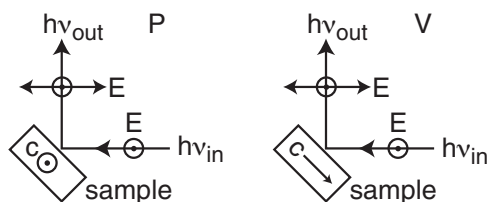


Fig. 1. Experimental configurations P ($\mathbf{E} // c$) and V ($\mathbf{E} \perp c$) for Ti K_{α} XES (polarized configuration). $h\nu_{in}$ and $h\nu_{out}$ represent incident and emitted photons, respectively, and \mathbf{E} a polarization vector of incident photons.

2. Experimental

The Ti K XAS and K_{α} XES experiments for Ti_2O_3 single crystal were carried out on beamlines BL7C and BL15B1 of KEK-PF both equipped with a Si(1 1 1) double-crystal monochromator. The XAS spectra were collected at 300 and 520 K with the total electron yield mode for the $\mathbf{E} // c$ and $\mathbf{E} \perp c$ conditions. The XES experiments were carried out at 300 K with the polarized configuration also for the $\mathbf{E} // c$ and $\mathbf{E} \perp c$ conditions (Fig. 1), and the XES spectra were taken using a cylindrically bent Ge(400) crystal and a position-sensitive proportional counter with the charge-division method [8]. Single crystals of Ti_2O_3 were grown by the floating zone method. The samples were cut into pieces with (1 1 $\bar{2}$ 0) surface, on which the Ti ion pair along the c -axis exists, by the discharge method.

3. Results and discussion

Fig. 2 shows the polarization-dependent Ti K XAS spectra of Ti_2O_3 single crystal measured at 300 K in the low temperature phase and 520 K in the high temperature phase. The spectra have tentatively been normalized to the intensity of the main peak at $h\nu \sim 4985$ eV. The spectra are roughly classified into pre-edge region below ~ 4972 eV and main absorption region above ~ 4972 eV. The structures around 5000 eV are due to the extended-X-ray fine structure (EXAFS). The pre-edge region shows only a broad feature, in contrast to $3d^0$ systems such as TiO_2 [9] and $SrTiO_3$ [10] with the complicated structures due to the pure $1s$ – $3d$ quadrupole transition and the dipole transition from $1s$ to $4p$ states hybridized with $3d$ states.

We notice that the XAS spectra taken at 300 K exhibit the polarization dependence slightly in the pre-edge region and remarkably

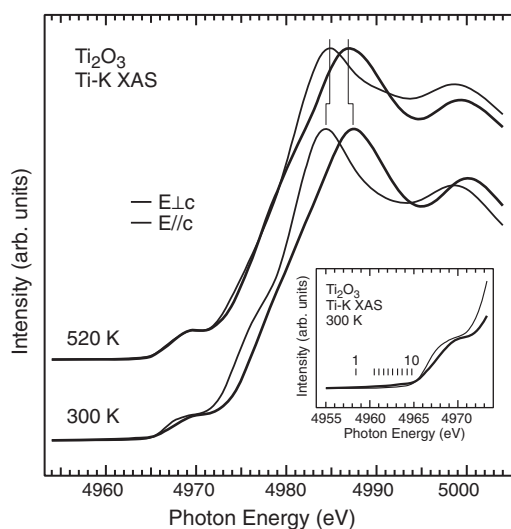


Fig. 2. Polarization-dependent Ti K_{α} XES spectra measured at 300 and 520 K. In inset, the excitation energies for Ti K_{α} XES are indicated by vertical bars.

in the main absorption region. The main peak of the $\mathbf{E} // c$ -spectrum is observed at 4984.4 eV, lower by 3 eV than that of the $\mathbf{E} \perp c$ -spectrum at 4987.4 eV. Since the main peak region originates from the Ti $1s$ – $4p$ transition [11], the XAS spectra reflect the unoccupied $4p$ states. The observed polarization dependence, thus, indicates that the unoccupied $4p$ bands are strongly polarized between the $4p_{//}$ and $4p_{\perp}$, and that the unoccupied $4p_{//}$ bands locate in the lower energy region than the $4p_{\perp}$ bands. With increasing temperature to 520 K above MIT temperature, the main peak of the $\mathbf{E} // c$ -spectrum is observed at higher energy of 4984.9 eV, while that of the $\mathbf{E} \perp c$ -spectrum at lower energy of 4986.9 eV, in comparison with the results at 300 K. The energy separation of the main peaks is reduced to be 2 eV, in consistent with the reduced anisotropy of the electronic structure observed in the polarization-dependent Ti L XAS experiments [3]. The polarization dependence in the pre-edge region and around 4977 eV also decreases at 520 K.

According to the theoretical analyses of the Ti L XAS spectra, the Ti a_{1g} orbital is mainly occupied at 300 K [3]. Intuitively, the occupied a_{1g} orbital, which extends along the c -axis, is expected to give rise to the higher lying $4p_{//}$ bands. However, the behavior of XAS spectra is opposite to our intuition. The present XAS results are qualitatively understood if we consider rather that the spectra are affected by the displacements of the three O ions triangularly surrounding the Ti–Ti bond axis of the Ti pair along the c -axis; Ti–O₃–Ti. It is known that the three O ions in Ti–O₃–Ti are displaced away from the Ti–Ti pair bond [12]. Since the $4p_{//}$ orbital extends along the Ti–Ti pair bond, the outward displacement of the O ions lowers the energy of the $4p_{//}$ bands. With increasing temperature, the O ion outward displacement becomes small in accordance with the elongation of the Ti pair bond and raises the energy of the $4p_{//}$ bands. The present XAS results are, thus, qualitatively understood from the displacements of the O ions. The theoretical studies are indispensable for further discussion of the Ti K XAS spectra.

Fig. 3(a) shows the polarization-dependent Ti K_{α} XES spectra with the polarized configurations (see Fig. 1) measured at 300 K. The excitation energies are below the pre-edge region of the Ti K XAS spectra and are indicated by vertical bars with Nos. 1–10 in inset in Fig. 2. The emission energies of the XES spectra are around $K_{\alpha 1}$ and $K_{\alpha 2}$ fluorescence regions (~ 4500 eV). The spectra in Fig. 3 are plotted as a function of the Raman shift, that is, the difference between the incidence and emission energies. The spectra are collected with the two experimental conditions $\mathbf{E} // c$ and $\mathbf{E} \perp c$. The thin and thick lines present the spectra with the configurations of P ($\mathbf{E} // c$) and V ($\mathbf{E} \perp c$) in Fig. 1, respectively. The spectra have tentatively been normalized to the tail region from 485 to 500 eV [13].

We notice the strong polarization dependence and several fine structures in the XES spectra in Fig. 3(a) as the Ti K XAS spectra. In the spectra #9, two prominent peaks F_1 and F_2 are observed at 456 and 460.5 eV, respectively. These structures begin to clearly grow from \sim #6 and are continuously connected to the $K_{\alpha 1}$ and $K_{\alpha 2}$ fluorescence lines with the constant emission energies above $h\nu \sim 4967$ eV. This indicates that the $1s$ – $4p$ dipole transition becomes already dominant in the Ti K XAS spectra at $h\nu \sim 4967$ eV. Other than the F_1 and F_2 peaks, the structures A and C are detected around 1 eV below the F_1 and F_2 peaks and the structures B and D around 3 eV below the F_1 and F_2 peaks. It should be addressed that these fine structures are clearly noticed by measuring the XES spectra with the two experimental conditions. The F_2 , C and D structures are the Ti $2p$ spin–orbit partners of the F_1 , A and B structures, respectively. We also notice broad structures Z around 475 eV.

In order to make clear the polarization dependence in 455–470 eV region of the XES spectra, we have subtracted the contributions of the broad structures Z from the each XES spectra. The contributions have appropriately been estimated as shown by dashed lines on the spectra #2 in Fig. 3(a). The subtracted results

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