P H Y S I C A L   R E V I E W   L E T T E R S

Determination of the Orbital Polarization in YTiO$_3$ by Using Soft X-Ray Linear Dichroism

F. Iga,[1] M. Tsubota,[1] M. Sawada,[2] H. B. Huang,[1] S. Kura,[1] M. Takemura,[1] K. Yaji,[3] M. Nagira,[3] A. Kimura,[3] T. Jo,[1] T. Takabatake,[1] H. Namatame,[2] and M. Taniguchi[2,3]

[1]*Department of Quantum Matter, ADSM, Hiroshima University, Higashi-Hiroshima, 739-8530, Japan*
[2]*Hiroshima Synchrotron Radiation Center, Hiroshima University, Higashi-Hiroshima, 739-8526, Japan*
[3]*Department of Physics, Faculty of Science, Hiroshima University, Higashi-Hiroshima, 739-8526, Japan*
(Received 23 July 2004; published 15 December 2004)

We report measurements of linear dichroism in x-ray absorption at Ti $L_{2,3}$ edges of a Mott-insulating ferromagnet YTiO$_3$, where orbital ordering occurs in the triply degenerate Ti 3d t_{2g} states. Dichroic spectra and their integrated intensities are obtained for the incident electric field with polarizations parallel to a, b, and c axes. The comparison of the spectra with atomic multiplet calculations removes the ambiguity about the orbital polarization, i.e., the relative weights of $|xy\rangle$, $|yz\rangle$, and $|zx\rangle$ orbits, which are crucial for the origin of ferromagnetism. The result is consistent with the previous analysis of nuclear magnetic resonance in the Mizokawa-Fujimori scheme.

In transition-metal oxides, an interplay among the spin, charge, and orbital orderings has attracted much attention [1–4]. The orbital ordering, i.e., ordering of the polarization of occupation among degenerate 3d orbits of transition-metal ions, affects the physical properties such as transport, magnetic, and thermal properties. For example, colossal magnetoresistance associated with a metal-insulator transition in manganese oxides is a current topic, and the orbital ordering is known to take an important role in it [1,3]. In the case of spin orderings, whose order parameters are represented by the difference between the occupied up and down spin electron numbers, various methods have been used to measure them. For orbital polarizations, on the other hand, the order parameters are represented in terms of a component of quadrupole or higher multipole moments or a superposition of the degenerate atomic orbits [5–8]. To determine them, three methods have been used: polarized neutron diffraction (PND) [9], nuclear magnetic resonance (NMR) [10], and resonant x-ray scattering (RXS) [11,12]. There have been, however, controversies about an interpretation of the results of RXS in some transition-metal oxides [13]. Furthermore, the experiments of PND and NMR were done in the magnetically ordered state. For YTiO$_3$ with Ti 3d antiferro-orbital ordering, the measured order parameter of the Ti 3d orbital state is not consistent among PND, NMR, and RXS. The order parameter is crucial for the occurrence of ferromagnetism in this compound [14]. Furthermore, in order to establish the concept of orbital polarization, an alternative experimental method to directly measure its order parameters seems to be indispensable.

In this Letter, we report a comprehensive study of YTiO$_3$ by using the linear dichroism of x-ray absorption spectroscopy (XAS) technique at the absorption edge of the inner shell of the transition-metal site. Recently, this method has been used to determine the orbital polarization of a doubly degenerate e_g-electron tetragonal system

La$_{1+x}$Sr$_{1-x}$MnO$_4$ [15]. The present study of YTiO$_3$ has determined the orbital polarization among the triply degenerate t_{2g} states of the trivalent Ti ion with one t_{2g} electron even in a paramagnetic state. YTiO$_3$ is well known to be a Mott-insulating ferromagnet (Curie temperature $T_C = 30$ K) with a distorted perovskite structure (orthorhombic GdFeO$_3$-type space group: *Pbnm*) [16–20]. In a cubic crystal field, one 3d electron of the Ti^{3+} ion may occupy the triply degenerate t_{2g} states. The Jahn-Teller distortion of a TiO$_6$ octahedron in YTiO$_3$ splits the energy levels of t_{2g} states. As shown in Fig. 1, the local coordinates of x, y, and z axes are taken to Ti-O bonding directions in each TiO$_6$ octahedron, respectively. Our Rietveld analysis of powder x-ray diffraction showed that the three Ti-O bonding lengths are 0.2077, 0.2021, and 0.2025 nm, respectively [21]. It is noted that at least three types of local coordination have been used in literature [9,12,14]. Here, the z axis for each Ti site is set as the direction of the most elongated Ti-O bonding [22].

The numbering of the four inequivalent Ti sites in Fig. 1 is according to the notation used for the PND study [9]. In the elongated TiO$_6$ octahedrons, one 3d electron must occupy either the $|zx\rangle$ or the $|yz\rangle$ orbit to minimize the Coulomb interaction energy between Ti^{3+} and O^{2-} ions, thereby triply degenerate t_{2g} states split into an excited $|xy\rangle$ state and doubly degenerate ground states composed of $|yz\rangle$ and $|zx\rangle$ orbits. The sites 1, 2, and 3, 4 are occupied by an electron of the orbits $c_1|zx\rangle - c_2|yz\rangle$ and $c_1|zx\rangle + c_2|yz\rangle$, respectively, where c_1 and c_2 are coefficients satisfying $c_1^2 + c_2^2 = 1$. The values of $c_1 \sim 0.8$ and $c_2 \sim 0.6$ were obtained by the Hartree-Fock calculation to minimize the total energy [14]. This means that the occupied 3d orbits are alternately arranged in the a-b plane with a spatial modulation vector $(1/2, 1/2, 0)$ in YTiO$_3$. For the relation between the antiferro-orbital ordering and the magnetic structure, a simplified model is often proposed. For example, in LaMnO$_3$ with one e_g
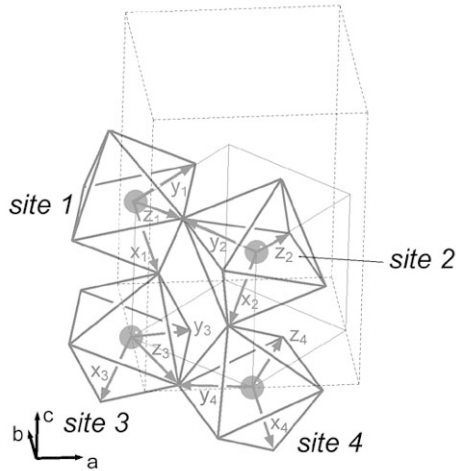
FIG. 1.   Crystal structure of $YTiO_3$ and local coordinate axes at four inequivalent Ti sites. The TiO_6 octahedrons are distorted by the Jahn-Teller effect. The z axis at each Ti site is selected to be the most elongated Ti-O bonding direction.
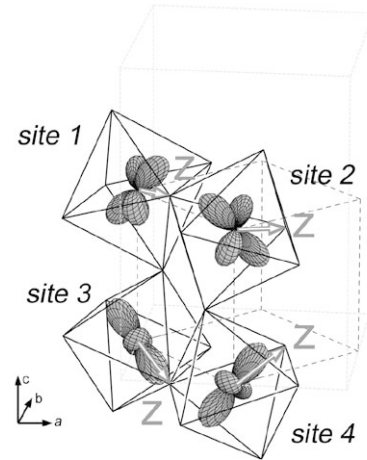

FIG. 2.   Orbital ordering pattern in $YTiO_3$ proposed by previous experiments [9,10,12]. The wave functions are described by $c_1|zx\rangle \pm c_2|yz\rangle$. For $c_1 > 0.7$ the orbital is elongated in the c direction, whereas for $c_1 < 0.7$ the orbital lies on the a-b plane.

electron, the alternate arrangement of $3x^2 - r^2$ and $3y^2 - r^2$ orbits in the a-b plane is argued to be responsible for the parallel spin coupling in the plane [6]. In the case of triply degenerate t_{2g} states, the mixing of $|zx\rangle$ and $|yz\rangle$ orbits is indispensable, while it is unfavorable for the occurrence of ferromagnetism. According to Mizokawa and Fujimori [14], a compromise between the mixing and the $GdFeO_3$-type tilting leads to ferromagnetism. In this sense, a precise determination of c_1 is very important to elucidate the origin of ferromagnetism.

Experimentally, different values of the coefficients have been obtained, depending on the method. From the PND study, $c_1 \sim 0.6$ was obtained [9] (a correction for the extinction effect altered this value to $c_1 \sim 0.7$ [23]). The RXS study also gave $c_1 \sim 0.7$ [12] and NMR measurement led to $c_1 \sim 0.8$ [10]. For $c_1 = 0.7$, the pattern of orbital order in $YTiO_3$ is displayed in Fig. 2.

XAS at the $L_{2,3}$ edge of $3d$ elements utilizes the excitation of one electron from the $2p$ orbital to the unoccupied $3d$ orbital. The transition intensity as a function of incident x-ray energy can be measured by the total yield from the secondary electrons originating from the subsequent Auger decay in the core holes. The total photocurrent yield was directly measured as the electrical current from the sample to the ground by means of a picoammeter. Electric dipole transition is usually dominant in such x-ray absorption near the $L_{2,3}$ edge. The transition probability therefore depends on the orbital polarizations in both the initial and final states characterized by the orbital quantum number l and the magnetic quantum number m. When the transition is induced by the electric field E parallel to the z axis, m must be conserved. However, in the case of E perpendicular to the z axis, m changes by ± 1. The x-ray linear dichroism (XLD) spectra correspond to the difference between the responses for horizontal and perpendicular polarizations

of E. Therefore, in XLD, one can directly observe the orbital polarization by using the above selection rule. Apart from orbital orderings, XLD has also been used to determine occupied orbits, for example, in V_2O_3 [24]. In the case of x-ray magnetic circular dichroism, its signal is obtained only for ferromagnets or ferrimagnets, and no signal is obtained for antiferromagnets, since the contribution of each sublattice cancels with each other. For XLD, on the other hand, its signal is found to be obtained for many transition-metal oxides with antiferro-orbital orderings [25].

In manganites, where trivalent Mn ions have one e_g electron, the basic pattern of XLD is only of one kind [25]. Therefore, the XLD experiment with the incident electric polarizations parallel and perpendicular to the tetragonal c axis may be enough. In $YTiO_3$ with triply degenerate Ti $3d$ t_{2g} states, however, the XLD spectral shape depends on the order parameter, i.e., *the relative ratio of the three kinds of orbits*. We will show that the absorption spectra measured for E parallel to a, b, and c axes give reliable information in this system with large $GdFeO_3$-type tilting.

The use of single crystals is essential in XLD. Single crystalline samples of $YTiO_3$ were grown by the floating-zone method using an image furnace with four halogen lamps [26]. The growth was done in a reductive atmosphere of the flowing mixture of Ar 50% and H_2 50%. The typical size of a single crystal was of 7 mm in diameter and 30 mm in length. The sample was annealed in air at $400\,°C$ for 4 h to increase the oxygen content to the stoichiometric value. The full occupation of oxygen was confirmed by thermogravimetric analysis. Powder x-ray diffraction analysis determined the lattice constants a, b, and c of the $GdFeO_3$-type structure to be 0.53376, 0.56827, and 0.76147 nm, respectively. By using Laue photos we oriented the crystal parallel to the a, b, and c

planes and cut the three surfaces within an accuracy of $1°$. To examine whether the crystal rod is of a single domain or twinned domains, Laue diffraction patterns were taken at several spots on the same surface. Furthermore, rocking curves measured by using an x-ray diffractometer showed several symmetric peaks for diffraction lines from each plane. Thus, the single domain nature was confirmed for the samples, which were cut into rectangular rods of 4×4 mm^2 square cross sections and 5–7 mm in length.

At the BL-14 line in the Hiroshima Synchrotron Radiation Center, the energy dependent XAS spectra were recorded by measuring the photocurrent at a 10^{-12} A level flowing from the sample to the earth probe via the sample holder. Because of the time decay of the ring current, the obtained spectra were normalized with respect to the incident photon flux intensity. Since the $Ti^{3+}(3d^1)$ state on the surface of the sample easily changes to the $Ti^{4+}(3d^0)$ state as $Y_2Ti_2O_7$, a fresh surface of $YTiO_3$ was obtained by *in situ* cleaving the crystal rods in a high vacuum of 1–2×10^{-8} Pa at 300 K. The surface was set normal to the direction of the incident photon flux whose electric field is polarized horizontally. The surface of the *a* plane was, for example, first set for $E \parallel b$. One scan from $h\nu = 450$ to 490 eV was recorded for 15 min. Then, the sample holder was rotated by $90°$ so that the polarization direction is changed to $E \parallel c$. After the measurement for another 15 min, it was reversed to the initial configuration for $E \parallel b$ in order to estimate the increase of the Ti^{4+} component in XAS within the period of 30 min. It was found that this contribution is less than 5% of the intensity of the XLD spectrum, $F_b - F_c$, that is, the difference between the spectra for $E \parallel b$ and $E \parallel c$. Furthermore, the two spectra obtained by rotating the sample by $180°$ were identical, and thus the effect of the irregularly cleaved surface can be also neglected in the following analysis of the XLD spectra.

Figure 3 shows the example of polarization dependent XAS spectra for the *a* plane at 300 K. The XLD spectrum for the *a* plane is given by $F_b - F_c$. In a similar way, XLD spectra for the *b* and *c* planes are obtained as $F_c - F_a$ and $F_a - F_b$, respectively. These spectra need to be normalized to make quantitative comparisons with the calculated ones. A simple normalization factor would be the total integrated intensity $I = I_a + I_b + I_c$, with I_a being the one obtained by integrating F_a, etc. However, the F_a spectrum cannot be measured for the *a* plane for geometric reasons. Therefore, the $F_b - F_c$ spectrum was normalized by $3/2 \times (I_b + I_c)$ instead of by $I_a + I_b + I_c$. The same normalization was applied to other planes. This approximation is allowed because the intensity of the XLD spectra is much weaker than that of the XAS spectra, as shown in Fig. 3. In this way, the normalized XLD spectra were obtained and compared with the calculated ones.

The XAS spectra of $YTiO_3$ are now compared with calculations based on the Mizokawa-Fujimori model [14].
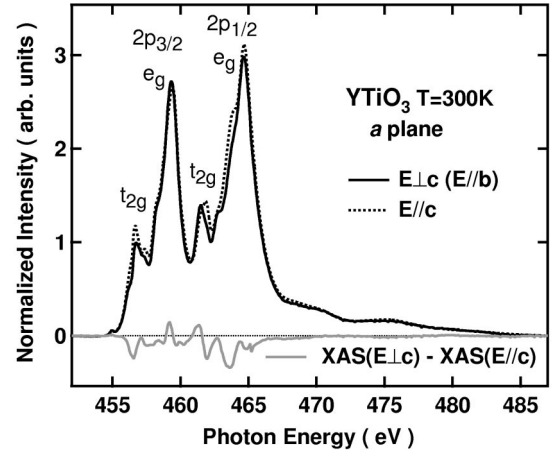

FIG. 3.   XAS spectra on the *a* plane of $YTiO_3$ for an electric field in the direction of perpendicular ($E \parallel b$, solid line) and horizontal ($E \parallel c$, dashed line) axes. The gray line shows a differential spectrum, that is, XLD at the Ti $L_{2,3}$ edge.

The $L_{2,3}$ XAS spectra of the Ti^{3+} ion for a given direction of E were calculated by exactly diagonalizing the single-ion Hamiltonian, including the $3d$-$3d$ and $3d$-$2p$ multipole interactions, the $3d$ and $2p$ spin-orbit interactions, and the cubic crystal field $10Dq = 1.5$ eV. The details of the method and parameters used for this calculation were reported by de Groot *et al.* [27] and Huang and Jo [28].

Table I summarizes the energy integrated values of the normalized XLD spectra for three planes, $(I_b - I_c)/I$, $(I_c - I_a)/I$, and $(I_a - I_b)/I$. The values calculated by varying the parameter c_1 from 0.6 to 0.9 are also listed. In principle, the sum of the three values must be zero for any value of c_1. The small but finite value of the experimental sum may be caused by the error in the evaluation of total intensity $I_a + I_b + I_c$. For choosing the best parameter c_1, another criterion is to reproduce the ratios $(I_b - I_c)/(I_a - I_b)$ and $(I_c - I_a)/(I_a - I_b)$, given in the Table I. We find that the two ratios are best reproduced by the calculation for $c_1 = 0.8$. This value of $c_1 = 0.8$ is consistent with the orbital ordering proposed by the NMR measurement [10].

By using the above parameter $c_1 = 0.8$, the XLD spectra were calculated for the three planes. The results are compared with the experimental ones in Fig. 4. Most of the fine structures in the energy dependence of XLD spectra are well reproduced for any plane except for the region above 465 eV. This disagreement is expected to be removed to some extent if the configuration mixing is taken into account, since its effect on $L_{2,3}$ XAS is small but is not negligible, especially in the L_2 region. In Fig. 4(b), the normalized spectrum of $(F_c - F_a)/I$ for the *b* plane is compared with $-\{(F_b - F_c)/I + (F_a - F_b)/I\}$ obtained by the measurements in the *a* and *c* planes, both of which must be identical in principle. Both spectra do agree well, including the fine profiles. This guarantees that the XLD measurements are consistent for the three planes. We may name this method "trichroism," which is

TABLE I.   The c_1 dependence of integrated XLD intensities calculated on the basis of the Mizokawa-Fujimori model wave functions, $c_1|zx\rangle \pm c_2|yz\rangle$, is compared with experimental results. I_a, I_b, and I_c denote integrated values of XAS spectra for the electric fields $E \parallel a$, b, and c, respectively.

		exp	$c_1 = 0.9$	$c_1 = 0.8$	$c_1 = 0.7$	$c_1 = 0.6$
a plane	$(I_b - I_c)/I$	-0.0271	-0.01474	-0.02036	-0.02903	-0.03675
b plane	$(I_c - I_a)/I$	-0.00556	-0.00769	-0.00100	$+0.01011$	$+0.02100$
c plane	$(I_a - I_b)/I$	$+0.0261$	$+0.02243$	$+0.02136$	$+0.01892$	$+0.01573$
	$\{(I_b - I_c) + (I_c - I_a) + (I_a - I_b)\}/I$	-0.0066	0	0	0	0
	$(I_b - I_c)/(I_a - I_b)$	-1.038	-0.365	-0.95	-1.53	-2.33
	$(I_c - I_a)/(I_a - I_b)$	-0.213	-0.635	-0.05	$+0.534$	$+1.333$

a new method to determine the orbital polarization of transition-metal ions by using polarized x rays.

In conclusion, we have observed fine structures in x-ray absorption linear dichroism spectra for YTiO$_3$, which is the prototype showing orbital order. The observed spectra at the Ti $L_{2,3}$ edge are well reproduced by using the wave functions $0.8|zx\rangle - 0.6|yz\rangle$ and $0.8|zx\rangle + 0.6|yz\rangle$, which are alternately arranged in the Ti sites 1, 2 and 3, 4, respectively. The above values determined by the *trichroism* method are consistent with those proposed by the nuclear magnetic resonance measurement in the ferromagnetic state of YTiO$_3$. Since the XLD method by using synchrotron radiation is applicable to the paramagnetic system without applying a magnetic field, it is a promis-

ing technique to determine the orbital order in various $3d$-transitional metal oxides as well as f-electron compounds.

[1]   Y. Tokura and N. Nagaosa, Science **288**, 462 (2000).
[2]   J. B. Goodenough, Phys. Rev. **100**, 564 (1955).
[3]   M. Imada, A. Fujimori, and Y. Tokura, Rev. Mod. Phys. **70**, 1039 (1998).
[4]   Y. Tokura *et al.*, Phys. Rev. B **48**, 14063 (1993).
[5]   J. Kanamori, J. Appl. Phys. **S31**, 14S (1960).
[6]   K. I. Kugel and D. I. Khomski, JETP Lett. **15**, 446 (1972).
[7]   F. J. Ohkawa, J. Phys. Soc. Jpn. **52**, 3897 (1983).
[8]   R. Shiina, H. Shiba, and P. Thalmeier, J. Phys. Soc. Jpn. **66**, 1741 (1997).
[9]   J. Akimitsu *et al.*, J. Phys. Soc. Jpn. **70**, 3475 (2001).
[10]   M. Itoh *et al.*, J. Phys. Soc. Jpn. **68**, 2783 (1999).
[11]   Y. Murakami *et al.*, Phys. Rev. Lett. **80**, 1932 (1998).
[12]   H. Nakao *et al.*, Phys. Rev. B **66**, 184419 (2002).
[13]   S. Ishihara, Phys. Rev. B **69**, 075118 (2004); P. Benedetti *et al.*, Phys. Rev. B **63**, 60408 (2001); M. Benfatto, Y. Joly, and C. R. Natoli, Phys. Rev. Lett. **83**, 636 (1999); M. Takahashi *et al.*, J. Phys. Soc. Jpn. **68**, 2530 (1999).
[14]   T. Mizokawa and A. Fujimori, Phys. Rev. B **54**, 5368 (1996).
[15]   D. J. Huang *et al.*, Phys. Rev. Lett. **92**, 087202 (2004).
[16]   J. E. Greedan, J. Less-Common Met. **111**, 335 (1985).
[17]   Y. Taguchi *et al.*, Phys. Rev. B **48**, 511 (1993).
[18]   K. Kumagai *et al.*, Phys. Rev. B **48**, 7636 (1993).
[19]   Y. Okimoto *et al.*, Phys. Rev. B **51**, 9581 (1995).
[20]   C. Ulrich *et al.*, Phys. Rev. Lett. **89**, 167202 (2002).
[21]   M. Tsubota *et al.* (unpublished).
[22]   This notation is different from those used for the model calculation based on the Mizokawa-Fujimori model [14].
[23]   J. Akimitsu (private communication).
[24]   J.-H. Park *et al.*, Phys. Rev. B **61**, 11506 (2000).
[25]   H. B. Huang *et al.*, J. Phys. Soc. Jpn. **69**, 2399 (2000); H. B. Huang and T. Jo, *ibid.* **71**, 3094 (2002).
[26]   M. Tsubota *et al.*, J. Phys. Soc. Jpn. **72**, 3182 (2003).
[27]   F. M. F. de Groot *et al.*, Phys. Rev. B **42**, 5459 (1990).
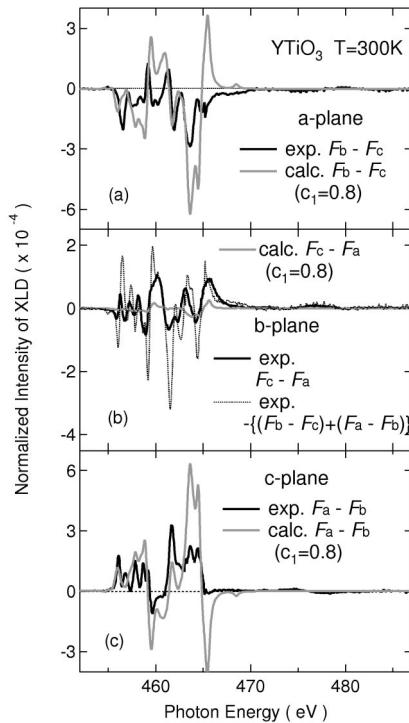[28]   H. B. Huang and T. Jo, J. Phys. Soc. Jpn. **73**, 2480 (2004).

FIG. 4.   The best fit results of XLD for the (a) a, (b) b, and (c) c planes of YTiO$_3$ by using parameter $c_1 = 0.8$ in the wave functions proposed by Mizokawa and Fujimori [14]. (b) The normalized spectrum of $(F_c - F_a)/I$ for the b plane was compared with $-\{(F_b - F_c) + (F_a - F_b)\}/I$ for the a and c planes.

Erratum: Determination of the Orbital Polarization in YTiO$_3$ by Using Soft X-Ray Linear Dichroism [Phys. Rev. Lett. 93, 257207 (2004)]

F. Iga, M. Tsubota, M. Sawada, H. B. Huang, S. Kura, M. Takemura, K. Yaji, M. Nagira, A. Kimura, T. Jo, T. Takabatake, H. Namatame, and M. Taniguchi

After the publication of the Letter, A. Tanaka and T. Shishidou, Department of Quantum Matter, ADSM, Hiroshima University, recalculated the linear dichroism (LD) spectra of YTiO$_3$ and found a mistake in the previous calculation. A paper including the recalculated results will be submitted soon to an appropriate journal. Table I and related discussions and conclusions in our previous Letter need to be revised as described below.

(1) On page 3, right-hand column, "c_1 from 0.6" in 12th line should be changed to "c_1 from 0.4". In the 20th line, "$c_1 = 0.8$" should be changed to "$c_1 = 0.55$". (2) In the next sentence, "This value of $c_1 = 0.8$ is consistent with the orbital ordering proposed by the NMR measurement [10]" should be deleted. (3) Although all experimental LD spectra are correct, the calculated ones for $c_1 = 0.8$ in Fig. 4 are wrong. (4) On page 4, the 7th line should be changed to "$0.55|xz\rangle + 0.84|yz\rangle$ and $0.55|xz\rangle - 0.84|yz\rangle$". (5) The sentence from the 9th line should be changed as follows. "The above values determined by the *trichroism* method are significantly different from previously proposed ones by the nuclear magnetic resonance, resonant x-ray scattering, and polarized neutron diffraction measurements of YTiO$_3$".

TABLE I. The c_1 dependence of integrated x-ray linear dichroism (XLD) intensities calculated on the basis of the Mizokawa-Fujimori model wave functions, $c_1|zx\rangle \pm c_2|yz\rangle$, is compared with experimental results. I_a, I_b, and I_c denote integrated values of x-ray-absorption spectroscopy (XAS) spectra for the electric field $\boldsymbol{E}||a$, b, and c, respectively.

		Experiment	$c_1 = 0.9$	0.8	0.7	0.6	0.5	0.4
a plane	$(I_b - I_c)/I$	-0.0271	$+0.0084$	-0.0007	-0.0097	-0.0182	-0.0259	-0.0327
b plane	$(I_c - I_a)/I$	-0.0056	-0.0394	-0.0305	-0.0197	-0.0085	$+0.0025$	$+0.0130$
c plane	$(I_a - I_b)/I$	$+0.0261$	$+0.0310$	$+0.0312$	$+0.0295$	$+0.0267$	$+0.0234$	$+0.0197$
	$\{(I_b - I_c) + (I_c - I_a) + (I_a - I_b)\}/I$	-0.0066	0	0	0	0	0	0
	$(I_b - I_c)/(I_a - I_b)$	-1.038	-0.271	-0.022	-0.329	-0.682	-1.107	-1.660
	$(I_c - I_a)/(I_a - I_b)$	-0.213	-1.271	-0.978	-0.668	-0.318	$+0.107$	$+0.660$