Indication of intrinsic room-temperature ferromagnetism in Ti$_{1-x}$Co$_x$O$_{2-\delta}$
thin film: An x-ray magnetic circular dichroism study

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Soft x-ray magnetic circular dichroism (XMCD) measurements at the Co $L_{2,3}$ edges of Co-doped rutile TiO$_2$ at room temperature revealed clear multiplet features characteristic of ferromagnetic Co$^{2+}$ ions coordinated by O$^{2-}$ ions, being in sharp contrast to the featureless XMCD spectrum of Co metal or metallic clusters. The absorption and XMCD spectra agree well with a full atomic-multiplet calculation for the Co$^{2+}$ high-spin state in the $D_{2h}$-symmetry crystal field at the Ti site in rutile TiO$_2$. The results indicate that the ferromagnetism arises from the Co$^{2+}$ ions substituting the Ti$^{4+}$ ions.


Dilute magnetic semiconductors with room-temperature ferromagnetism are promising materials for spintronics devices, in which both spin and charge degrees of freedom are utilized.$^{1,2}$ The finding of ferromagnetism at room temperature in Co-doped rutile and anatase TiO$_2$ (Refs. 3 and 4) triggered subsequent intensive studies of various oxide semiconductors doped with magnetic ions.$^{5,6}$ Shinde *et al.* studied ferromagnetic nanoparticles that vanish with high-temperature annealing and on intrinsic ferromagnetism remaining after a heat treatment in anatase-type Ti$_{1-x}$Co$_x$O$_{2-\delta}$ films.$^7$ Measurements of the anomalous Hall effect (AHE) and visible-UV magnetic circular dichroism (MCD) in rutile-type Ti$_{1-x}$Co$_x$O$_{2-\delta}$ indicated that charge carriers are responsible for intrinsic ferromagnetism. However, the claim for intrinsic ferromagnetism by AHE was disputed by subsequent work,$^10$ suspecting that Co nanoparticles may be responsible for the AHE. Thus, whether the ferromagnetism is intrinsic or extrinsic has been the subject of much debate.

Soft x-ray magnetic circular dichroism (XMCD) in core-level absorption is especially suitable for approaching the present issue, because it provides element-specific, valence-orbital-selective, microscopic information about the electronic and magnetic states. XMCD measurements were reported on, e.g., Mn-doped GaAs (Ref. 11) and on Co-doped ZnO.$^{12}$ showing ferromagnetism at low temperatures. Shimizu *et al.*$^{13}$ measured Co $K$-edge x-ray absorption spectra (XAS) in anatase-type Co-doped TiO$_2$ films, confirming the valence state of Co as $2^+$, and detected an XMCD signal, which probes the Co 4$p$ states directly, but not the magnetic Co 3$d$ states. Kim *et al.*$^{14}$ have studied Co-doped anatase-type Ti$_{1-x}$Co$_x$O$_2$ thin films with various $x$ by XMCD measurements at the Co $L_{2,3}$ edges. On the contrary, they observed an XMCD spectral line shape nearly identical to that of metallic Co, and found that this XMCD signal increased with annealing the sample. It was therefore suspected that the ferromagnetism in Ti$_{1-x}$Co$_x$O$_2$ was due to segregated metallic Co clusters.$^{14}$ Thus, it is still open whether the reported room-temperature ferromagnetism is intrinsic or not.

Here, we report on a combined experimental and theoretical Co $L_{2,3}$-edge XMCD study of rutile-type Ti$_{0.97}$Co$_{0.03}$O$_{2-\delta}$ as-deposited films. We observed clear multiplet features at the Co $L_{2,3}$ edges in the XMCD spectrum corresponding to those in XAS of Ti$_{0.97}$Co$_{0.03}$O$_{2-\delta}$. The experimentally observed XMCD multiplet features agree qualitatively well with the results of a full atomic-multiplet calculation for high-spin Co$^{2+}$ ions under $D_{2h}$-symmetry crystal field around the Co site in rutile TiO$_2$. Our experimental and theoretical observations strongly indicate intrinsic ferromagnetism arising from Co$^{2+}$ ions substituting the Ti$^{4+}$ ions.

Rutile-type Ti$_{0.97}$Co$_{0.03}$O$_{2-\delta}$ epitaxial films were synthesized by the pulsed laser deposition method at 400 °C at oxygen pressure of $1 \times 10^{-7}$ Torr. Ferromagnetism was confirmed at room temperature for the present films by both anomalous Hall effect and magnetization measurements.$^3$
The present samples also showed a MCD signal in the visible-UV region at room temperature. XAS and XMCD spectra at the Co L₂,₃ edges were measured on bending-magnet (BL-11A) and helical-undulator (AR-NE1B) beamlines at the Photon Factory. Polarization-dependent high resolution XAS were measured at room temperature with the total electron-yield method without Ar ion sputtering or annealing in order to avoid the segregation of metallic Co nanoclusters induced by surface treatments. Magnetic fields of ±1 T were applied to the samples.

Figure 1 shows the Co L₂,₃-edge XAS and XMCD spectra of the as-deposited rutile-type Ti₀.₉₇Co₀.₀₃O₂₋δ film. Here, \( \mu_+ \) and \( \mu_- \) stand for the absorption coefficients for the photon helicity, \( h \), parallel and antiparallel to the Co 3d majority-spin direction, respectively. Both the XAS and XMCD \( \Delta \mu \) spectra were corrected for the degree of circular polarization of the incident light. The XAS of the rutile-type Ti₁₋₀.₀₃Co₀.₀₃O₂₋δ thin film showed multiplet features. In the following, we refer to each multiplet feature as A–G. The XMCD spectrum showed clear multiplet features that almost corresponded one-to-one to those in the XAS.

Figure 2 shows the expanded XAS and XMCD spectra of Ti₀.₉₇Co₀.₀₃O₂₋δ in the Co L₂,₃-edge region. The XMCD spectrum of metallic Co is also shown in Fig. 2 for a comparison. A striking point here is that the XMCD spectrum of Ti₀.₉₇Co₀.₀₃O₂₋δ showed a clear negative peak at the energy corresponding to feature D in the XAS. It is emphasized that this negative XMCD peak at D was not observed in the XMCD spectrum of metallic Co. The dominant negative peak in the XMCD spectrum showed a line shape more flattened than that in the XMCD spectrum of metallic Co, indicating overlapping, unresolved multiplet features corresponding to features A–E in the XAS. This peculiar XMCD spectrum is in sharp contrast to the smooth and featureless XMCD spectrum of metallic Co, which is plotted for a comparison on a scale reduced by a factor of 0.06.

We now compare in Fig. 3 the experimental XAS and XMCD spectra with the results of full atomic-multiplet calculations. The calculation method is described elsewhere. The calculations were made for a low-spin Co²⁺ ion in a crystal field with \( O_h \) symmetry, the high-spin Co²⁺ ion in a crystal field with \( O_h \) and \( D_{2h} \) symmetries. \( D_{2h} \) is the local symmetry around the Ti site in the rutile-type structure. The possibility of the low-spin Co²⁺ ion is immediately excluded from a clear disagreement of the experimental XAS and
Comparison with the experimental XMCD spectrum. The calculated XMCD spectra were scaled by a factor of 1/30 for a comparison with the calculated spectra for the Co2+ high-spin configuration and are located at the Ti sites of TiO2. By using the integrals18

\[ \text{AL}_{\text{orb}} = \text{AL}_{\text{spin}} + 7 \text{m}_T = \frac{2(2\text{AL}_{\text{L}_3} - 2\text{AL}_{\text{L}_2})}{\text{AL}_{\text{L}_3} + \text{AL}_{\text{L}_2}} \times n_m \mu_B, \]

where \( \text{AL}_{\text{L}_2} \) and \( \text{AL}_{\text{L}_3} \) are the \( \text{L}_2 \) and \( \text{L}_3 \) edge integrated XAS and XMCD intensities, respectively, \( n_m \) is the 3D hole number, and \( m_T \) is the magnetic quadrupole moment. By using the integrals18 \( p, q, r \) and \( r \) in Fig. 1, and assuming a nominal value of \( n_m = 3.0 \) in a Co2+ ion, the orbital and the effective spin moments were determined to be \( m_{\text{orb}}(\text{Co}) = (0.013 \pm 0.002) \mu_B \) and \( m_{\text{spin}}(\text{Co}) + 7m_T(\text{Co}) = (0.12 \pm 0.01) \mu_B \). We thus obtained the total moment \( m_{\text{total}}(\text{Co}) = m_{\text{spin}} + m_{\text{orb}} + 7m_T = (0.13 \pm 0.01) \mu_B \). The value of \( m_{\text{total}} = 0.13 \mu_B \) is smaller by a factor of \(~7~8\) than \( m_{\text{total}}(\text{Co}) = 1.0 \mu_B \), determined by magnetization measurements.6 The origin of this discrepancy is not clear at present, but a possible cause is the formation of a magnetically dead layer on the film surface.

In conclusion, we have verified that the ferromagnetism in a rutile-type Ti3O7Co0.03O2−δ film is caused by high-spin Co2+ ions substituting the Ti4+ ions on the basis of an element-specific XMCD study. The present result provides key information for understanding of dilute magnetic semiconductors based on wide band-gap oxides and for the development of spintronic devices using them.

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