Bulk and surface magnetization of Co atoms in rutile Ti$_{1-x}$Co$_x$O$_{2-\delta}$ thin films revealed by x-ray magnetic circular dichroism

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Abstract

We have studied magnetism in Ti$_{1-x}$Co$_x$O$_{2-\delta}$ thin films with various $x$ and $\delta$ by soft x-ray magnetic circular dichroism (XMCD) measurements at the Co L$_{2,3}$ absorption edges. The estimated ferromagnetic moment by XMCD was 0.15–0.24 $\mu_B$/Co at the surface, while in the bulk it was 0.82–2.25 $\mu_B$/Co, which is in the same range as the saturation magnetization of 1.0–1.5 $\mu_B$/Co. These results suggest an intrinsic origin of the ferromagnetism. The smaller moment of the Co atom at the surface is an indication of a magnetically dead layer of a few nanometers thick at the surface of the thin films.

(Some figures in this article are in colour only in the electronic version)
with various Co concentrations \( x \) and oxygen vacancy \( \delta \) to clarify the origin of the ferromagnetism. XAS is well known as a very useful method to determine the electronic structure of transition-metal atoms, and its XMCD signal reflects the magnetic state of the same atoms. Mamiya et al.’s XMCD spectra of \( \text{Tl}_{1-x} \text{Co}_x \text{O}_2 \) \([11]\) are distinctly different from the previous results by Kim et al.\([5]\), where they studied \( \text{Tl}_{1-x} \text{Co}_x \text{O}_2 \) samples heat-treated prior to the measurements. They observed no multiplet features at the Co L\(_{2,3}\) edges in their XMCD spectra, attributing the XMCD signals to those of segregated metallic Co clusters. The segregated Co clusters in their samples obviously arose from high annealing temperature (673 K) in a vacuum, as indicated by the systematic increase of the XAS and XMCD signals of metallic Co \([5]\), and may not be due to the intrinsic properties of \( \text{Tl}_{1-x} \text{Co}_x \text{O}_2 \). Mamiya et al.’s Co L\(_{2,3}\) result \([11]\) clearly indicates that the Co\(^{2+}\) ions in rutile \( \text{Tl}_{1-x} \text{Co}_x \text{O}_2 \) are in the divalent high-spin ionic state, Co\(^{2+}\), indicating that the doped Co atoms substituted for the Ti sites and are responsible for the ferromagnetism \([11]\). However, the XMCD signal corresponds to only \( \sim 0.1 \mu_B/\text{Co} \), much smaller than the saturation magnetization of \( \sim 1.0 \mu_B/\text{Co} \) deduced from superconducting quantum interference device (SQUID) measurements for bulk \([15]\). In this study, we compare XMCD results taken using the surface sensitivity in agreement with Mamiya et al.’s \([11]\) total electron yield (TEY) and those taken using the bulk-sensitive total fluorescence yield (TFY) mode, together with SQUID measurements. In the TEY mode, we observed a small XMCD signal at the Co L\(_{2,3}\) edges, which corresponds to \( \sim 0.15–0.24 \mu_B/\text{Co} \), while in the TFY mode it was 0.82–2.25 \( \mu_B/\text{Co} \), which is much larger than Mamiya et al.’s \([11]\) result and consistent with SQUID measurements. We have thus found that the Co ion indeed has a large moment corresponding to the bulk magnetization. The spectral line shape can be accounted for by that of the Co\(^{2+}\) atom, showing that the origin of magnetization should be Co atoms in the \( \text{Tl}_{1-x} \text{Co}_x \text{O}_2 \) oxide matrix.

Rutile \( \text{Tl}_{1-x} \text{Co}_x \text{O}_2 \) (101) epitaxial thin films with \( x = 0.03, 0.05 \) and 0.10 were synthesized by the pulsed laser deposition method on r-sapphire substrates at 673 K at different oxygen pressures, \( P_{\text{O}_2} = 10^{-6} \) or \( 10^{-7} \) Torr \([2]\). The samples fabricated in oxygen pressure \( P_{\text{O}_2} = 10^{-6} \) and \( 10^{-7} \) Torr are named as low-\( \delta \) and high-\( \delta \), respectively, since the number of oxygen vacancies increases with decreasing oxygen pressure. Segregation of secondary phases was not observed under careful inspection by x-ray diffraction, atomic force microscopy (AFM), scanning electron microscopy (SEM), and transmission electron microscopy (TEM). Its ferromagnetism at room temperature was confirmed by Hall effect measurements, magnetization measurements, and MCD measurements in the visible region \([2, 14, 15]\). The XAS and XMCD measurements were performed at BL-11A of the National Synchrotron Radiation Research Center, Taiwan. In XMCD measurements, magnetic fields were applied to the sample along the out-of-plane direction. XAS and XMCD spectra were obtained in the TEY and TFY modes without surface preparation in order to avoid possible destruction of the sample surfaces. The probing depth of the TEY mode and TFY mode was \( \sim 5 \) and 100 nm, respectively.

Figures 1(a) and (b) show the magnetic properties of \( \text{Tl}_{1-x} \text{Co}_x \text{O}_2 \) at 300 K with different \( x \) and electron carrier density \( n_e \). It is clear from figure 1 that the magnetization \( M(H) \) in the range 1.0–1.5 \( \mu_B/\text{Co} \) with coercive force around several tens of Oersted, and increases with \( \delta \) or \( n_e \). In \( M(H) \) measurements, magnetic field was applied to the sample out-of-plane, i.e. in the direction of rutile (101). AHE measurements for \( \text{Tl}_{1-x} \text{Co}_x \text{O}_2 \) with different \( n_e \) and \( x \) also showed the same magnetic field dependences. The resultant magnetic ‘phase diagram’ shows that higher \( n_e \) and \( x \) induce the ferromagnetic phase as shown in figure 1(b).

In figure 2, we show the Co L\(_{2,3}\)-edge XAS and XMCD spectra of \( \text{Tl}_{1-x} \text{Co}_x \text{O}_2 \) \((x = 0.03, 0.05, \text{ and } 0.10 \text{ with low-} \delta \text{ and high-} \delta \) thin films taken in the TEY mode. In the figure, \( \mu_+ \) and \( \mu_- \) stand for the absorption coefficients for photon helicity parallel and antiparallel to the Co majority spin direction, respectively. The XMCD spectra \((\Delta \mu = \mu_+ - \mu_-)\) have been corrected for the degree of circular polarization of the incident
light. The XAS spectra of the rutile-type $\text{Ti}_{1-x}\text{Co}_x\text{O}_{2-\delta}$ thin films showed multiplet features. Here, we follow Mamiya et al. [11] and refer to each multiplet feature as A-G. The XMCD spectra show clear multiplet features that correspond almost one-to-one to those in the XAS spectra. The line shapes of the XAS and XMCD spectra are almost the same as in Mamiya et al. [11]. While the saturation moments deduced from the SQUID magnetization measurements are $1.0–1.2\,\mu_B/\text{Co}$, consistent with Mamiya et al. [11], the present experiment clearly reveals multiplet features in the XMCD spectra corresponding to those in XAS without annealing, consistent with the ferromagnetism arising from $\text{Co}^{2+}$ ions, which are coordinated by $\text{O}^{2-}$ ions [11].

The experimental data, i.e. XAS and XMCD spectra, show qualitatively the good agreement with the calculated spectra for the $\text{Co}^{2+}$ high-spin configuration in the $D_{2h}$ crystal field [11].

Table 1. Electronic structure parameters for rutile Co-doped $\text{TiO}_2$ thin film used in the cluster model calculations in units of eV: the charge-transfer energy $\Delta$, the on-site 3d–3d Coulomb energy $U_{dd}$, and the 3d–2p Coulomb energy $U_{dc}$ on the Co ion, the hopping integral between Co 3d and O 2p $V_{Eg}$, and the crystal field 10 $Dq$.

| Crystal symmetry | $\Delta$ | $U_{dd}$ | $U_{dc}$ | $V_{Eg}$ | 10 $Dq$ | weight (%) |
|------------------|----------|----------|----------|---------|--------|-----------|
| $D_{2h}$ low spin| 4        | 5        | 7        | 1.1     | 1.1–1.2 | 38        |
| $O_h$ low spin   | 3        | 6        | 7.5      | 1.1     | 1.1–1.2 | 38        |
| $O_h$ high spin  | 2        | 5        | 7.5      | 1.1     | 0.8–0.9 | 24        |

Figure 4 shows the magnetization estimated from the XMCD spectra taken in the TFY and TEY modes using the calculated spectra for the $\text{Co}^{2+}$ in bulk $\text{Ti}_{1-x}\text{Co}_x\text{O}_2$ with random crystal fields$. The parameters used in the calculations are listed in Table 1.

Figure 4 shows the magnetization estimated from the XMCD spectra taken in the TFY and TEY modes using

7 The calculated spectra are the weighted sum of 38% of $D_{2h}$ low-spin, 38% of $O_h$ low-spin, and 24% of $O_h$ high-spin crystal fields. This result again suggests that the majority of the ferromagnetic Co ions in bulk $\text{Ti}_{1-x}\text{Co}_x\text{O}_2$ have $\text{Co}^{2+}$ with random crystal fields.

Figure 2. (a) Co L$_{2,3}$ XAS and (b) and (c) XAS and XMCD spectra of rutile-type $\text{Ti}_{1-x}\text{Co}_x\text{O}_{2-\delta}$ samples for $x = 0.05$, high-$\delta$ taken in the TEY mode at $T = 300\,\text{K}$ and $H = 1\,\text{T}$.
Figure 3. (a) Co L\textsubscript{2,3} XAS and (b) and (c) XAS and XMCD spectra of rutile-type Ti\textsubscript{1−x}Co\textsubscript{x}O\textsubscript{2−δ} samples for x = 0.05, high-δ taken in the TFY mode at T = 300 K and H = 1 T.

Figure 4. M−H relation of SQUID magnetization and the magnetization estimated from the XMCD spectra Ti\textsubscript{1−x}Co\textsubscript{x}O\textsubscript{2−δ}. optical sum rules [19] compared with the M−H curves from magnetization measurements as well as cluster model calculations. For the validity of the sum rule in this case we divided the obtained spin magnetic moment by a correction factor 0.92 [16]. The magnetic moment obtained from the cluster model calculation is 1.48 μ\textsubscript{B}/Co. Nevertheless, the
Co magnetic moment is found to be obviously much larger in the bulk region than in the surface region. Since the TFY suffers from self-absorption then the magnetic moment obtained by the optical sum rule is not as accurate as the TEY mode. The magnetizations estimated from the XMCD spectra taken in the bulk-sensitive TFY mode are similar to those estimated from the SQUID measurements as well as from cluster model calculations, which strongly suggest that the Co ions in the bulk region are responsible for the ferromagnetism, while the surface layer of the film looks like a magnetically dead layer, as confirmed by the XMCD taken in the surface-sensitive TEY mode. TiO$_2$ has an extraordinary chemical stability, hence we can rule out possible surface degradation as a cause of decrease in surface magnetization. From surface characterization techniques such as AFM and reflection high energy electron diffraction, we have not observed any change in the surface state. Also, from spectroscopic techniques, we have not observed a significant time dependence of XMCD and x-ray photoemission spectroscopy. Figure 1(a) shows magnetic hysteresis of Ti$_{1-x}$Co$_x$O$_{2-δ}$ with different $x$. The coercive force is so small that the hysteresis is difficult to resolve by the XMCD setup. The magnetic anisotropy with out-of-plane easy axis is not so strong in Ti$_{1-x}$Co$_x$O$_{2-δ}$. As reported by Fukumura et al [15], even the out-of-plane anisotropy depends on Co content and carrier density. Thus, it is difficult to form a unified explanation of the magnetic anisotropy at present.

In conclusion, we have studied the high temperature ferromagnetism observed in rutile-type Ti$_{1-x}$Co$_x$O$_{2-δ}$ films using x-ray magnetic circular dichroism at the Co L$_2$ edges (both in the TEY and TFY mode). These results show that the high temperature ferromagnetism originates from the Co$^{2+}$ atoms; charge carriers induce the ferromagnetism most probably. The magnetic moment of the Co ions as long as 0.82–2.25 $\mu_B$/Co was first observed by the bulk-sensitive TFY method. The magnetic moment value deduced with the TEY mode (0.15–0.24 $\mu_B$/Co) indicates the presence of a magnetically dead layer of $\sim$5 nm thickness on the sample surface.

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