Soft x-ray magnetic circular dichroism study of Ca_{1-x}Sr_{x}RuO_{3} across the ferromagnetic quantum phase transition


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Ca_{1-x}Sr_{x}RuO_{3}, which is ferromagnetic for Sr concentration x > 0.3, has been studied by x-ray magnetic circular dichroism (XMCD) in Ru 3p and O 1s core-level x-ray absorption. XMCD signals appear at x ~ 0.3 and monotonically increase with x in the ferromagnetic phase. While the monotonic increase of the XMCD signals with x is of a typical Stoner-type, the absence of appreciable change in the spectral line shapes of both the Ru 3p and O 1s XMCD spectra indicate that the itinerant-electron ferromagnetism in Ca_{1-x}Sr_{x}RuO_{3} is influenced by strong electron correlation.

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Recently a number of unconventional superconductors in the vicinity of magnetic phases have been discovered, such as UGe_{2}, URhGe, and ZrZn_{2}. Although the pairing mechanism has not been established in these materials, it is presumed that quantum critical fluctuations are involved for the coexistence/competing ferromagnetism and superconductivity. Magnetic quantum critical transitions have also been observed in Ru oxides. The single-layer Sr_{2}RuO_{4} is a spin-triplet superconductor with quasi-two-dimensional Fermi liquid state, while non-Fermi-liquid behavior appears in triplet superconductor with quasi-two-dimensional Fermi liquid.

SrRuO_{3}, the n ~ 3 member of the Ruddlesden-Popper type Ru oxides Sr_{n+1}RuO_{3+n}, is one of few ferromagnetic metallic oxides (T_{C} ~ 160 K), and its unique ferromagnetism has fascinated many researchers for several decades. Neumeier et al. have shown that the Curie temperature decreases under hydrostatic pressure. The Rhodes-Wohlfarth ratio \mu_{eff}/\mu_{ord} ~ 1.3 for SrRuO_{3} is similar to Ni metal, indicating that the magnetic properties of SrRuO_{3} are close to those of localized electron systems. According to photoemission studies of SrRuO_{3}, electron-correlation effects in the Ru 4d bands are relatively strong. Recent optical studies have shown that SrRuO_{3} is strongly deviated from a conventional Fermi liquid. With substitution of Ca for Sr, the Curie temperature decreases and a ferromagnetic-to-paramagnetic transition occurs at the Sr concentration of x ~ 0.3. With Ca substitution, the Ru-O-Ru bond angle decreases from ~165° to 150° but no change in the Ru-O distance has been observed, which means that the Ca substitution decreases the Ru 4d band width and that electron correlation within the Ru 4d band is enhanced. CaRuO_{3} is also metallic but does not show long-range magnetic order down to 4.2 K. At high temperatures, it shows a negative Weiss temperature, suggesting antiferromagnetic correlations. Mukuda et al., however, using NMR deduced that CaRuO_{3} is close to a ferromagnetic metal since the Stoner factor was estimated to be close to 1. He and Cava have reported that ferromagnetic interaction is observed by replacing Ru by nonmagnetic Ti (Ti^{4+} has electron configuration 3d^{0}) by as small amount as 2%. Therefore, CaRuO_{3} is considered to be a metal close to a ferromagnetic instability, and ferromagnetic transition in Ca_{1-x}Sr_{x}RuO_{3} is expected to be a paramagnetic to ferromagnetic quantum phase transition.

Recently, Park et al. and Takizawa et al. have studied the electronic structures of Ca_{1-x}Sr_{x}RuO_{3} using epitaxial thin films by photoemission and x-ray absorption spectroscopy and confirmed that electron-correlation effects increase in going from SrRuO_{3} to CaRuO_{3} due to the spectral weight transfer from the coherent to incoherent parts of the Ru 4d band spectra. However, the relationship between the systematic change in the electron correlation strength and the change in the magnetic properties is not clear. In this paper, in order to gain further information about the magnetic properties of the system, a series of Ca_{1-x}Sr_{x}RuO_{3} samples (0 ~ x ~ 1) have been studied by soft x-ray magnetic circular dichroism (XMCD) in core-level soft x-ray absorption spectroscopy (XAS).

Sintered polycrystalline samples of Ca_{1-x}Sr_{x}RuO_{3} were prepared in the following procedure. A stoichiometric mixture of RuO_{3}, SrCO_{3}, and CaCO_{3} powders was prefired at 1000 °C for 24 h in air. Then the mixture was pressed into a pellet and fired at 1200 °C for 48 h in air. The product was milled, pressed into a pellet again (~2000 K g/cm^{2}) and fired again at 1400 °C for 48 h in air. XAS and XMCD spectra from the Ru 3p and O 1s core levels were measured at the soft x-ray beamline BL23-SU of SPring-8 in the total-electron-yield mode. The energy resolution was ~130 meV.
FIG. 1. (Color online) Magnetization curves of Ca$_{1-x}$Sr$_x$RuO$_3$ (0 ≤ x ≤ 1) measured using a SQUID magnetometer at 30 K. The inset shows the magnetization at 2 T as a function of x.

at hν ~ 700 eV and the degree of circular polarization was estimated to be ≥95% at the Ni L$_{2,3}$ edge from comparison with Ni 2p XMCD reported in the literature. The base pressure of the measurement chamber was 1 × 10$^{-8}$ Pa. A fresh surface was obtained before each series of measurements by scraping the samples under an ultrahigh vacuum at 30 K. XMCD was measured by switching the helicity of the incident circularly polarized light under a fixed applied magnetic field of 2 T. Then, the magnetic field was inverted and the two XMCD spectra were averaged to eliminate suspicious signals. Magnetization of Ca$_{1-x}$Sr$_x$RuO$_3$ were measured using a superconducting quantum interference device (SQUID) magnetometer.

Figure 1 shows the magnetization curves of the Ca$_{1-x}$Sr$_x$RuO$_3$ samples (0 ≤ x ≤ 1) measured at 30 K. Hystereses loops were observed for x ≥ 0.4, i.e., in the ferromagnetic phase. The magnetization was not saturated up to 2 T, which can be attributed to the increase of the exchange splitting of the Ru 4d $t_{2g}$ band under the high magnetic field. Even though hystereses loops were not observed for x ≤ 0.3, the magnetization at 2 T increases gradually with Sr concentration as shown in the inset of Fig. 1. Above the critical concentration of x ~ 0.3, the magnetization at 2 T increases strongly compared with that in the paramagnetic phase of x ≤ 0.3. Coercive force also increases with the Sr concentration for x ≥ 0.4. This is in accordance with the scenario that ferromagnetic transition in Ca$_{1-x}$Sr$_x$RuO$_3$ is a paramagnetic to ferromagnetic transition and that the ferromagnetic interaction increases with Sr concentration in the ferromagnetic phase.

Figure 2(a) shows the Ru 3p XAS spectra for photon helicity parallel ($\mu^+$) and antiparallel ($\mu^-$) to the Ru 4d majority-spin direction and the XMCD spectrum $\Delta \mu = \mu^+ - \mu^-$ of SrRuO$_3$. The absorption peaks at ~463 and ~485 eV are due to transitions from the Ru 3p$_{3/2}$ and 3p$_{1/2}$ core levels into the Ru 4d band. Other structures located around ~476 and ~498 eV are attributed to transitions into Ru 5s states. The background is due to transition to the continuum above the Fermi level and is composed of two step functions at the Ru 3p$_{3/2}$ (463 eV) and 3p$_{1/2}$ (485 eV) XAS peaks with the intensity proportional to the degeneracy of the core level. The Ru 3p XAS [(\(\mu^+ + \mu^-)/2\)] spectra and XMCD spectra of Ca$_{1-x}$Sr$_x$RuO$_3$ (0 ≤ x ≤ 1) are shown in Figs. 2(b) and 2(c), respectively. In both Ru 3p$_{3/2}$ and 3p$_{1/2}$ XAS spectra, not only peaks but also shoulder structures were observed on the lower photon energy sides of the peaks. In the inset of Fig. 2(b), the Ru 3p$_{3/2}$ XAS spectra of CaRuO$_3$ and SrRuO$_3$ are compared with the Ru 4d partial density of states of CaRuO$_3$ and SrRuO$_3$. They have been broadened with a Gaussian function of 1 eV FWHM and shifted by 461.3 eV for CaRuO$_3$ and 461.7 eV for SrRuO$_3$. We attribute these
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For $x > 0.3$ XMCD signal increased in proportion to the increased Sr concentration as shown in the inset of Fig. 2(c) and in Fig. 4. This is consistent with the above observation (Fig. 1) that the magnetization in the Ru 4d band increased linearly as the Sr concentration $x$ increased beyond the critical value of $x \sim 0.3$. Such a behavior is different from the simple Stoner model of itinerant ferromagnetism, according to which changes in the line shape of the XMCD spectra are expected to occur across the ferromagnetic transition due to the exchange splitting of the Ru 4d band.

In order to investigate the influence of the magnetization on the ligand O 2p states, XMCD measurements were also made in O 1s XAS. Figure 3 shows the O 1s XAS and XMCD spectra of Ca$_{1-x}$Sr$_x$RuO$_3$. The O 1s XAS spectra represent the unoccupied part of the Ru 4d band mixed with O 2p orbitals: Transitions into the Ru 4d $t_{2g}$ and $e_g$ bands are in the regions 528–530.5 eV and 530.5–534 eV, respectively. The peak at $\sim$529 eV and the shoulder structure around 530 eV correspond to the coherent and incoherent parts of the Ru 4d $t_{2g}$ bands, respectively, as reported by Takizawa et al., indicating strong electron correlation in the Ru 4d $t_{2g}$ band. The Sr 4d and Ca 3d states are in the region 534–540 eV, and the Ru 5s states are in the region 540–550 eV. Significantly, a large negative XMCD structure was observed in the Ru 4d $t_{2g}$ band region, indicating that the influence of the magnetization is strong only in the Ru 4d $t_{2g}$ band region and negligibly small in the other regions. The XMCD signal became the largest at $x = 1$ amounting to $\sim 7\%$ of the O 1s peak intensity.

Figure 3(b) shows that as the Sr concentration $x$ increases, the intensity of O 1s XAS decreases in the incoherent part and increases in the coherent part. Since the number of electrons in the Ru 4d band does not change with $x$, this means that spectral weight is transferred from the incoherent part to the coherent part within the Ru 4d $t_{2g}$ band, i.e., electron correlation strength decreases within the Ru 4d $t_{2g}$ band. As for the O 1s XMCD spectra shown in Fig. 3(c), the XMCD intensity increases linearly as the Sr concentration $x$ increases in the ferromagnetic phase ($x \approx 0.3$) without any appreciable change in the spectral line shape. Since the energy-integrated intensity of the O 1s XMCD spectrum is proportional to the orbital magnetic moment of the O 2p states, the orbital magnetic moment of the O 2p states increases linearly in the ferromagnetic phase.

By applying the orbital$^{28}$ and spin sum rules$^{29}$ to the Ru 3p XMCD spectra, we can estimate the orbital and spin magnetic moments of the Ru 4d states. In the case of compounds, especially, transition-metal oxides, however, magnetic moments estimated by the XMCD sum rules tend to be smaller than the magnetization measured by SQUID.$^{30,31}$ One of the causes of the discrepancy is the mixing of $p_{3/2}$ and $p_{1/2}$ components. In order to compensate the underestimation of the spin magnetic moment due to the electron–core-hole interaction, which mixes $p_{3/2}$ and $p_{1/2}$ components, correction factors were calculated.$^{12}$ Although these correction factors were calculated only for the 3d transition-metal ions, expected correction factor for the Ru 3p XMCD would be smaller and cannot explain this discrepancy, because the influence of the electron–core-hole interaction decreases along the transition-metal series with increasing spin-orbit splitting$^{32,33}$ and the spin-orbit splitting in the Ru 3p core level is as large as $\sim 20$ V.
Another possible cause of the discrepancy is that the magnetization of the O 2p electrons is also substantial. The magnetic moment of the O 2p orbitals is induced by charge transfer from the O 2p orbitals to the spin-polarized Ru 4d, however, there is no method to estimate the spin magnetic moment of the O 2p electrons. Another possible cause is that the magnetization is reduced at the surface compared to that in the bulk. Since the effective probing depth of the XAS measurement is at most 10 nm in the total electron yield mode, the estimated magnetization may be substantially influenced by electronic states at the surface. The estimated magnetization may increase by using cleaved samples or single-crystalline film samples. Finally, the use of the XMCD sum rules is strictly valid for atomic wave functions and may not be quantitatively applicable to the itinerant Ru 4d electrons.

We have estimated the orbital ($M_{\text{orb}}$) and spin ($M_{\text{spin}}$) magnetic moments of the Ru 4d states using the XMCD sum rules as follows:

$$M_{\text{orb}} = -2 \frac{\Delta A_{M_1} + \Delta A_{M_2}}{3(A_{M_1} + A_{M_2})} (10 - N_{4d}),$$  
$$M_{\text{spin}} + 7M_T = - \frac{\Delta A_{M_1} - 2\Delta A_{M_2}}{A_{M_1} + A_{M_2}} (10 - N_{4d}),$$

where $M_{\text{orb}}$, $M_{\text{spin}}$, and the magnetic-dipole moment $M_T$ are given in units of $\mu_B/\text{atom}$, $N_{4d}$ is the 4d electron occupation number which is assumed to be 4, $\Delta A_{M_1}$ and $\Delta A_{M_2}$ are the energy integrals of the 3p$_{3/2}$ and 3p$_{1/2}$ XMCD intensities, and $A_{M_1}$ and $A_{M_2}$ are the energy integrals of the 3p$_{3/2}$ and 3p$_{1/2}$ XAS intensities, respectively. In estimating the XAS intensities, background has been subtracted from the XAS spectra as shown in Fig. 2(a). In estimating the spin magnetic moment from the XAS and XMCD spectra, we have to separate the Ru 3p XMCD spectra into the 3p$_{3/2}$ and 3p$_{1/2}$ components. We have divided the Ru 3p spectra into the two components at 478 eV, where the Ru 3p XAS shows a minimum. Since our measurements were made on polycrystalline samples, the angle average would result in a vanishing magnetic-dipole term and therefore we have ignored $M_T$ in estimating the spin magnetic moment using Eq. (2).

In Fig. 4, we compare the XMCD intensities of Ru 3p$_{3/2}$ ($\sim$461.5 eV) and O 1s ($\sim$529 eV) with the magnetization measured at 2 T and the orbital and spin magnetic moments of Ru 4d estimated from the Ru 3p XMCD spectra. In the paramagnetic phase ($x \leq 0.3$), however, no orbital magnetic moment is estimated from the Ru 3p XMCD spectra since no XMCD signals are observed in the Ru 3p within experimental error in as shown in Fig. 2(c). This indirectly means that the magnetism of Ca$_{1-x}$Sr$_x$RuO$_3$ is strongly influenced by the change of electron correlation through magnetic transition. As for the O 2p states, the O 1s XMCD spectra were relatively sharp but the energy integral of the XMCD intensity was very tiny compared with that of the XAS intensity, leading to nearly the same orbital moment as that of the Ru 4d.

The orbital magnetic moment of O 2p was estimated to be as small as $\leq 1 \times 10^{-2} \mu_B/\text{atom}$ in the entire Sr concentration range on the assumption that the number of holes in the O 2p orbitals is $\sim 1$. Although the absolute value estimated from XMCD was only $\sim 60\%$ of the magnetization, the overall $x$ dependence of the XMCD intensities and estimated magnetic moments qualitatively followed the $x$ dependence of the magnetization.

The XMCD peak intensities and the magnetization increased linearly above $x \sim 0.3$ as shown in Fig. 4. These observations are consistent with the Stoner-type ferromagnetism. On the other hand, as no appreciable spectral change in the Ru 3p and O 1s XMCD spectra was observed as a function of $x$, there was no clear indication of the exchange splitting of the Ru 4d band. These observations as well as the large Rhodes-Wohlfarth ratio mean that ferromagnetism in Ca$_{1-x}$Sr$_x$RuO$_3$ is strongly influenced by electron correlation of the Ru 4d $t_{2g}$ band and is different from the Stoner-type itinerant ferromagnetism.

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21 The calculations have been done using the generalized gradient approximation method.


24 In the O 1s XAS spectra of Ca1−xSrRuO3 in Fig. 3, the dip structure at ~534 eV may be due to the contamination state owing to carbon oxides. Because of little influence on the region mixed with the Ru 4d states we ignore it in the following discussion.


31 In our preliminary study of a single-crystalline thin film of SrRuO3, XMCD signal in Ru 3p XAS became stronger than the present polycrystalline work by ~10%.