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 $x \sim 0.3$ and monotonically increase with $x$ in the ferromagnetic phase. While the monotonous 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 novel 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 coexisting/competing ferromagnetism and superconductivity. Magnetic quantum critical transitions have also been observed in Ru oxides. The single-layer Sr$_2$RuO$_3$ is a spin-triplet superconductor with quasi-two-dimensional Fermi liquid state, while non-Fermi-liquid behavior appears in Sr$_2$Ru$_{1-x}$Ti$_x$O$_4$ in the vicinity of antiferromagnetic ordering for the critical impurity concentration of $x_c \sim 0.0025$. The bilayer perovskite Sr$_3$Ru$_2$O$_7$ shows metamagnetism for a field of $\sim 5.5$ T below 10 K, and near the metamagnetic field the resistivity shows non-Fermi-liquid behavior at low temperature.

SrRuO$_3$, the $n=\infty$ member of the Ruddelsden-Popper type Ru oxides Sr$_{n+1}$Ru$_n$O$_{3n+1}$, is one of few ferromagnetic metallic oxides ($T_C \sim 160$ K) and its unique ferromagnetism has fascinated many researchers for several decades. Neuheimer et al. have shown that the Curie temperature decreases under hydrostatic pressure. The Rhodes-Wolfarth ratio $\mu_{eff}/\mu_{ord} \sim 1.3$ 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 $x \sim 0.3$. With Ca substitution, the Ru-O-Ru bond angle decreases from $\sim 165^\circ$ to $150^\circ$ 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. 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$\leq x \leq 1$) 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$_2$, SrCO$_3$ and CaCO$_3$ powders was
prefired at 1000 °C for 24 hours in air. Then the mixture was pressed into a pellet and fired at 1200 °C for 48 hours in air. The product was milled, pressed into a pellet again (∼2000 Kg/cm²) and fired again at 1400 °C for 48 hours in air. The magnetization was not saturated to eliminate suspicious signals. Magnetization of CaRuO₃ was measured by scraping the samples under an ultra-high vacuum at 30 K. XMCD was measured by switching the 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 ultra-high 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 Ca₁₋ₓSrₓRuO₃ were measured using a superconducting quantum interference device (SQUID) magnetometer.

Figure 1 shows the magnetization curves of Ca₁₋ₓSrₓRuO₃ (0≤x≤1) measured at 30 K. The inset shows the magnetization at 2 T as a function of x.

Figure 2(a) shows the Ru 3p XAS spectra μ⁺ and μ⁻ and XMCD spectra Δµ = μ⁺ - μ⁻ of Ca₁₋ₓSrₓRuO₃ (0≤x≤1). (a) XAS and XMCD spectra of SrRuO₃. Vertical lines correspond to the position of XAS and XMCD peaks. The broken line shows the background of XAS spectrum. (b) Ru 3p XAS ([μ⁺ + μ⁻]/2) spectra. In the inset of (b), the Ru 3p₃/2 XAS spectra of CaRuO₃ and SrRuO₃ are compared with the Ru 4d partial density of states broadened with a Gaussian function of 1 eV FWHM. (c) Ru 3p XMCD spectra. All the spectra have been normalized to the Ru 3p₃/2 XAS peak height. The horizontal lines in (c) show zero levels of the XMCD spectra.

FIG. 1: (Color Online) Magnetization curves of Ca₁₋ₓSrₓRuO₃ (0≤x≤1) measured using a SQUID magnetometer at 30 K. The inset shows the magnetization at 2 T as a function of x.

FIG. 2: (Color online) Ru 3p XAS spectra μ⁺ and μ⁻ and XMCD spectra Δµ = μ⁺ - μ⁻ of Ca₁₋ₓSrₓRuO₃ (0≤x≤1). (a) XAS and XMCD spectra of SrRuO₃. Vertical lines correspond to the position of XAS and XMCD peaks. The broken line shows the background of XAS spectrum. (b) Ru 3p XAS ([μ⁺ + μ⁻]/2) spectra. In the inset of (b), the Ru 3p₃/2 XAS spectra of CaRuO₃ and SrRuO₃ are compared with the Ru 4d partial density of states broadened with a Gaussian function of 1 eV FWHM. (c) Ru 3p XMCD spectra. All the spectra have been normalized to the Ru 3p₃/2 XAS peak height. The horizontal lines in (c) show zero levels of the XMCD spectra.

Magnetic interaction increases with Sr concentration in the ferromagnetic phase.

Figure 2(a) shows the Ru 3p XAS spectra for photon helicity parallel (μ⁺) and antiparallel (μ⁻) to the Ru 4d majority-spin direction and the XMCD spectrum Δµ = μ⁺ - μ⁻ of SrRuO₃. The absorption peaks at ∼463 eV and ∼485 eV are due to transitions from the Ru 3p₃/2 and 3p₁/₂ core levels into the Ru 4d band. Other structures located around ∼476 eV 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 3p₃/2 (463 eV) and 3p₁/₂ (485 eV) XAS peaks with the intensity proportional to the degeneracy of the core level. The Ru 3p XAS ([μ⁺ + μ⁻]/2) spectra and XMCD
spectra of Ca$_{1-x}$Sr$_x$RuO$_3$ (0 ≤ x ≤ 1) are shown in Figs. 2(b) and (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 peaks and shoulders to the transition to the Ru 4d $t_{2g}$ and $e_g$ bands, respectively. The fact that Ru 3p XMCD signals were only observed for the shoulder structures is consistent with this assignment. The XMCD signal showed symmetric peaks and no appreciable change was observed in the whole Sr concentration range. For the Ru 3p XAS spectra, their line shape changes throughout the whole Sr concentration range. The energy separation between the shoulder structure and the peak position for CaRuO$_3$ seems to be larger than that for SrRuO$_3$ and this separation gradually becomes smaller as the Sr concentration increases. This agrees with the result of the band-structure calculation that the tilting of the RuO$_6$ octahedra increases the energy separation between the antibonding Ru 4d $t_{2g}$ and $e_g$ bands. In addition, as the Sr concentration increases, the intensity of the shoulder structure increases. This well corresponds to the observation that in the Ru 3p XAS of Ca$_{1-x}$Sr$_x$RuO$_3$ the density of states near the Fermi level increases with Sr concentration.

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. 3. 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 $x$ ∼ 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 ∼ 529 eV and the shoulder structure around 530 eV correspond to the incoherent part and increases in the coherent part around 530 eV correspond to the incoherent part and increases in 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 ($x ≥ 0.3$) 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 orbitals $^{28}$ 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.\textsuperscript{30,31} One of the cause 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.\textsuperscript{32,33} 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\textsuperscript{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.\textsuperscript{34} 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:

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

$$M_{\text{spin}} + 7M_T = -\frac{\Delta A_{M_3} - 2\Delta A_{M_2}}{A_{M_3} + A_{M_2}}(10 - N_{4d}),$$

where $M_{\text{orb}}$, $M_{\text{spin}}$ and the magnetic-dipole moment $M_T$ are given in units of $\mu_B$/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\textsuperscript{35} 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 $\lesssim 1 \times 10^{-2} \mu_B$/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.

**FIG. 4:** (Color online) Orbital and spin magnetic moments of the Ru 4d states estimated from the Ru 3p XMCD compared with the magnetization measurements at 30 K under 2 T.
and is different from the Stoner-type itinerant ferromagnetism.

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