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Orbital magnetism in $Cd_2Os_2O_7$ studied by x-ray magnetic circular dichroism

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X-ray magnetic circular dichroism (XMCD) at the $L_{2,3}$-edge of Os has been investigated in the antiferromagnetic phase of $Cd_2Os_2O_7$, which exhibits a metal-insulator transition around 227 K. According to the sum rule, the XMCD spectra at 10 and 37 T clearly show that the ratio between the orbital magnetic moment (m_L) and spin magnetic moment (m_S) is $m_L/m_S = 0.16 \pm 0.02$, and that m_L and m_S are coupled in parallel ($m_L||m_S$). These phenomena are unusual in that the expected ground state of $Os^{5+}(5d^3)$ is an orbital singlet in a cubic crystal field, and m_L and m_S should be antiparallel for a less than half-filled system in accordance with Hund's third rule. It is likely that the spin-orbit coupling is important for explaining the observed orbital magnetism.

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I. INTRODUCTION

Spatial extension of the wave function of $5d$ electrons is generally larger than that of $3d$ or $4f$ electrons. Hence, the bandwidth (W) is large, and the electron correlation due to intra-atomic Coulomb repulsion (U) is considered to be weak in $5d$ electron systems. Since various types of exotic phenomena such as high-T_c superconductivity and heavy fermions are mostly observed in $3d$ and $4f$ electron systems where $U/W \gg 1$, $5d$ electron systems, like normal metals, might be expected to have rather simple properties. However, the recent discovery of the spin-orbit (SO) Mott state in Sr_2IrO_4[1] indicates that $5d$ electron systems such as Ir, Os, and Re oxides can exhibit a variety of intriguing phenomena. Although the correlation is thought to originate in the intermediate regime ($U/W \sim 1$) for $5d$ systems, a strong correlation can occur through the significant SO interaction. In Sr_2IrO_4, the SO interaction enhances the localized character of the $5d$ electrons ($U/W \gg 1$), resulting in the Mott insulating state.[1]

Another interesting phenomenon found in $5d$ electron systems is a continuous metal-insulator transition (MIT) in $Cd_2Os_2O_7$ near 225 K, which was first reported in 1974.[2] The MIT has attracted much attention[2–6] because of its peculiar characteristics, and the origin of the MIT remains unclear at present. According to theoretical calculations,[4] the Fermi level is located in the $5d$ band, and a semimetallic state is predicted. The MIT in $Cd_2Os_2O_7$ has been reported to be closely related to its magnetic state. Antiferromagnetic (AFM) order with weak ferromagnetism appears below the transition temperature.[3] Interestingly, no structural change has been observed at the MIT in $Cd_2Os_2O_7$,[3] in contrast to the MIT accompanying Jahn-Teller distortion in $3d$ systems such as Mn perovskite oxides.[7] One might also expect the SO interaction to be important in understanding the MIT, as in the case of Sr_2IrO_4. However, orbital magnetism and SO coupling in $Cd_2Os_2O_7$ have not yet been studied experimentally.

In the present study, we measured the x-ray magnetic circular dichroism (XMCD) in a high magnetic field to examine the orbital magnetism and SO coupling in $Cd_2Os_2O_7$. The XMCD experiment employed a synchrotron x-ray beam, which is among the most powerful tools for studying the electronic state of matter. The orbital magnetic moment m_L and spin magnetic moment m_S, where the total magnetization $m = m_L + m_S$, are separately obtained from XMCD spectra by using the sum rule.[8,9] We found a finite orbital magnetic moment in $Cd_2Os_2O_7$. We analyzed the results in terms of crystal field and SO interaction, and found that the SO coupling can be very strong. Moreover, the observed spin and orbital magnetic moments were found to be parallel with each other. Since Os^{5+} ($5d^3$) is a less than half-filled system, the spin and orbital magnetic moments are expected to be antiparallel according to Hund's third rule. This phenomenon may suggest the noncollinear arrangement of spin and orbital magnetic moments.

II. EXPERIMENTAL

The XMCD experiment on $Cd_2Os_2O_7$ was carried out on BL39XU at SPring-8. Pulsed high magnetic fields up to 37 T were generated by a miniature pulsed magnet,[10] and DC magnetic fields up to 10 T were generated by a superconducting DC magnet.[11] Polycrystalline $Cd_2Os_2O_7$ was grown from CdO and Os in a sealed quartz tube. The absorption was measured by the direct transmission method. The $Cd_2Os_2O_7$ crystals were powdered and mixed with epoxy resin so that the effective thickness was appropriate to obtain the x-ray absorption intensity $\mu t \sim 1$, where μ and t are the absorption coefficient and the thickness of the sample, respectively. The XMCD signal ($\Delta\mu t$) is the difference in absorption between the right-handed (μt^+) and left-handed (μt^-) circular polarizations: $\Delta\mu t = \mu t^+ - \mu t^-$. The details of the experimental XMCD techniques using a pulsed high field[10] and DC field on BL39XU[11] have been described elsewhere. The magnetization of $Cd_2Os_2O_7$ was measured to evaluate the sample quality and to investigate the magnetic state in a high field. The magnetization in a low magnetic field was measured on a superconducting quantum interference device (SQUID). The magnetization in a high magnetic field up to 50 T was obtained by the induction method using a conventional pulsed magnet.[12]

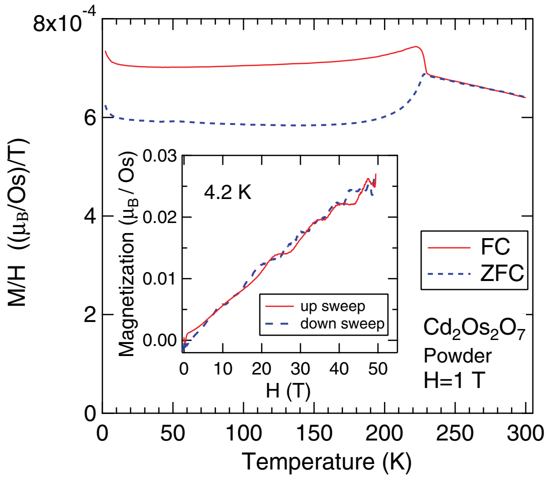

FIG. 1. (Color online) Temperature dependence of effective magnetic susceptibility, M/H. Field-cooling (FC) and zero-field-cooling (ZFC) data are shown by solid and dashed curves, respectively. Inset shows the magnetization curve up to 50 T at 4.2 K.

III. RESULTS AND ANALYSIS

Figure 1 shows the temperature dependence of the effective magnetic susceptibility, M/H, where M is the magnetization and H is the magnetic field. An abrupt change was seen in both the field-cooling (FC) and zero-field-cooling (ZFC) curves around 227 K, which is in agreement with the literature value (226 K) of the MIT;[3] thus, the observed change is attributed to the MIT. The large difference between FC and ZFC is explained by a weak ferromagnetic component.[3] The upturn seen below 10 K is considered an impurity effect. The magnetization in a high magnetic field is shown in the inset of Fig. 1. Since the magnetization is small even at 50 T, signal intensity (induction voltage of a pick-up coil) is as large as the resolution limit of the measurement system. The small oscillation-like features are due to experimental error because they do not correspond to the field-increasing and field-decreasing processes. The field dependence of the magnetization is nearly linear with slight curvature (convex upward).

The XMCD spectra at the L_3 and L_2 edges of Os are shown in Fig. 2(a) and 2(b), respectively. The x-ray absorption spectrum (XAS) and the XMCD spectrum are plotted together for the L_2 or L_3 edge of Os. The XMCD signal is as small as $10^{-2} \sim 10^{-3}$ times the absorption peak intensity, corresponding to the small magnetization (inset of Fig. 1). The signal-to-noise ratio is worse in the pulsed field data (37 T) than in the DC field data (10 T), because the duty ratio of the pulsed magnet is low in our system: The pulse duration is about 1 ms, and the cool-down waiting time of the coil is 10 min for each shot, resulting in a duty ratio of approximately 1.7×10^{-6}.[13] Although the signal-to-noise ratio of the pulsed-field data is low, the DC field data multiplied by 3.7 overlap with the pulsed-field data. This overlap is consistent with the linear field dependence of the magnetization as shown in the inset of Fig. 1. The sign of XMCD is negative at the L_3 edge and positive at the L_2 edge. The signal intensity at the L_3 edge is larger than that at the L_2 edge. As we discuss below, these results reveal that (1) the spin magnetic moment m_S has the same direction as the external magnetic field, and (2) the orbital magnetic moment m_L makes a finite contribution and is parallel with m_S.

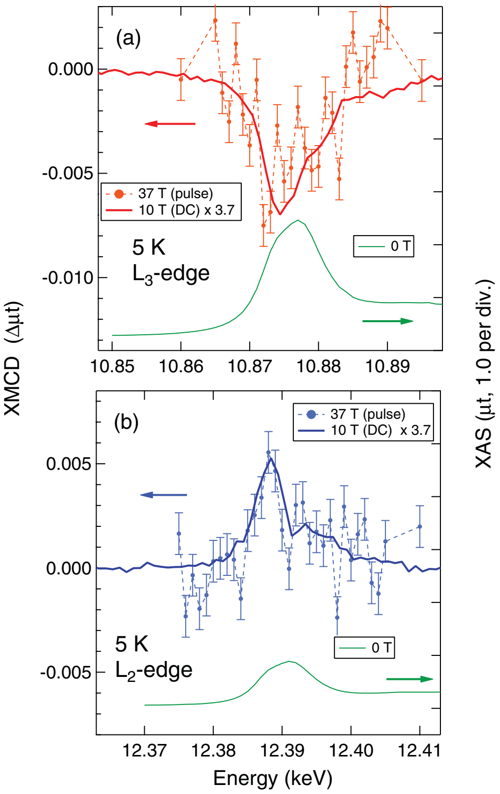

FIG. 2. (Color online) (a) XMCD spectra and XAS at L_3 edge of Os at 5 K. (b) XMCD spectra and XAS at L_2 edge of Os at 5 K.

As mentioned above, the MIT in $Cd_2Os_2O_7$ occurs at the AFM ordering temperature, suggesting that the origin of the MIT is closely related to the magnetic state. One might speculate that a magnetic field-induced insulator-to-metal transition can occur through collapse of AFM order in a high magnetic field. As shown in the inset of Fig. 1, however, only low magnetization appears, even in a high magnetic field; the magnetization of Os was found to be 0.025 μ_B/Os at 50 T. When considered at the atomic level, the $Os^{5+}(3d^3)$ state is expected to be $S = 3/2$ and the magnetization is expected to be 3 μ_B/Os if we assume that the orbital angular momentum is quenched and the g value is 2. When we assume $g = 2$ and $S = 3/2$, the magnetic field corresponding to the MIT temperature (227 K) is 112 T.

In $3d$ transition metal compounds, the orbital magnetic moment is generally small and sometimes can be disregarded, owing to the quenching effect of the crystal field. However, in $5d$ electron systems, the SO interaction is as large as the crystal field splitting.[1] By using the sum rule of the XMCD,[8,9] the orbital magnetic moment is distinguished from the spin magnetic moment. The sum rule equations are[14]

$$m_L = -\frac{2}{3}\left(\frac{I_{L_3}+I_{L_2}}{I_{\text{Abs}}}\right) n_h \mu_B \tag{1}$$

and

$$m_S = -\left(\frac{I_{L_3}-2I_{L_2}}{I_{\text{Abs}}}\right) n_h \mu_B + 7\,T_z, \tag{2}$$

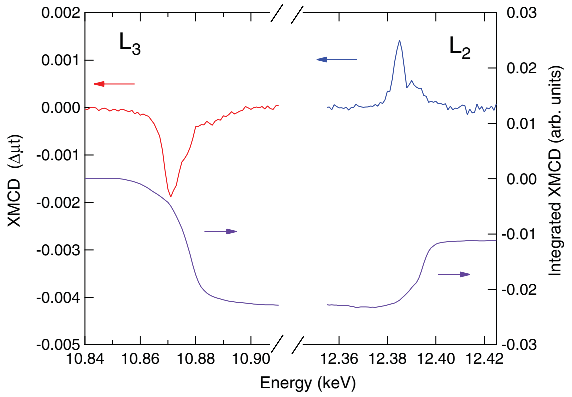

FIG. 3. (Color online) XMCD spectra and XMCD integrals at 10 T.

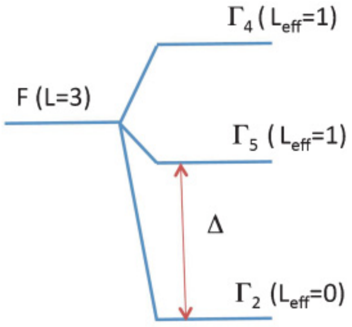

FIG. 4. (Color online) Schematic energy level diagram of d^3 state in a cubic crystal field.

where I_{L_3} and I_{L_2} are integrated XMCD signal intensities for L_3 and L_2 edges, respectively, and I_{Abs} is the integrated absorption intensity for the L_3 and L_2 edges, n_h denotes the hole number of the $5d$ band of Os, and μ_B is the Bohr magneton.

The XMCD integral $I_{L_3} + I_{L_2}$ at 10 T is plotted as a function of energy in Fig. 3, along with the XMCD spectra. The integration ranges are from 10.84 to 10.91 keV for L_3 and from 12.355 to 12.425 keV for L_2 edges. The end value of the XMCD integral is found to be -0.011. This value corresponds to the numerator of Eq. (1) and indicates the finite value of the orbital magnetic moment m_L. Using this value, m_L is determined to be $(2.45 \pm 0.25) \times 10^{-4} n_h \mu_B$. Since the dipole exchange interaction term T_z is canceled out[15] in a powder sample of a cubic crystal, the spin magnetic moment m_S is calculated to be $(1.50 \pm 0.03) \times 10^{-3} n_h \mu_B$ from the XMCD spectra and Eq. (2). Therefore, the ratio m_L/m_S is 0.16 ± 0.02, suggesting that the orbital magnetic moment contributes to the magnetism to a certain extent and cannot be completely disregarded.

Note that the obtained m_L/m_S value is positive, and that the orbital and spin magnetic moments are indicated to be coupled in parallel. According to Hund's third rule, however, m_L and m_S should be coupled in antiparallel because $Os^{5+}(5d^3)$ is a less than half-filled system. Similar phenomena have been reported in an Fe/W multilayer[16] and in $Co_{100-x}Ir_x$ alloys,[17] where Hund's third rule appears not to hold. Wilhelm *et al.*[16] and Krishnamurthy *et al.*[17] have pointed out that the strong hybridization between the different magnetic ions, namely, between Fe and W in the Fe/W multilayer and between Co and Ir in $Co_{100-x}Ir_x$ alloys, may induce the violation of Hund's third rule. In $Cd_2Os_2O_7$, however, only Os is a magnetic ion, and the origin of the phenomenon should be different from that in the previously reported cases.

IV. DISCUSSION

Here let us reconsider the meaning of the observed finite orbital component of the magnetization in $Cd_2Os_2O_7$. As we mentioned at the beginning of this paper, the orbital magnetic moment and the SO interaction are significant in Sr_2IrO_4, where Ir has $5d^5$.[1] In that case, five d electrons occupy the t_{2g} level based on the strong crystal field model, and the total spin is 1/2 (low spin state). The effective orbital angular momentum $L_{\mathrm{eff}} = 1$ couples with the spin $S = 1/2$, resulting in the effective total angular momentum $J_{\mathrm{eff}} = 1/2$.[1]

Considering the case of $5d^3$ in $Cd_2Os_2O_7$, we find that, based on the strong crystal field model, there is no orbital degree of freedom when three d electrons occupy the t_{2g} level; that is, $L_{\mathrm{eff}} = 0$. Since the spatial extension of the wave function of $5d$ electrons is large, the strong crystal field model seems reasonable not only for Sr_2IrO_4 but also for $Cd_2Os_2O_7$. However, this conclusion, that $S = 3/2$ and $L_{\mathrm{eff}} = 0$ for $Cd_2Os_2O_7$, is not in agreement with our XMCD results: We experimentally observed a finite orbital magnetic moment. We show below that the SO interaction can be important in explaining this disagreement.

According to crystal field theory, the atomic F state of a d^3 system splits into an orbital singlet state (Γ_2) and two orbital triplet states (Γ_5 and Γ_4) as shown schematically in Fig. 4. The ground state Γ_2 corresponds to the configuration where three d electrons occupy the t_{2g} orbital and the orbital singlet state is realized. Since there are matrix elements of the SO coupling between Γ_2 and Γ_5, the orbital triplet component ($L_{\mathrm{eff}} = 1$) mixes with the orbital singlet ground state. According to the literature,[18] the ratio between the orbital and spin magnetization, $\langle L\rangle/\langle 2S\rangle$, is expected to be on the order of $(\lambda/\Delta)^2$, where λ and Δ, respectively, are the SO coupling constant and the energy difference between Γ_2 and Γ_5 states. There are four spin triplet $S = 3/2$ states of Γ_2. When we consider only the lowest state in magnetic fields $|-\frac{3}{2}\rangle = |\Gamma_2, -\frac{3}{2}\rangle + \frac{3\lambda}{\Delta}|\Gamma_5(0), -\frac{3}{2}\rangle - \frac{\sqrt{6}\lambda}{\Delta}|\Gamma_5(-1), -\frac{1}{2}\rangle$, it is deduced that $\langle L\rangle = -6(\lambda/\Delta)^2$ and $\langle 2S\rangle = -3 - 33(\lambda/\Delta)^2$. Then $\langle L\rangle/\langle 2S\rangle = 2\alpha/(1 + 11\alpha)$, where α is $(\lambda/\Delta)^2$. Since $m_L/m_S = \langle L\rangle/\langle 2S\rangle \sim 0.16$ from the XMCD experiment, it is found that $\lambda/\Delta = \sqrt{0.67} \sim 0.8$. This finding suggests that the SO coupling is as large as the crystal field splitting. However, it is obvious that the crystal field model assumed is not appropriate anymore because the perturbation theory breaks down when $(\lambda/\Delta) \sim 1$. Therefore, the system considered here should be in the intermediate regime between the strong crystal field and the strong SO coupling limit as in the case of $BaIrO_3$ reported recently.[19] Another indication of the strong SO coupling is the branching ratio (BR) between the absorption peaks (white lines) of L_2 and L_3 edges. The BR is found to be about 3 in $Cd_2Os_2O_7$ as shown in Fig. 2. BR is expected to be 2 if there is no SO coupling, and the large deviation from 2 suggests the strong SO coupling.[19]

Up to this point we regarded the system as a localized spin system. The significant peak structure at the absorption edges shown in Fig. 2 indicates the local density of states of $5d$ electrons. However, the $5d$ electrons may have some itinerant character because of the large spatial extension of the wave functions even though the system shows the insulating antiferromagnetic behavior. One may also think that the hybridization effect between the Os-$5d$ electrons and the O-$2p$ electrons can be considerable. Therefore, the occupation number of the $5d$ electrons might be different from 3 ($5d^3$). At the present, however, there appears to be no reliable information on the occupation number of the $5d$-shell in $Cd_2Os_2O_7$. Further experimental and theoretical investigations are required.

Since the magnetic moment deduced from the XMCD spectra in this study is just the component (projection) of the magnetic moment along the applied magnetic field, and the magnetization is not saturated as shown in the inset of Fig. 1, it can be difficult to evaluate the hole number n_h correctly from the XMCD spectra. The magnetic moment deduced from XMCD can deviate from the magnetization measured by a conventional method when the magnetization is below the saturation value.[20] If we use $n_h = 7$ (for $5d^3$), the magnetic moment $m = m_L + m_S \sim 1.2 \times 10^{-3}\mu_B$ at 10 T, which is approximately two times larger than the magnetization obtained. (See the inset of Fig. 1.)

In the present system, the magnetic moments are ordered antiferromagnetically, and most probably the moments are noncollinear due to the geometrical frustration effect of the pyrochlore lattice.[3] Hence, the Os spins are oriented in different directions from that of applied magnetic fields, and the magnetization is induced by slight tilt of spins from the ordered direction by the applied magnetic field. The situation seems to be similar to the condition that a magnetic field is applied perpendicular to the easy-magnetization direction where the orbital and spin magnetic moments are not parallel.[20] One may speculate that spin and orbital moments are coupled antiparallel in accord with Hund's third rule, but they are forced out from the initial direction by magnetic field as schematically shown in Fig. 5, resulting in the induced moments being parallel with the applied magnetic field. We also note here that the band structure and the band filling can be important for understanding breaking the Hund's rule as discussed in the literature.[21,22] Since the band structure is directly related to the MIT, further investigation of the band structure including the strong SO coupling is required.

In conclusion, high magnetic field XMCD analysis of $Cd_2Os_2O_7$ using the sum rule clearly shows that the orbital magnetic moment contributes to the magnetism of this unusual compound. A possible explanation for the orbital magnetism observed is that the strong SO interaction induces mixing between the orbital singlet and triplet states of $5d^3(Os^{5+})$. The ratio between the spin and orbital magnetic moments, m_L/m_S, is found to be 0.16 ± 0.02. The positive value of m_L/m_S indicates parallel coupling between the spin and orbital angular momentums; this result appears incompatible with Hund's third rule because the $5d^3$ system is less than half-filled. This phenomenon can be related to the magnetic structure of this material. The magnetic-field-angle-dependent XMCD experiment of a single crystal will give valuable information to solve this problem.

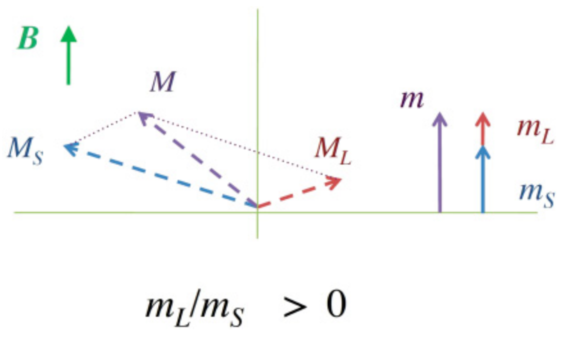

FIG. 5. (Color online) Schematic possible diagram of an arrangement of spin and orbital magnetic moments. The induced spin and orbital magnetizations, m_L and m_S, are along with the applied magnetic field. M_L and M_S are the net magnetic moments of an orbital and spin, respectively.

The observed orbital magnetism and implication of importance of the SO interaction would shed new light on understanding the electronic structure and MIT of $Cd_2Os_2O_7$. To confirm the validity of our findings, further studies for evaluation of the hole number n_h and the band effect are strongly required; the oxygen K-edge XMCD will give us the information on the hybridization between Os-$5d$ and O-$2p$ electrons. Another intriguing experiment would be a magnetization measurement in ultra-high magnetic fields in the range of several hundreds of tesla;[23] the magnetic moment of Os can be determined directly by the saturation value of the magnetization.

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