Soft X-ray Absorption Magnetic Circular Dichroism Study of Ferromagnetic Superconductor UGe₂

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X-ray absorption magnetic circular dichroism (XMCD) at the U N₄s edge was measured for the ferromagnetic superconductor UGe₂ in the normal state. The orbital and spin magnetic moments deduced from the sum rule analysis of the XMCD data indicate that the U atom in UGe₂ is considered to be closer to the trivalent state rather than the tetravalent state. The temperature dependence of the XMCD signal does not show any significant anomaly at T* ~ 30 K, where the resistivity anomaly was observed at ambient pressure. The XMCD measurement at the U N₂₃ edge indicates that the U 6d electrons have negligibly small magnetic contributions.

KEYWORDS: uranium compounds, ferromagnetism, superconductivity, x-ray absorption, magnetic circular dichroism

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1. Introduction

Recently, UGe₂ has attracted considerable attention, because the coexistence of superconductivity and ferromagnetism was found under pressure.¹,²) UGe₂ crystallizes in the orthorhombic ZrGa₂ structure (space group Cmcm). At ambient pressure, UGe₂ orders ferromagnetically below the Curie temperature T_Curie = 52 K with the ordered moment of 1.4μ₄B. The magnetic properties are strongly anisotropic, and the easy magnetization axis is the crystallographic a axis of the ZrGa₂ structure. Superconductivity is found in the pressure range of 1.0–1.6 GPa. The highest superconducting critical temperature T_SC is 0.8 K at the pressure P_C of 1.2 GPa, while T_Curie is 35 K at that pressure. As the induced pressure increases, the superconductivity disappears where the ferromagnetism disappears at around 1.7 GPa. Therefore, the superconductivity and ferromagnetism in UGe₂ seem to be closely related, although the mechanism of superconductivity has not been understood yet, and it is very important to experimentally characterize the magnetic properties of UGe₂. In particular, the strong magnetic anisotropy indicates the importance of spin–orbit coupling and hence the orbital magnetic moment of the U 5f electron. Experimental information about the orbital magnetic moment μ₄ as well as the spin magnetic moment μₛ therefore gives important clues to understand the electronic structure of UGe₂. Orbital contributions are particularly important in 5f electron systems because of the strong spin–orbit interaction compared to 3d and 4f electron systems.

X-ray absorption magnetic circular dichroism (XMCD) measurement combined with orbital and spin sum rules⁽¹,⁴⁾ is a powerful technique to obtain μ₄ and μₛ separately for a given electronic shell of a specific element. XMCD at the U M₄₅ (3d₃/₂,5/₂ → 5f) and U N₄₃ (4d₃/₂,5/₂ → 5f) absorption edges provides the information about the magnetic contribution of U 5f electrons. So far, XMCD studies at U core levels have been mostly made for the M₄₅ edges in the range of hv ~ 3.5 keV,²⁻⁷ measured in the total fluorescence yield mode. The M₄₅ XMCD studies had the disadvantage that the large absorption correction was applied to the raw data to obtain X-ray absorption (XAS) spectra, resulting in an uncertainty in the deduced magnetic moments. The large (~180 eV) spin–orbit splitting at the M₄₅ edges may also enlarge the uncertainty, because the M₄ and M₅ edges need quite different corrections. The N₄₃ XMCD measured in the total electron yield (TEY) mode is simpler and is a more precise way to estimate the U 5f magnetic moments, since the absorption correction is unimportant.

In addition, a resistivity anomaly within the ferromagnetic phase was observed as a round shoulder at the characteristic temperature T* ~ 30 K at ambient pressure.²⁻⁸) T* decreases with pressure and disappears at P_C where T_SC is the highest. Therefore, the anomaly is considered to be related to the appearance of superconductivity. For the origin of the anomaly at T*, the possibility of the transition due to the formation of a charge-density wave (CDW) or spin-density wave (SDW) was proposed because the nesting was expected from the topology of the Fermi surface,¹,²) although the existence of CDW or SDW has not been experimentally

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confirmed yet. Based on this scenario, a small modification of the magnitude of the ordered moment in zero field at $T^*$ is expected. Whether this anomaly is related to the magnetism or not, temperature-dependent study of XMCD would give microscopic information.

In the present study, we have performed XMCD measurements of UGe$_2$ at the U N$_{4.5}$ and U N$_{5.3}$ ($4p_{1/2}\rightarrow 6d$) edges to study the contribution of the U 5$f$ electrons and the U 6$d$ electrons to the magnetic moment, respectively. We have also investigated the temperature dependence of the XMCD signal at the U N$_{4.5}$ edges, in an attempt to detect a corresponding anomaly around $T^*$.

2. Experimental

Single crystalline samples of UGe$_2$ were grown by the Czochralski method. The XMCD measurements were performed at beamline BL23SU of SPring-8, which is specially designed for soft X-ray spectroscopic experiments of radioactive materials. As far as we know, the U N-edge XMCD experiment, which requires measurement for unsealed radio-active samples, has been performed only by us. The XAS spectra were obtained in the TEY mode. The energy resolution $E/\Delta E$ in the N$_{4.5}$ region edges was about 5000. In the XMCD measurements, circularly polarized X-rays produced by the APPLE-II type undulator were irradiated on the sample along one of the crystallographic $a$ axis, which was normal to the sample surface, and a magnetic field of 2T, which was sufficient to saturate the magnetization, was applied along the same axis. The N$_{4.5}$ XMCD was measured as the helicity of X-rays was fixed and the direction of magnetic field was reversed, while the N$_{5}$ XMCD was measured as the direction of magnetic field was fixed and the helicity of X-rays was reversed. The sample temperature was varied from 42 to 25 K, which is below $T_{\text{Curie}}$ and contains $T^*$. Clean sample surfaces were obtained by in situ cleaving prior to each series of measurements.

3. Results and Discussion

The upper part of Fig. 1 shows the XAS spectra of UGe$_2$ at the U N$_{4.5}$ edges measured with the photon helicity parallel ($\gamma_+$) and antiparallel ($\gamma_-$) to the direction of the magnetization of the sample. The XAS spectra have a rather simple line shape composed of two white line peaks at the N$_3$ and N$_4$ edges and no distinct fine structures due to multiplet splitting were observed. The spectra of the magnetized samples are dependent on the helicity of circularly polarized X-rays. The XMCD signals have been deduced as a difference between $\gamma_+$ and $\gamma_-$, as shown in the lower part of Fig. 1. The XMCD signals at the N$_3$ and N$_4$ edges have the same sign, and the XMCD signals at the N$_4$ edge have a much higher intensity than those at the N$_3$ edge. These behaviors were commonly observed in the XMCD spectra at the U M$_{4.5}$ edges of other ferromagnetic uranium compounds, from which one can conclude that $\mu_L$ and $\mu_S$ are directed in the opposite direction to each other.

From the integrated intensity of the XAS and XMCD spectra, one can evaluate $\mu_L$ and $\mu_S$ by applying the orbital and spin sum rules.

![Fig. 1. Upper part: XAS spectra of UGe$_2$ at the U N$_{4.5}$ edges for the helicity of the incident X-rays parallel ($\gamma_+$) and antiparallel ($\gamma_-$) to the direction of the magnetization. Lower part: XMCD spectra taken at $\Delta\gamma = \gamma_+ - \gamma_-$.](image)

\[\rho = \frac{(L_2)}{3n_h} = \frac{\int_{N_{4.5}} \Delta\gamma(E) dE}{3 \int_{N_{4.5}} \gamma(E) dE}, \quad \delta = \frac{2(S_2)}{3n_h} = \frac{\int_{N_{4.5}} \Delta\gamma(E) dE - \frac{3}{2} \int_{N_4} \gamma(E) dE}{\frac{3}{2} \int_{N_{4.5}+N_4} \gamma(E) dE}. \]

Here, $\gamma(E)$ and $\Delta\gamma(E)$ denote the XAS and XMCD spectra, respectively. $(L_2)$, $(S_2)$ and $(T_2)$ are the expectation values of the $x$ component of the orbital angular momentum, the spin angular momentum and the magnetic dipole operator of the 5$f$ shell, respectively. $(S_2)$ is the so-called effective spin. $n_h$ is the number of holes in the 5$f$ shell.

The application of the spin sum rule is valid only when the spin-orbit splitting of the core level is sufficiently large compared with other interaction including the core-valence Coulomb and exchange interaction. The condition may not be so clear at the U N$_{4.5}$ edges because the spin-orbit splitting is considerably smaller than that at the U M$_{4.5}$ edges. We have therefore calculated the influence of the N$_4$–N$_5$ overlap effect on the spin sum rule using the same atomic multiplet theory as that in ref. 13 and deduced that the correction required is less than 5%. As the deviation from the spin sum rule is mainly caused by the exchange interaction between the $f$ electron and the core hole, the smallness of the deviation compared to the M$_{4.5}$ edge of rare-earth ions is due to the fact that the value of the Slater integral for the 4$d$–5$f$ exchange interaction $G_{4f}^{-1}$ is less than one fifth of that for the 3$d$–4$f$ exchange interaction. Thus, we consider that the spin sum rule is applicable to the U N$_{4.5}$ edges.
In order to evaluate the values of $\mu_L = -(L_2)\mu_B$ and $\mu_S = -2(S_2)\mu_B$ separately from the XMCD spectra, $n_b$ and $(T_2)$ have to be known. However, $n_b$ and $(T_2)$ cannot be experimentally determined. On the other hand, $n_b$ is not necessary to obtain the ratio $(L_2)/(S_2) = 2\rho/\delta$. In addition, errors in the estimation of the background of the XAS spectra does not affect the deduction of $(L_2)/(S_2)$. The value of $(L_2)/(S_2) = 2\rho/\delta$ is evaluated to be $-1.76$ from the integrated intensities of the XMCD signals at the $N_4$ and $N_5$ edges in Fig. 1, which is comparable to the $(L_2)/(S_2)$ value of $-1.65$ for US estimated from the U $M_{4,5}$ XMCD experiment.\(^{5}\)

To eliminate the $(T_2)$ term in the expression of $(S_2)$, we have assumed that the magnitude of magnetic dipole $(T_2)$ can be scaled to the spin momentum $(S_2)$, and have used the theoretically-obtained value of the ratio $R_T = (T_2)/(S_2)$ based on the intermediate coupling scheme, that is 1.16 and 0.62 for the free ions of the $5f^2$ ($U^{4+}$) and $5f^3$ ($U^{3+}$) configurations, respectively.\(^{14}\) Then, the ratio $\mu_L/\mu_S$ is written as

$$\frac{\mu_L}{\mu_S} = (1 + 3R_T) \frac{\int_{n_b+S_2} \Delta \gamma(E) \, dE}{\int_{S_2} \Delta \gamma(E) \, dE - \frac{3}{2} \int_{n_b} \Delta \gamma(E) \, dE},$$

and is thus estimated to be $-3.94$ if the valence of U is assumed to be tetravalent, or $-2.51$ if the valence of U is assumed to be trivalent. From the $\mu_L/\mu_S$ values and the total magnetic moment $\mu_{tot} = \mu_L + \mu_S$ of 1.41$\mu_B$ at 25K obtained from the neutron diffraction experiment,\(^{13,14}\) one can evaluate the $\mu_L$ and $\mu_S$ values: $\mu_L = 1.89\mu_B$ and $\mu_S = -0.48\mu_B$ for the $5f^2$ ($U^{4+}$) configuration, and $\mu_L = 2.35\mu_B$ and $\mu_S = -0.94\mu_B$ for the $5f^3$ ($U^{3+}$) configuration.

Kernavanso et al.\(^{16}\) analyzed the neutron diffraction results of UGe$_2$ using a form factor $f(h,k,l) = (j_0) + C_2 (j_2)$, where $(j_0)$ and $(j_2)$ are the radial integrals of the $5f$ single-electron wave function of the uranium ion either in the $5f^2$ ($U^{4+}$) or $5f^3$ ($U^{3+}$) configuration and $C_2 = \mu_L/\mu_{tot}$. They obtained $\mu_L = 2.37\mu_B$ and $\mu_S = -0.91\mu_B$ for the $U^{4+}$ ion, and $\mu_L = 2.62\mu_B$ and $\mu_S = -1.17\mu_B$ for the $U^{3+}$ ion at $T = 6K$. The ratio $\mu_L/\mu_S$ is $-2.60$ for the $U^{4+}$ ion and $-2.24$ for the $U^{3+}$ ion. While the differences of $\mu_L/\mu_S$ or $\mu_S$ between the $U^{4+}$ and $U^{3+}$ values are moderate in the estimation by the neutron diffraction, they are quite large in the estimation by XMCD. Therefore, the XMCD values can be used as a sensitive tool to judge the valence of U to be tetravalent or tetravalent, by checking the consistency with other experiments or theoretical estimation. Since the $U^{4+}$ XMCD value of $|\mu_L/\mu_S| (|\mu_S|)$ seems to be too large (small) compared to the neutron value, the XMCD values of $\mu_L$, $\mu_S$, and $\mu_L/\mu_S$ are more consistent with the neutron results if the $U^{4+}$ ion is assumed rather than the $U^{4+}$ ion. This is also consistent with recent LDA+U calculation by Shick et al.\(^{17}\) which gave the U $5f$ occupation of 2.8. Therefore, it is reasonable to consider that the U atom in UGe$_2$ is closer to the trivalent state rather than to the tetravalent state. On the other hand, some discrepancy remains between the XMCD and the neutron results for the $U^{3+}$ ion. The discrepancy may partly be due to the ionic approximation used in the analyses of both the XMCD and the neutron results.

If the resistivity anomaly at $T^*$ is associated with the CDW/SDW formation, a small modification of the magnitude of the ordered moment may be expected.\(^{2,19}\) Therefore, we have investigated the temperature dependence of the integrated intensity of the XMCD signal at the U $N_4$ edges, as shown in Fig. 2. However, no distinct anomaly around $T^* \sim 30\,K$ is observed within the accuracy of the measurements. The values of $(L_2)/(S_2)$ also does not show anomaly around $T^*$ and is stable within the range from $-1.75$ to $-1.77$ at the temperature region. The influence of the anomaly at $T^*$ on the magnetic moment is therefore very small, less than 0.1$\mu_B$, if existed. In the magnetization measurement, enhancement of the magnetization below $T^*$ was observed only in the vicinity of $P_\sigma \sim 1.2\,GPa$, while this anomaly would be broadened and become undetectable at ambient pressure.\(^{13}\) XMCD measurements with better S/N ratio or under pressure are desired to clarify whether an anomaly on the magnetic moment exists or not.

In order to investigate the contribution of the U 6d electrons to the magnetization, we have measured XMCD at the U $N_3$ edge, too. The upper panel of Fig. 3 shows the XAS spectra measured with the plus and minus helicities, and the lower panel of Fig. 3 shows the XMCD signals, i.e., the difference between the $\gamma_+$ and $\gamma_-$ spectra. One can see that no appreciable XMCD signals are observed at the U $N_3$ edge. In addition, we have also measured XMCD in the region of the Ge $L_{2,3}$ and U $N_2$ absorption edges, as shown in Fig. 4. The Gd $M_{4,5}$ XAS signals observed in the region with distinct XMCD signals of minus sign at $\sim 1185\,eV$ and plus sign at $\sim 1215\,eV$ arises from the sample holder. Besides the Gd signals, the XAS spectrum in the region has a quite complicated line shape and it is hard to separate the U $N_2$ XAS signal from the Ge $L_{2,3}$ XAS signals. However, the XMCD signals have a relatively simple line shape and one can see two small XMCD structures of minus sign at $\sim 1228$ and $\sim 1255\,eV$ besides the Gd XMCD signals. These signals may be originated from the Ge $L_{2,3}$ edges, since the energy separation between those structures is close to the spin–orbit splitting of the Ge $L_{2,3}$ core level $\sim 30\,eV$. The observation of XMCD at the Ge $L_{2,3}$ edges was reported in
the XMCD study of the Fe/Ge interfaces. In this report, both the \(L_2\) and \(L_3\) Ge XMCD signals have a strongly asymmetric line shape composed of two lobes with opposite signs, while the sign of the overall signal is reversed between the \(L_3\) and \(L_2\) edges. If we assume that similar line shape is observed in the XMCD spectrum of Fig. 4, the strong XMCD signal with a plus sign at \(\sim 1215\) eV may indicate not only Gd \(M_4\) contribution but also the Ge \(L_2\) contribution, and the broad hump at around 1270 eV may include the Ge \(L_2\) contribution with a plus sign. Thus, the XMCD signals at \(\sim 1228\) and \(\sim 1255\) eV can be interpreted as due to the Ge \(L_{2,3}\) X-ray absorption, and the result may indicate that a small magnetic moment, which is coupled in parallel to the U \(5f\) moment, is induced on Ge 4s electrons due to hybridization with the U \(5f\) states. Appreciable XMCD signals were also observed at the Ge \(K\) edge. On the other hand, the existence or absence of XMCD at the U \(N_{2}\) edge (\(\sim 1270\) eV) is unclear because of the possible overlap of the Ge \(L_2\) XMCD signal. However, from the absence of XMCD at the U \(N_3\) edge, we conclude that the magnetic contribution of the U 6d electrons is negligibly small (within \(\pm 0.05\mu_B\)) compared to that of the U \(5f\) electrons.

4. Conclusion

We have estimated the ratio of orbital and spin magnetic moments \(\mu_o / \mu_S\) of the U \(5f\) electrons to be \(-3.94\) for the \(5f^2\) (\(U_{2+}\)) configuration and \(-2.51\) for the \(5f^3\) (\(U_{3+}\)) configuration from the sum-rule analysis of the U \(N_{4,5}\) XMCD data. Comparison between the XMCD data and the previous neutron diffraction results indicates that the U atom in UGe\(_2\) is close to be trivalent rather than tetravalent. The temperature dependence of the XMCD signal does not show any significant anomaly around \(T^*\). The magnetic contribution of the U 6d electrons is negligibly small compared to that of the U \(5f\) electrons.

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15) Reference [2] describes that the temperature dependence of \(\mu_{orb}\) is expressed as \(\mu_{orb} \propto (1 - T/T_{Curie})^{0.3}\) above 30K and \(\mu_{orb} \propto (1 - (T/T_{Curie})^{0.3}\) below 30K, while \(\mu_{orb}\) at 5K was estimated to be 1.48\(\mu_B\).
22) In our XMCD measurement of uranium monochalcogenides too, no sizable XMCD signals were observed both at the N2 and N3 edges.