X-ray magnetic circular dichroism at the U \( N_{4,5} \) edges of uranium monochalcogenides US, USe and UTe

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Abstract

Magnetic circular dichroism (MCD) has been measured at the U \( N_{4,5} \) absorption edges of ferromagnetic uranium monochalcogenides US, USe and UTe. The MCD signals are weaker in US than in USe and UTe. Both the spin and orbital moments are increased in going from US to USe, and then reduced from USe to UTe.

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1. Introduction

A number of uranium compounds order magnetically, while the nature of magnetic ordering has not been fully understood. The difficulty lies in the nature of 5f electrons which play major roles in the magnetism. Due to the relatively large spin–orbit interaction of 5f electrons, the magnitude of the orbital moment is often expected to be larger than that of the spin moment in uranium compounds. The delocalization of uranium 5f electrons should be correlated with the magnitude of the orbital moment. It is important to evaluate experimentally the orbital moment \( \mu_L \) and the spin moment \( \mu_S \) separately for each constituent atom in order to properly describe the mechanism of 5f electron magnetism in uranium compounds.

X-ray absorption magnetic circular dichroism (MCD) measurement combined with several sum rules \cite{1,2} is a powerful experimental technique to obtain the orbital and spin moments separately for a given electronic shell of a specific element. MCD at the \( M_{4,5} (3d \rightarrow 5f) \) and \( N_{4,5} (4d \rightarrow 5f) \) absorption edges of uranium provides the information about the magnetic moment of 5f electrons.

Uranium monochalcogenides US, USe and UTe crystallize in the NaCl structure and order ferromagnetically below the Curie temperatures \( T_c \) of 177, 160 and 104 K, respectively \cite{3}. The magnetic moment deduced from neutron diffraction experiments becomes larger in the order US,
US, UTe, while the lattice parameter also becomes larger in the same order [3]. For US, MCD was measured at the $M_{4,5}$ edges [4,5], although the estimation of $\mu_\uparrow$ and $\mu_\downarrow$ depends on some unknown parameters used in the sum rules. The large absorption correction made in these studies may have caused ambiguity in the estimation of the magnetic moments. In addition, the large energy separation between the $M_4$ and $M_5$ peaks is disadvantageous for a precise application of the sum rules. MCD for USe and UTe has not been measured so far, while the measurement for $\mathrm{USb}_{0.5}\mathrm{Te}_{0.5}$ was performed [6].

We have performed the MCD measurement at the $U\,N_{4,5}$ edges of US, USe and UTe, using synchrotron radiation soft X-ray at SPring-8. To our knowledge, this is the first experiment of MCD at the $U\,N_{4,5}$ edges of uranium compounds.

2. Experiment

Single crystalline samples of US, USe and UTe were grown by the Bridgman method, starting from a uranium metal of 99.95% and chalcogenides of 99.999%.

The MCD measurements were performed at beamline BL23SU of the SPring-8, which is specially designed for the soft X-ray experiments of radioactive materials. The X-ray absorption (XAS) spectra were obtained in the total-electron yield method. The energy resolution $E/\Delta E$ in the region around the $U\,N_{4,5}$ edges was about 5000. The vacuum in the measurement chamber was kept below $5 \times 10^{-8}$ Pa.

In the MCD measurements, the circularly polarized X-rays irradiated the sample along the [001] direction. The helicity of the X-rays was fixed, and the magnetic field of 2 T was induced in parallel and antiparallel to the incident X-rays. The degree of circular polarization was estimated to be $\geq 95\%$. The sample temperature during the measurements was fixed at 50 K, which is well below $T_c$ for all the samples. Clean sample surface was obtained by in situ cleaving along the (100) plane just before each series of measurements.

3. Results and discussion

The upper panel of Fig. 1 shows the XAS spectra of US, USe, and UTe measured at the $U\,N_{4,5}$ edges. The $\gamma_+$ and $\gamma_-$ spectra were measured as the photon helicity parallel and antiparallel to the direction of the magnetization. The XAS spectra with a cancelled polarization, $\gamma = (\gamma_+ + \gamma_-)/2$, has a rather simple line shape composed of
two white-line peaks at the $N_5$ and $N_4$ edges. No distinct fine structures due to multiplet splitting were observed. The small structure at around 820 eV in the spectra of UTe is due to the Te M$_3$ absorption. In going from US, USe to UTe, the peak positions of the white lines are shifted to the lower-energy side, and their line widths tend to decrease. The decrease in the line width can be related to the decrease in the bandwidth of the empty U 5f states, namely the localization of U 5f electrons in going from US, USe to UTe [7].

The MCD spectra obtained as $\Delta \gamma = \gamma_+ - \gamma_-$ are shown in the lower panel of Fig. 1. The MCD signals at the $N_5$ and $N_4$ edges have the same sign (minus in the figure), and the MCD signals at the $N_4$ edge have much larger intensity than that at the $N_5$ edge. These properties are the same as observed in the MCD measurements at the $M_{4,5}$ edges [4,5].

The magnitude of the MCD signals becomes clearly larger in going from US to USe, and remains almost the same or slightly decreases from USe to UTe, while the line shape is not significantly changed. Therefore, it appears that the magnetic nature of the uranium monochalcogenides is different between US and the other compounds.

To evaluate the spin and orbital magnetic moments from the MCD spectra, the following sum rules are usually applied to the integrated intensity of the MCD and XAS spectra [1,2,4].

$$\rho = \frac{\langle L_z \rangle}{3n_h} = \frac{1}{3} \int_{N_4 + N_5} \frac{\Delta \gamma(E) \, dE}{\gamma(E) \, dE},$$  \hspace{1cm} (1)

$$\delta = \frac{2}{3n_h} \int_{N_5} \frac{\Delta \gamma(E) \, dE - \frac{3}{2} \int_{N_4} \Delta \gamma(E) \, dE}{\frac{3}{2} \int_{N_4 + N_5} \gamma(E) \, dE},$$  \hspace{1cm} (2)

$$\langle S_e \rangle = \langle S_z \rangle + 3 \langle T_z \rangle.$$  \hspace{1cm} (3)

In the equations, $\langle L_z \rangle$, $\langle S_z \rangle$ and $\langle T_z \rangle$ are the expectation values of the $z$ projections of the orbital angular momentum, the spin angular momentum and the magnetic dipole operator of the 5f shell, respectively. $\langle S_e \rangle$ is the so-called effective spin, which is conventionally used. $n_h$ is the number of holes in the 5f shell. From the integrated values of the spectra in Fig. 1, we have estimated the value of $\rho$ and $\delta$ as $-0.088$ and $0.108$ for US, $-0.118$ and $0.144$ for USe, $-0.113$ and $0.140$ for UTe, respectively. The value of $\rho$ and $\delta$ for US is close to those obtained in the previous MCD studies at the $M_{4,5}$ edges [4,5].

For the purpose of the evaluation of $\langle L_z \rangle$ and $\langle S_z \rangle$ from the MCD spectra, $n_h$ and $\langle T_z \rangle$ still remains as unknown parameters, which cannot be experimentally determined. We use the values of $n_h$ calculated by the band calculation using the spin-polarized relativistic LAPW method, 11.21, 11.11 and 11.01 for US, USe and UTe, respectively [8]. We first evaluated $\langle L_z \rangle$ using Eq. (1), and then estimated the value of $\langle S_z \rangle$ from the $\langle L_z \rangle$ value and the total moment $\mu_{\text{total}} = \mu_L + \mu_S = -2 \langle S_z \rangle \mu_B - 2 \langle S_e \rangle \mu_B$ of 1.7, 2.0 and 2.25 $\mu_B$ for US, USe and UTe, respectively, obtained from the neutron diffraction experiments [3]. Finally, the value of $\langle T_z \rangle$ is determined using Eqs. (2) and (3). All the estimated values are summarized in Table 1.

The estimated values of $\mu_L$ and $\mu_S$ for US agree well with the values $\mu_L = -3.0 \mu_B$ and $\mu_S = 1.31 \mu_B$ estimated from the form factor analysis of the neutron diffraction data [9]. Both the values of $|\mu_L|$ and $|\mu_S|$ are significantly enhanced in going from US to USe, probably reflecting a localization of 5f electrons. However, they are reduced in going from USe to UTe, although the total moment deduced from the neutron diffraction experiments increases [3]. The increase of the total moments in going from USe to UTe is mainly caused by the decrease in $\mu_S$. Similar tendency was observed in the magnetic Compton scattering (MCS) experiments, although $|\mu_L|$ and $|\mu_S|$ estimated here for USe and UTe are noticeably larger than those obtained by MCS [10]. The behavior from USe to UTe can be explained by considering the hybridization between U 5f electrons and the valence...
electrons of chalcogen. The ratio $|\mu_L/\mu_S|$ decreases in going from US to USe, and then increases from USe to UTe. $\langle T_2 \rangle$ has a tendency to increase in the order US, USe, UTe. It is interesting to note that the ratio $\langle L_z \rangle/\langle S_z \rangle$, namely the ratio between $\delta$ and $\rho$, which is determined only from the MCD spectra, remains relatively unchanged among US, USe and UTe.

In summary, the MCD spectra of uranium monochalcogenides, which are related to the magnetic moments of the U 5f electrons, show clear dependence on the chalcogen elements. The MCD signals are weaker in US than in USe and UTe. Both the spin and orbital moments estimated using the sum rules increases in going from US to USe, but decreases from USe to UTe.

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References