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X-ray magnetic circular dichroism studies in $Ce(Fe_{1-x}Co_x)_2$

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Abstract

We have measured XAS and MCD spectra at Ce $L_{2,3}$-edges in $Ce(Fe_{1-x}Co_x)_2$. All the XAS spectra of $Ce(Fe_{1-x}Co_x)_2$ around the Ce-L_3 edge exhibit a double-peak structure that is the characteristic feature of the mixed-valence system. The ratio of the $4f^1$ peak intensity to the $4f^0$ peak intensity in the Ce $L_{2,3}$-edges increased as the composition of Co increased. But the MCD and XAS spectral shape changed slightly for $Ce(Fe_{1-x}Co_x)_2$. As the Co composition increased, MCD intensity decreased. Applying to Sum rules, we estimated the values of $\langle L_z \rangle$, $\langle S_z \rangle$, and $\langle L_z \rangle + 2\langle S_z \rangle$, respectively. The orbital magnetic moment of Ce-5d electrons is very small but does exist in $Ce(Fe_{1-x}Co_x)_2$.

Keywords: Laves compound; Ferro–antiferro-magnetic phase transition; Magnetic circular dichroism; X-ray absorption spectroscopy

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1. Introduction

The compounds $CeFe_2$ with the C15 Laves phase ($MgCu_2$-type) structure is a unique ferromagnet with the Curie temperature $T_c = 230$ K and the spontaneous magnetization $M_s = 2.30\ \mu_B$/f.u. at 4.2 K [1]. These values are significantly reduced, compared to other RFe_2 (R = rare earth metals) compounds. These anomalies were initially ascribed to the transfer of Ce-4f electrons to the conduction band [2]. However, recent theoretical studies [3,4] and some experimental results [5,6] emphasize the important role played by hybridization between 4f and 5d and/or 3d electrons in determining these physical properties for $CeFe_2$.

Another interesting magnetic characteristic of this compound is the loss of ferromagnetism at lower temperatures by substituting a small amount of impurity for Fe. With the substitution of Al, Co and Ru for Fe, a ferromagnetic (F) state is replaced by an antiferromagnetic (AF) one below a temperature T_0 lower than T_c [7–9]. In the case of $Ce(Fe_{1-x}Co_x)_2$, the AF ground state appears for $0.04 < x < 0.3$ [8]. Long-range AF order was confirmed by neutron diffraction measurements [10]. Sharp discontinuity is observed in the temperature dependence of electrical resistivity as well as that of lattice parameter at T_0 for $0.1 \leq x \leq 0.2$, indicating that the AF–F transition is of first order [11,12]. On the other hand, the average hyperfine field, estimated form Mössbauer spectra, shows a smooth temperature variation without any significant change at T_0, suggesting no dramatic change in the magnitude of the Fe moment by the AF–F transition [13]. Beyond $x = 0.3$ ferromagnetism is stabilized down to the lowest temperature. T_c shows a broad maximum at around $x = 0.5$ and decreases with increasing x, falling to zero at around $x = 0.9$. These behaviors of $Ce(Fe_{1-x}Co_x)_2$ are caused by the hybridization of the 3d–4f bands.

Magnetic circular dichroism (MCD) in the core-level absorption spectrum (XAS) in soft X-ray regions, namely the difference of the absorption spectra between parallel and anti-parallel geometries of the magnetized sample with respect to the helicity of an incoming circularly polarized X-ray, has recently been used for the spectroscopic study on ferro- and ferri-magnetic materials. The XAS technique gives not only information on constituent elements of a magnetic material but also that on orbital states of each element, because the

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core electron is excited according to the selection rule and the transition probability.

The information on the selectivity of XAS allows us to investigate the magnetic polarization around the selected elements; namely, it becomes possible to study the origin of magnetism in the magnetic material from a microscopic point of view. Analyzing the XAS at the $L_{2,3}$ (2p → 5d transitions) edges of the R element, the 5d state of R is revealed. In addition, MCD experiment provides us with quantitative information on magnetic polarization and enables us to estimate the magnetic moments, orbital and angular moments, projected to the incident light direction. Moreover, analysis for XAS and MCD signals based on the sum rules provides us with the orbital magnetic moment as well as the spin magnetic moment [14,15]. To estimate the expected value of spin moment from the experimental spectra, the expectation value of the magnetic dipole operator, which cannot be obtained from XAS-MCD measurements only, is needed.

In this paper, we pay attention to the hybridization between 4f and 5d and/or 3d electrons that is a very important interaction for the R-Fe_2 system. Therefore, we used the XAS and MCD measurements, which are element-selective and orbital-selective, to investigate the Ce valence and the 4f–5d–3d hybridization in $Ce(Fe_{1-x}Co_x)_2$.

2. Experimental methods

$Ce(Fe_{1-x}Co_x)_2$ samples with $x = 0$, 0.2, and 0.3 were prepared by argon arc-melting of pure constituents of at least nominal 99.9% purity, followed by annealing at 850 °C in an evacuated quartz tube for 1 week. The powder X-ray diffraction patterns revealed that the sample show a single phased C15 Laves structure without any impurity phases.

The XAS and MCD spectra at Ce $L_{2,3}$-edges were recorded in the transmission mode using the helicity-modulation (HM) method [16] with a fixed magnetic field of 2.0 T on the undulator beamline 39XU of SPring-8. The beamline was composed of a rotated-inclined double-crystal monochromator equipped with a Si 111 crystal and a Pt-coated mirror for higher harmonics rejection. A diamond phase retarder was used in the Laue geometry with the 220 reflection plane in order to produce circularly polarized X-rays having plus and minus helicities in the a.c. mode with a frequency of 40 Hz by using a piezo oscillator. The X-ray intensity was monitored using an ionization chamber filled with N_2 gas before and after the sample. The degree of circular polarization was estimated to be 0.9 in the energy range used, as determined by polarization analysis. Energy resolution was estimated to be $\Delta E/E < 1.0 \times 10^{-4}$ at Ce $L_{2,3}$-edges. The XAS and MCD measurements were carried out at $T = 100$ K and $T = 20$ K. The temperature of the sample was monitored by using a GaAlAs diode installed in the sample holder.

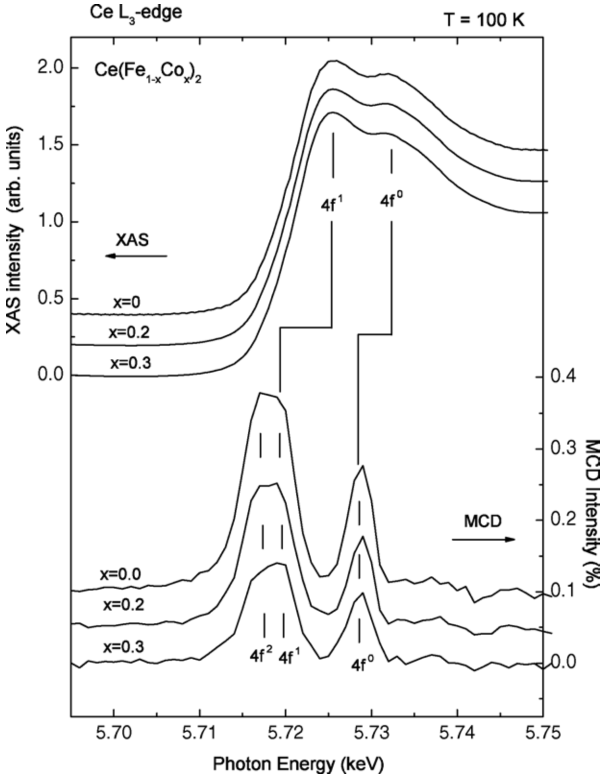

Fig. 1. The XAS and MCD spectra at the Ce L_3-edge in $Ce(Fe_{1-x}Co_x)_2$.

3. Results and discussion

Figs. 1 and 2 show the XAS and MCD spectra at the Ce $L_{2,3}$-edges in $Ce(Fe_{1-x}Co_x)_2$ ($x = 0.0$, 0.2, and 0.3). The top (bottom) of these figures corresponds to the XAS (MCD) spectra.

All the XAS spectra of $Ce(Fe_{1-x}Co_x)_2$ around the Ce-L_3 edge exhibit a double-peak structure that is the characteristic feature of the mixed-valence system [17]. According to Harada et al., the lower energy peak corresponds to $4f^1$ configuration (the $4f^1$ peak) and the higher energy peak to $4f^0$ configuration (the $4f^0$ peak) [18,19]. No significant changes are found in the width and relative energy position of the two peaks. Our results indicate that the Ce mixed valence behaviour is retained in all the $Ce(Fe_{1-x}Co_x)_2$. In order to make it clear the behaviour of the mixed valence of Ce, the ratio of the $4f^1$ peak intensity to the $4f^0$ peak intensity in the Ce $L_{2,3}$-edges was analyzed. This ratio increased as the composition of Co increased. This result means that the number of electrons and the configuration of $4f^1$ increased by introduction of Co. Moreover, this result confirmed the hybridization of the 3d–4f–5d bands is important for $Ce(Fe_{1-x}Co_x)_2$ (Fig. 3).

In all the cases, the MCD spectra at the Ce-$L_{2,3}$ edges in the $Ce(Fe_{1-x}Co_x)_2$ series exhibit a double-peak structure. The higher energy peak in the MCD spectra corresponds to $4f^0$ configuration as in the case of XAS spectra. On the other hand, the lower energy peak in the MCD spectra corresponds

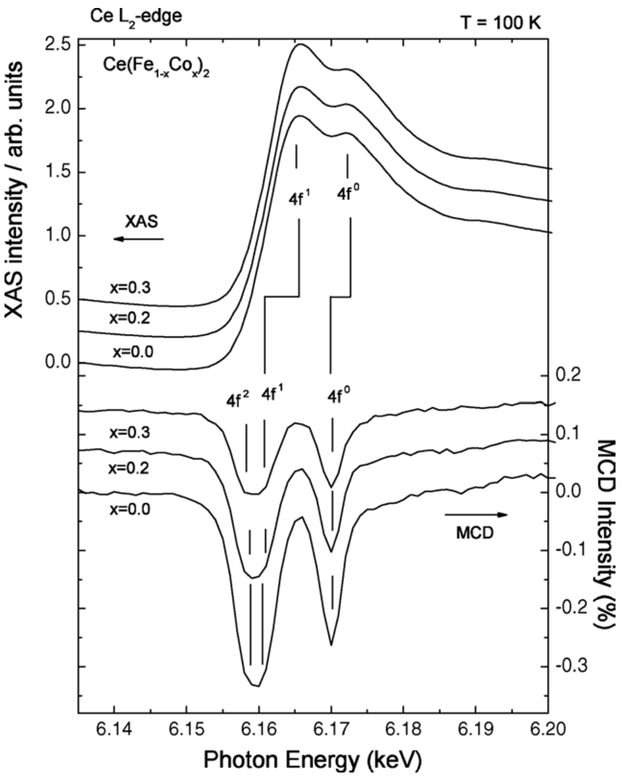

Fig. 2. The XAS and MCD spectra at the Ce L_2-edge in Ce(Fe$_{1-x}$Co$_x$)$_2$.

to 4f^1 and 4f^2 configuration, which are different from XAS spectra.

The energy position of the 4f^1 peak and the 4f^0 peak in XAS spectra is higher than the energy position of the 4f^1 peak and the 4f^0 peak in MCD spectra, respectively. According to Harada and co-workers [18,19], the difference between XAS and MCD is caused by the reason as follows. The XAS spectrum spreads because the unoccupied 5d states exist over the range 7–8 eV above Fermi energy. On the other hand, the polarization of Ce-5d electrons originates from the hybridization between the Fe-3d and Ce-5d electrons and exists only near the Fermi energy. Therefore, the peak of the MCD spectra is lower than that of the XAS spectra. The energy separation of these two peaks mainly depends on the Coulomb interaction U_{fc} between the 4f electrons and the 2p core hole. In all the MCD spectra in Ce(Fe$_{1-x}$Co$_x$)$_2$, the energy separation of these two peaks is almost the same. That is to say, it is independent of the Co composition. As the Co composition increased, MCD intensity decreased. This is direct confirmation that the magnetic moment of Ce-5d electrons is induced by Fe magnetic moment.

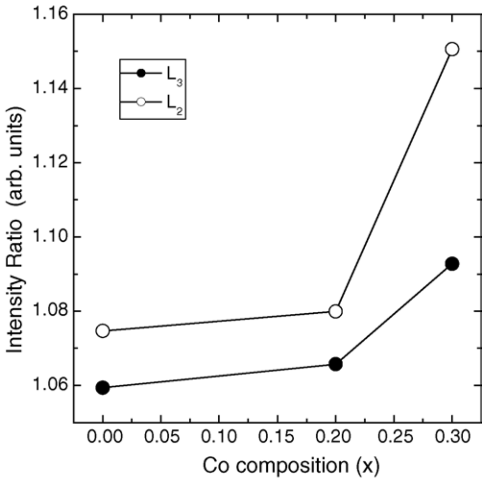

Fig. 3. The composition dependence of the ratio of the 4f^1 peak intensity to the 4f^0 peak intensity around the Ce-$L_{2,3}$ edges.

Table 1
The orbital, the spin and the total magnetic moment of Ce-5d electrons in Ce(Fe$_{1-x}$Co$_x$)$_2$

X	$\langle L_z \rangle$	$2\langle S_z \rangle$	$\langle L_z \rangle + 2\langle S_z \rangle$
0.0	−0.022	0.306	0.284
0.2	−0.011	0.211	0.200
0.3	−0.008	0.140	0.132

Despite there being a general consensus concerning that there is a net moment on the Ce site, mostly spin, and antiparallel to that of Fe, there is a hot debate regarding the value of the moments (both 4f and 5d) [20]. Trying to obtain a deeper insight into the magnitude of Ce-5d magnetic moment in Ce(Fe$_{1-x}$Co$_x$)$_2$, we have applied the sum rules derived by Thole and co-workers [14,15]. For the Ce $L_{2,3}$ edges they can be written as follows.

$$\langle L_z \rangle = \frac{2n_{\mathrm{h}}(A_3 + A_2)}{W}$$

$$\langle S_z \rangle = \frac{3}{2}n_{\mathrm{h}}\frac{(A_3 - 2A_2)}{W} - \frac{7}{2\langle T_z \rangle}$$

where A_3 and A_2 are the MCD integrated intensity at the L_2 and L_3 edges respectively, n_{h} is the number of holes in the Ce-5d band, and W is the integrals over whitelines intensity at the L_2 and L_3 edges. $\langle L_z \rangle$, $\langle S_z \rangle$, and $\langle T_z \rangle$ represent the orbital magnetic moment, the spin magnetic moment and the magnetic dipole moment, respectively. According to Delobbe et al. [21], we have considered that the $\langle T_z \rangle$ term is zero. By using the number of holes in Ce-5d band is 8.5, we estimated the values of $\langle L_z \rangle$, $2\langle S_z \rangle$, and $\langle L_z \rangle + 2\langle S_z \rangle$. The obtained results are shown in Table 1. The total magnetic moment in this result is almost equal to the theoretical estimation [22]. As the Co composition increased, the values of $\langle L_z \rangle$, $2\langle S_z \rangle$, and $\langle L_z \rangle + 2\langle S_z \rangle$ decreased. The total magnetic moment of Ce-5d electrons almost consists of spin magnetic moment. The orbital magnetic moment of Ce-5d electrons is very small but does exist. Moreover, the orbital magnetic moment coupled with the spin magnetic moment antiferromagnetically. This means that Hund law is realized in Ce-5d orbital.

4. Conclusion

We have measured XAS and MCD spectra at Ce $L_{2,3}$-edges in Ce(Fe$_{1-x}$Co$_x$)$_2$. All the XAS spectra of Ce(Fe$_{1-x}$

$Co_x)_2$ around the Ce-L_3 edge exhibit a double-peak structure that is the characteristic feature of the mixed-valence system. The ratio of the $4f^1$ peak intensity to the $4f^0$ peak intensity in the Ce $L_{2,3}$-edges increases as the composition of Co increased. On the other hand, the MCD and XAS spectral shape change slightly for $Ce(Fe_{1-x}Co_x)_2$. As the Co composition increased, MCD intensity decreased. Applying to Sum rules, we estimated the values of $\langle L_z \rangle$, $2\langle S_z \rangle$, and $\langle L_z \rangle + 2\langle S_z \rangle$, respectively. The orbital magnetic moment of Ce-5d electrons is very small but does exist in $Ce(Fe_{1-x}Co_x)_2$.

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