A study of magnetic moments of CeRh₃B₂ by X-ray magnetic diffraction experiments

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Abstract. X-ray magnetic diffraction experiments of a ferromagnetic rare-earth compound CeRh₃B₂ have been performed, and the spin and orbital magnetic form factors have been measured. Density distributions of the spin and orbital magnetic moments in real space have been obtained by using Maximum Entropy Method. Low peaks at Rh sites as well as high peaks at Ce sites are observed in these distribution maps. We have estimated the spin and orbital magnetic moments at the Ce and Rh sites in the distribution maps, and have obtained small but nonnegligible spin and orbital magnetic moments of Rh. This is probably the first experimental evidence showing existence of the spin and orbital moments of Rh in this compound.

1. Introduction
A rare-earth compound CeRh₃B₂ has a hexagonal CeCo₃B₂-type crystal structure as shown in Fig. 1 [1], and is ferromagnetic below 115K [2]. This Curie temperature is the highest among the compounds of Ce with nonmagnetic elements. On the other hand, the magnetic moment per Ce atom, 0.4μₓ at 4.2K [3], is almost the smallest among them. This moment value is much smaller than the calculated value, 2.14μₓ, for Ce³⁺ free ion under Hund’s rule. These magnetic properties of this compound have been attracting much attention of many researchers, and a large number of theoretical and experimental studies have been made to reveal the origin of the magnetic properties. After arguments between theoretical models of itinerant electrons and those of localized ones, currently accepted models are those of localized Ce ⁴f electrons hybridized with Ce ⁵d, Rh ⁴d [7], or Ce ⁴f electrons of neighbouring atoms [8]. Among them, the Monte Carlo study [7] presented a possibility...
of polarization of Rh 4d electrons which provided magnetic moments of 0.15\(\mu_B\).

The polarized neutron diffraction (PND) experiments showed that the magnetic moments were contributed mainly by localized Ce 4f electrons (0.56±0.02\(\mu_B\)), slightly by delocalized electrons distributing along the c-axis between Ce atoms (−0.18±0.04\(\mu_B\)), but negligibly by Rh and B [9, 10]. The magnetic Compton scattering (MCS) experiments showed that the spin moments were contributed considerably by Ce 4f (−0.69±0.08\(\mu_B\)) and Ce 5d electrons (−0.41±0.04\(\mu_B\)) but negligibly by Rh 4d electrons (−0.03±0.04\(\mu_B\)), which suggested hybridization of Ce 4f with Ce 5d electrons [11, 12].

In this study, we have applied a new experimental method of X-ray magnetic diffraction (XMD) to CeRh3B2. XMD is nonresonant magnetic X-ray Bragg scattering, which utilizes elliptically polarized X-rays. A specific feature of the XMD is that we can measure spin and orbital magnetic form factors of ferromagnets separately [13]. In this study, we have measured these form factors of CeRh3B2, and have estimated the spin and orbital magnetic moments of the constituent atoms. We have paid attention on these moments of Rh. The preliminary result of the XMD data analysis was presented elsewhere [14].

2. Experimental

The XMD experiments have been performed on the beamline 3C of Photon Factory (PF) in High Energy Accelerator Research Organization (KEK). On this beamline the dedicated XMD experimental system was installed, which consists of a four-circle diffractometer, an electromagnet, a refrigerator and a pure-Ge solid-state detector (SSD) with related electronic circuits to count X-ray photons. Details of this system were presented elsewhere [15]. White X-rays of elliptically polarized synchrotron radiation from the bending magnet were incident on the specimen, and X-ray intensities diffracted at the pure-Ge SSD with related electronic circuits to count X-ray photons. Details of the SSD system were presented elsewhere [15]. White X-rays of elliptically polarized synchrotron radiation from the bending magnet were incident on the specimen, and X-ray intensities diffracted at the specimen with 90° scattering angle were measured with the SSD. The specimen was magnetized with the electromagnet along a direction perpendicular to the c-axis of CeRh3B2. We have measured relative change \(R\) in the diffraction intensity accompanied by reversal of the magnetic field direction. Magnetic field strength was 21.5kOe that was enough to saturate the magnetization of this compound along any direction in the plane perpendicular to the c-axis. As the geometrical relation between the crystal axis and the magnetic field direction in the XMD is different from that of the PND [9], the XMD could provide complimentary information to the PND. The specimen temperature was kept at 15 K that was far below the Curie temperature of this compound.

The \(R\) is expressed as, \(R = \gamma f_\alpha \mu_s(k)/F(k)\) [16]. Here, \(\gamma\) is the energy term expressed as \(\gamma = E/E_0\) where \(E\) is diffracted X-ray energy and \(E_0\) is electron rest mass energy. The term \(f_\alpha\) is the polarization factor expressed as \(f_\alpha = P_c/(1-P_l)\) where \(P_l\) and \(P_c\) are the linear and circular polarization of the incident X-rays. The term \(\mu_s(k)\) is a combined magnetic form factor represented as \(\mu_s(k) = \mu_{s Lionel}(k) + \mu_{s Dipole}(k)\) for Ce 4f electrons of a Ce\(^{3+}\) free ion under the dipole approximation [18], which are represented as \(\mu_{s Lionel}(s) = \mu_{0 s Lionel} \langle j_0(s) \rangle\rangle\) and \(\mu_{s Dipole}(s) = \mu_{0 s Dipole} \langle j_2(s) \rangle\rangle\). Here \(\mu_{0 s Lionel}\) and \(\mu_{0 s Dipole}\) are the spin and orbital...
magnetic moments of Ce 4f, and \( \langle j_n(s) \rangle \) is the radial integral of the wavefunction of Ce 4f electrons multiplied by the n-th order spherical Vessel function. We use the values of \( \mu_{S0} = -1.16 \mu_B \) and \( \mu_{L0} = 1.61 \mu_B \) from the literature 12 as is described below.

In Fig. 2 the followings are noted. (i) The observed values of \( \mu_s(s) \) are negative whereas those of \( \mu_L(s) \) are positive. This indicates that the major part of the magnetic moments is the orbital moment and the spin moment is oppositely coupled with the orbital moment. (ii) The observed \( \mu_L(s) \) is fairly reproduced by the theoretical dipole-approximation curve. (iii) The observed \( \mu_s(s) \) decreases more slowly than \( \mu_L(s) \) and is far from the theoretical curve. This behavior of \( \mu_s(s) \) is discussed later. (iv) The observed \( \mu_{S0}(s) \) and \( \mu_L(s) \) data are composed of two different series. One is the \( hk0 \) series where both \( h \) and \( k \) are even (even series), and the other is the one where either \( h \) or \( k \) is odd (odd series). Absolute values of the odd series are slightly smaller than those of the even series. Here let us remind the crystal structure factor of CeRh\(_3\)B\(_2\), \( f_{Ce} + 3f_{Rh} \) for the even series and \( f_{Ce} - f_{Rh} \) for the odd series where \( f_{Ce} \) and \( f_{Rh} \) are the atomic scattering factor of Ce and Rh (boron contribution is ignored here). Then the characteristic behavior of the observed \( \mu_{S0}(s) \) and \( \mu_L(s) \) for the even and odd series suggests that both \( \mu_{S0}(s) \) and \( \mu_L(s) \) are contributed by Rh as well as by Ce.

![Graph](image.png)

Fig. 2. (Color online.) Observed (a) spin magnetic form factor \( \mu_s(s) \) and (b) orbital magnetic form factor \( \mu_L(s) \) for twenty reciprocal lattice points of \( hk0 \). Solid circles and squares are for the even series and open circles and squares are for the odd series. It is noted that the direction of the ordinate of \( \mu_s(s) \) is reversed. Solid lines denote theoretical dipole-approximation curves of Ce 4f electrons of a Ce\(^{3+}\) free ion.

We have estimated the spin and orbital magnetic moments of Ce and Rh. We have adopted the maximum entropy method (MEM), and have obtained the density distributions of the spin and orbital magnetic moments in real space, \( M_S(r) \) and \( M_L(r) \). The obtained distribution maps projected along the c-axis are presented in Fig. 3 by using VESTA [19]. In Fig. 3, we notice high peaks at Ce sites and low peaks at Rh sites for both \( M_S(r) \) and \( M_L(r) \). Peaks of \( M_S(r) \) are sharper than those of \( M_L(r) \), and the peaks of \( M_L(r) \) at the Rh sites seem to extend toward Ce sites. Though the reason for latter is not clear at this moment, we discuss the reason for the former. The PND experiments [9, 10] have shown the existence of the magnetic (probably spin) moment of delocalized electrons which are distributed along the c-axis. The anisotropic distribution of the spin moment along the c-axis may relate to the sharp peaks of \( M_S(r) \) in the map projected along the c-axis, which could be concerned with the slow decrease of \( \mu_{S0}(s) \) in the reciprocal space as shown in Fig. 2 (a).

We have estimated the spin and orbital magnetic moments of Ce and Rh by integrating the density values of the maps in Fig. 3 as follows,

\[
K^{S(L)} \left( \delta^{S(L)}_{Ce} + 3 \delta^{S(L)}_{Rh} \right) = \mu^{S(L)}_0, \quad (1)
\]
\[ \mu_{\text{Ce}}^{S(L)} = K^{S(L)} A_{\text{Ce}}^{S(L)}, \quad (2) \]
\[ \mu_{\text{Rh}}^{S(L)} = K^{S(L)} A_{\text{Rh}}^{S(L)}. \quad (3) \]

Here, \( K^{S(L)} \) is a conversion factor for the spin (orbital) magnetic moment, \( A_{\text{Ce}}^{S(L)} \) and \( A_{\text{Rh}}^{S(L)} \) are integrated density values at the Ce and Rh sites for the spin (orbital) magnetic moment, and \( \mu_0^{S(L)} \) is the spin (orbital) magnetic moment per formula unit of CeRh\(_3\)B\(_2\). We have used \( \mu_0^{S} = -1.16 \mu_B \), which was deduced by the MCS experiment [12]. The value of \( \mu_0^{S(L)} \) has been derived from the equation \( \mu_0^{L} = \mu_0^{S} \), where \( \mu_0 \) is the magnetic moment per formula unit obtained by the magnetization measurement. Here, \( \mu_0^{L} = 0.42 \mu_B \) and \( \mu_0^{S(L)} = 1.61 \mu_B \). Then we have obtained the following values: \( \mu_{\text{Ce}}^{S(L)} = -0.98 \pm 0.12 \mu_B \), \( \mu_{\text{Ce}}^{L} = 1.52 \pm 0.12 \mu_B \), \( \mu_{\text{Rh}}^{S} = -0.06 \pm 0.02 \mu_B \), and \( \mu_{\text{Rh}}^{L} = 0.03 \pm 0.02 \mu_B \). The values of \( \mu_{\text{Rh}}^{S(L)} \) may be associated with 4d electrons. The values of \( \mu_{\text{Ce}}^{S(L)} \) may be contributed by both 4f and 5d electrons but each contribution cannot be distinguished in this study. The \( \mu_{\text{Ce}}^{S(L)} \) value is comparable to the sum of Ce 4f spin and Ce 5d spin, \(-1.10 \pm 0.09 \mu_B\), by the MCS experiment [12]. The magnetic moment per Ce atom, \( \mu_{\text{Ce}}^{L} + \mu_{\text{Ce}}^{S} = 0.54 \pm 0.14 \mu_B \), is also comparable to the corresponding value, \( 0.56 \pm 0.02 \mu_B \) by the PND experiments [9, 10]. In this study, we have observed small but nonnegligible spin and orbital magnetic moments of Rh. Future MCD experiment for Rh L edge will be helpful to check the existence of the magnetic moments of Rh in this compound.

**Fig. 3.** (Color online.) Density distribution of (a) the spin magnetic moment and (b) the orbital magnetic moment projected along the c-axis. Upper left figures of (a) and (b) show the distributions of the central Rh sites with contours lines the interval of which is 4% of their maximum values.

**4. Conclusion**

X-ray magnetic diffraction experiments of a ferromagnetic compound CeRh\(_3\)B\(_2\) have been performed, and the spin and orbital magnetic form factors have been measured separately. Both form factors have been shown to be contributed by Rh as well as Ce. Density distributions of the spin and orbital magnetic moments in real space have been obtained by using the Maximum Entropy Method. By integrating density values at the Ce and Rh sites, we have obtained the spin and orbital magnetic moments of Ce and Rh. As a result, we have observed small but nonnegligible spin and orbital magnetic moments of Rh. This is probably the first experimental evidence showing existence of the spin and orbital moments of Rh in CeRh\(_3\)B\(_2\).
Acknowledgments
The authors thank to H. Adachi, K. Hirano and X. Zhang for their support to the XMD experiments at KEK-PF. This research was partly supported by a Grant-in-Aid for Scientific Research from Ministry of Education, Science, Sports and Culture (20540331) and the XMD measurements were performed in the KEK-PAC proposal of 2006G046 and 2008G190.

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