Magnetic Field Induced $4f$ Octupole in CeB_6 Probed by Resonant X-Ray Diffraction

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A mysterious antiferroquadrupolar ordered phase of CeB_6 is considered as originating from the T_{xyz}-type magnetic octupole moment in magnetic fields. By resonant x-ray diffraction, we have verified that the T_{xyz}-type octupole is indeed induced in the $4f$ orbital of Ce with a propagation vector $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$, thereby supporting the theory. We observed an asymmetric field dependence of the intensity for an electric quadrupole ($E2$) resonance when the field was reversed and extracted a field dependence of the octupole by utilizing the interference with an electric dipole ($E1$) resonance. The result is in good agreement with that of the NMR-line splitting, which reflects the transferred hyperfine field at the boron nucleus from the anisotropic spin distribution of Ce with an O_{xy}-type quadrupole.

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A rich variety of electronic phases arising from multiple degrees of freedom of f electrons has attracted great interest in recent years. In addition to the magnetic dipole moment, the electric quadrupole and magnetic octupole, etc., behave as independent degrees of freedom in a crystal-field eigenstate with orbital degeneracy. Quadrupole orders are frequently realized in localized f-electron systems, and, more exotically, octupole orders can also take place as in NpO_2, $Ce_xLa_{1-x}B_6$ ($x \leq 0.8$) [1–5]. Furthermore, it has recently been recognized that these multipoles sometimes play fundamental roles when f electrons are hybridized with conduction electrons. In Pr-based filled skutterudites such as $PrRu_4P_{12}$, a $4f$-hexadecapole order is combined with Fermi-surface nesting, causing a metal-insulator transition [6]. In $PrOs_4Sb_{12}$, it is suggested that a quadrupolar excitation is associated with the heavy-fermion superconductivity [7]. Thus, understanding the physics of multipole moments is of fundamental importance.

One of the difficulties of multipole research is that they are hard to identify as is often expressed as a hidden order parameter. In most cases, a primary order parameter (OP) is initially inferred indirectly by combining various pieces of information from macroscopic and microscopic methods. Then detailed investigation of a secondary OP by neutron and x-ray diffraction, and of a hyperfine field by NMR, using a single crystal, may provide evidence for the multipole OP [1,2]. Among these microscopic probes, resonant x-ray diffraction (RXD) has a distinctive ability to directly probe ordered structures of multipole tensors up to rank 4, using an electric quadrupole ($E2$) resonant process [8]. With respect to the observation of an antiferroquadrupole (AFQ) order, there have already been several examples of successful applications of RXD mainly using an electric dipole ($E1$) resonance, typically for DyB_2C_2 [9]. On the other hand, with respect to an antiferro-octupole (AFO) order, there has been only one report on $Ce_{0.7}La_{0.3}B_6$ by Mannix *et al.* [4]. They successfully detected an $E2$ signal at zero field, measured the azimuthal-angle dependence, and concluded an AFO order, which was also confirmed by neutron diffraction [5]. However, it was pointed out that the contribution from the $4f$ quadrupole to the $E2$ signal cannot be ruled out [10]. Azimuthal dependence only is sometimes insufficient to separate contributions from different rank tensors to an $E2$ signal.

In this Letter, we report an effective method for extracting even and odd rank tensors, which will be quite useful in studying octupole orders, especially those induced in magnetic fields. Since various kinds of multipoles are induced in magnetic fields and affect the macroscopic properties, it is of fundamental importance to trace what kind of multipole is induced by the field.

A compound we study is CeB_6, a typical Γ_8-quartet system with a simple cubic structure. The Γ_8 has 15 degrees of freedom in total: 3 dipoles, 5 quadrupoles, and 7 octupoles [11]. At zero field, CeB_6 exhibits an O_{xy}-type AFQ order at $T_Q = 3.3$ K followed by an antiferromagnetic (AFM) order at $T_N = 2.3$ K [12–14]. In magnetic fields, T_Q exhibits an anomalous increase up to 8.3 K at 15 T [12], whose most important mechanism has been ascribed to an antiferro-type interaction between field-induced octupoles of T_{xyz} type [11]. Splitting of the boron-NMR line in the AFQ phase can be strong evidence for this interpretation [15,16]. It is explained by a phenomenological analysis of the hyperfine field at the boron nucleus in terms of the multipole moments of Ce based on symmetry arguments. To be exact, however, we have to mention that direct evidence for the existence of the octupole is still lacking. As pointed out by Hanzawa, the microscopic mechanism of the NMR splitting is due to the transferred hyperfine field (THF) via the $2p$ and $2s$ conduction electrons, reflecting the anisotropic spin distribution of Ce with an O_{xy}-type quadrupole [17]. The splitting can also be explained phenomenologically if one considers that the THF, e.g., for borons along the z axis, is proportional to $m_F\langle O_{xy}\rangle$, where m_F is a field-induced uniform magnetization [18].

However, $m_F\langle O_{xy}\rangle$ is not identical to T_{xyz} in the sense that $T_{xyz} \equiv (\sqrt{5}/3)(J_x O_{yz} + J_y O_{zx} + J_z O_{xy})$ represents a complex magnetization distribution where all three terms are equally induced even for the field along the z axis. The field-induced octupole is essentially a quantum mechanical phenomenon, and the increase of T_Q in magnetic fields requires consideration of this real T_{xyz} $4f$ octupole. Therefore, it is worth verifying whether the T_{xyz} octupole is induced in the Ce $4f$ orbital itself.

A RXD experiment has been performed at beam line 3A of the Photon Factory in the High Energy Accelerator Research Organization, using a vertical field superconducting magnet on a two-axis diffractometer. A sample with a mirror-polished (331) surface was mounted in the cryostat, so that the [001] and [110] axes were in the horizontal scattering plane and the field was along the $[\bar{1}10]$ axis. The geometry is illustrated in Fig. 1. The incident photon was π-polarized, and the energy was tuned to the Ce L_{III} absorption edge.

Figure 1 shows the energy spectra of the $(\frac{3}{2}, \frac{3}{2}, \frac{1}{2})$ superlattice reflection at 2.5 K in the AFQ phase for several magnetic fields with reversed directions. We immediately notice that the peaks at 5.724 ($E1$) and 5.718 keV ($E2$) become stronger and well resolved for fields in the plus direction, whereas for fields in the minus direction the $E2$ peak becomes obscure. From this result, we can extract the field dependence of the quadrupole and octupole moments as explained next.

The energy- and field-dependent structure factor for resonant diffraction is generally expressed as

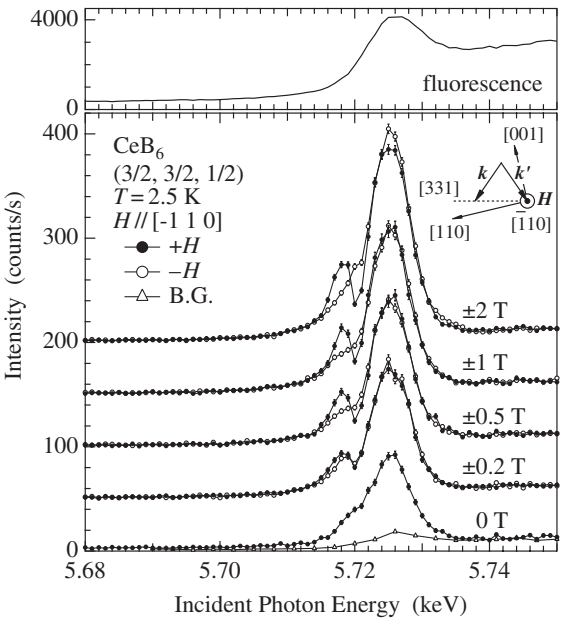

FIG. 1. Top: Fluorescence spectrum of CeB_6. Bottom: X-ray energy spectra of the $(\frac{3}{2}, \frac{3}{2}, \frac{1}{2})$ superlattice reflection in magnetic fields with reversed directions. The triangle shows the background due to the fluorescence.

$$F_{\mathrm{reso}}(E, H) = Z_{E1}(H)\{f'_{E1}(E) + if''_{E1}(E)\} + Z_{E2}(H) \times \{f'_{E2}(E) + if''_{E2}(E)\}, \quad (1)$$

where Z_{E1} and Z_{E2} are unit-cell structure factors for $E1$ and $E2$ processes, which are directly coupled with the atomic tensors $\langle T_q^{(K)}\rangle$ of $5d$ and $4f$ orbitals, respectively [8]. They are written as

$$Z_{E1} = \sum_n e^{i\boldsymbol{\kappa}\cdot\boldsymbol{R}_n} \sum_{K=0}^{2} \sum_q A_K \langle T_q^{(K)}\rangle_n^{(5d)} X_{-q}^{(K)} (-1)^q, \quad (2)$$

$$Z_{E2} = \sum_n e^{i\boldsymbol{\kappa}\cdot\boldsymbol{R}_n} \sum_{K=0}^{4} \sum_q B_K \langle T_q^{(K)}\rangle_n^{(4f)} H_{-q}^{(K)} (-1)^q. \quad (3)$$

Here A_K and B_K are constant factors for the rank-K terms, $X^{(K)}$ and $H^{(K)}$ are spherical tensors of the x-ray beam determined by the diffraction geometry, $\boldsymbol{R}_n$ is a position vector of the nth Ce ion in a unit cell, and $\boldsymbol{\kappa}$ is a scattering vector. $\langle T_q^{(K)}\rangle$ varies with the applied field. The energy-dependent term in Eq. (1) can be written as $f(E) = 1/(E - \Delta + i\Gamma/2)$ ($\Delta = \Delta_{E1}$ or Δ_{E2}) when a resonance can be modeled by a single oscillator. However, we leave it here as $f'(E) + if''(E)$ because the actual form is not so simple [10].

The asymmetry with respect to the field reversal can be understood by considering the following two effects. The first is that the $E1$ and $E2$ terms interfere; i.e., the intensity is proportional to $|Z_{E1}f_{E1} + Z_{E2}f_{E2}|^2$ and not to $|Z_{E1}f_{E1}|^2 + |Z_{E2}f_{E2}|^2$. The second is that the odd rank tensor (magnetic dipole and octupole) reverses its sign with the field reversal, whereas the even rank tensors (electric quadrupole and hexadecapole) do not change sign. That is, the even (odd) rank terms in Z are symmetric (asymmetric) with respect to the field reversal. To analyze the symmetry and asymmetry of the intensity, we write the Z factor in Eq. (1) as $Z^s + iZ^a$, where Z^s (Z^a) represents the symmetric (asymmetric) part. It is noted that the odd rank term is imaginary. The energy- and field-dependent intensity $I(E, H)$ can be calculated by $|F_{\mathrm{reso}}(E, H)|^2$, and the symmetric and asymmetric parts of the intensity, $I^s(E, H)$ and $I^a(E, H)$, are obtained by $\{I(E, H) + I(E, -H)\}/2$ and $\{I(E, H) - I(E, -H)\}/2$, respectively. They are expressed as

$$I^s(E, H) = \{(Z_{E1}^s)^2 + (Z_{E1}^a)^2\}\{(f'_{E1})^2 + (f''_{E1})^2\} + \{(Z_{E2}^s)^2 + (Z_{E2}^a)^2\}\{(f'_{E2})^2 + (f''_{E2})^2\} + 2(Z_{E1}^s Z_{E2}^s + Z_{E1}^a Z_{E2}^a)\mathrm{Re}\{f_{E1}^* f_{E2}\}, \quad (4)$$

$$I^a(E, H) = 2(Z_{E1}^a Z_{E2}^s - Z_{E1}^s Z_{E2}^a)\mathrm{Im}\{f_{E1}^* f_{E2}\}. \quad (5)$$

In Fig. 2, we show the field dependence of the integrated intensity for a rocking scan at each resonance energy. $I^s(E, H)$ and $I^a(E, H)$ deduced from the raw data are shown in the bottom figures. At $E = \Delta_{E1}$ the asymmetric intensity is negligibly small, whereas it clearly exists at $E = \Delta_{E2}$. From these data and Eqs. (4) and (5), the field dependence

of the multipole tensors can be extracted. Of course, to determine all of the parameters in general, we need information from azimuthal-angle dependence, polarization analysis, model calculation, and also from other experimental results. In the present case of CeB_6 for $H \parallel [\bar{1}10]$, however, some factors can be neglected, and the situation becomes quite simple, which is suited for a demonstration.

The sharp anomaly in intensity around 0.1 T corresponds to the one reported in Ref. [19]. This is a transition from the $\langle O_{xy} \rangle$ OP at zero field, with $\langle O_{yz} \rangle$ and $\langle O_{zx} \rangle$ domains equally populated, to the $\langle \alpha O_{yz} + \beta O_{zx} + \gamma O_{xy} \rangle$ OP, where (α, β, γ) is the unit vector of the field direction. This has also been observed by nonresonant x-ray diffraction [20]. Although this is also an important nature of the AFQ phase of CeB_6, we do not deal with it because it is outside the subject of this Letter.

Figure 3 shows the energy spectra of $I^s(E)$ and $I^a(E)$ deduced from the data for ± 2 T. We observe that $I^s(E = \Delta_{E1})$ is dominated by the first term in Eq. (4). In fitting $I^s(E)$ and $I^a(E)$, every term in Eqs. (4) and (5) was assumed as a Lorentzian, where the real and imaginary parts of $f^*_{E1} f_{E2}$ are connected by the Kramers-Kronig relation. The absorption effect and a Gaussian resolution of 2 eV were also taken into account in the fit. Although there are two contributions from Z^s_{E1} and Z^a_{E1} to $I^s(E = \Delta_{E1})$, Z^a_{E1}, reflecting the field-induced AFM dipole, can be neglected here. This is justified by the variation of $I(E = \Delta_{E1})$ as measured by rotating the crystal around the [331] axis. The result can be perfectly explained by considering only the AFQ OP of $\langle \alpha O_{yz} + \beta O_{zx} + \gamma O_{xy} \rangle$, indicating a negligible contribution from the induced AFM. In addition, below T_N, we could not detect any signal at superlattice spots of the AFM order such as $(\frac{5}{4}, \frac{5}{4}, \frac{1}{2})$, probably because it was too small. The dipole moment in the AFM phase estimated by neutron diffraction is $\sim 0.28 \mu_B$ [12], whereas that for the induced AFM in the AFQ phase is $\sim 0.05 \mu_B$ at $H = 2$ T [18]. That is, the dipole is not the main polarization of the $4f$ shell giving rise to the resonant signal.

By taking the square root of $I^s(E = \Delta_{E1})$, Z^s_{E1}, reflecting the AFQ moment of the $5d$ orbital, is obtained. This is proportional to that of the $4f$ orbital, which is $\langle O_{yz} - O_{zx} \rangle$ for $H \parallel [\bar{1}10]$ from the structure-factor calculation. Next, since Z^a_{E1} in Eq. (5) can be neglected, we can deduce Z^a_{E2} by dividing $I^a(E = \Delta_{E2})$ by Z^s_{E1}. As described above, the dipole contribution to Z^a_{E2} may also be neglected, and the obtained result is considered as reflecting only the $4f$ octupole. From the structure-factor calculation, Z^a_{E2} is proportional to $\langle T_{xyz} + 0.02 T^z_{1u} \rangle$ for $H \parallel [\bar{1}10]$, where $\langle T_{xyz} \rangle$ is dominant. These results are plotted in Fig. 4. Z^s_{E2}, reflecting the $4f$ quadrupole and hexadecapole with the same symmetry of $T^{yz}_{2g} - T^{zx}_{2g}$, can also be deduced after some data treatments, but this results in the same field dependence as that of Z^s_{E1} as expected.

In Fig. 4, the field dependence of the $4f$ octupole shows a good agreement with that of THF at the boron site as deduced from NMR [18,21]. In addition, it exhibits a convex dependence like a Brillouin function. This is quite a contrast to the concave field dependence of the induced AFM as measured by neutron diffraction [22]. This fact also supports that Z^a_{E2} is dominated by the octupole contribution.

One of the reasons we could obtain this elegant result is that the scattering geometry for $H \parallel [\bar{1}10]$ provides an

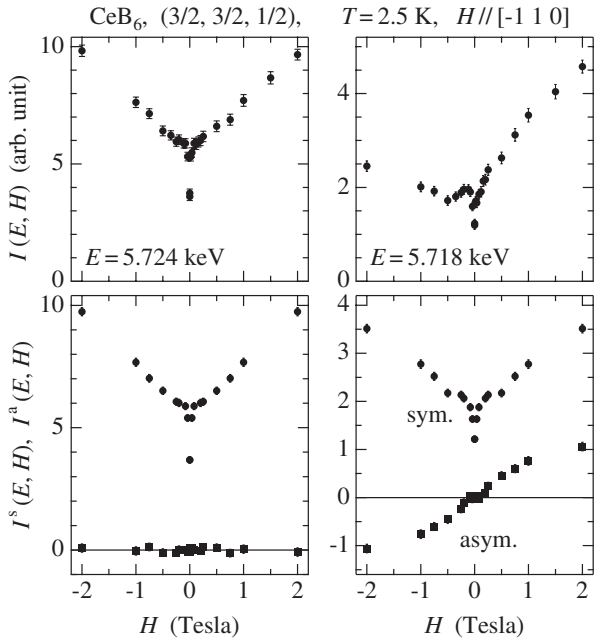

FIG. 2. Top: Magnetic-field dependence of the integrated intensity of the $(\frac{3}{2}, \frac{3}{2}, \frac{1}{2})$ resonant Bragg diffraction measured at $E = 5.724$ (left) and 5.718 keV (right), corresponding to the $E1$ and $E2$ processes, respectively. Bottom: Symmetric (circles) and asymmetric (squares) components of the intensity for the respective processes.

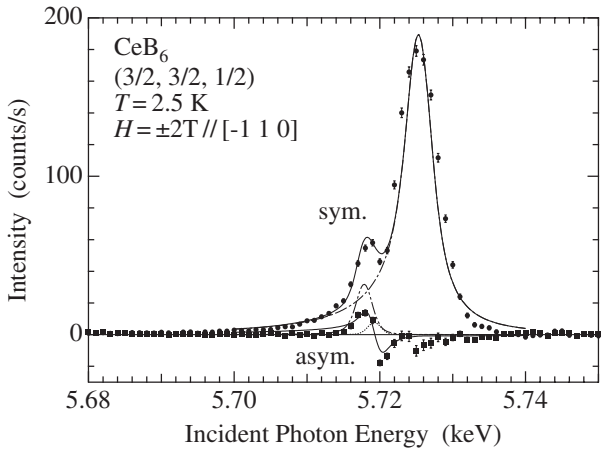

FIG. 3. X-ray energy dependence of the symmetric and asymmetric components deduced from the data for ± 2 T. The solid lines are the fits to the data with Lorentzian components. The single-dotted, double-dotted, and dotted lines represent the 1st, 2nd, and 3rd term in Eq. (4), respectively.

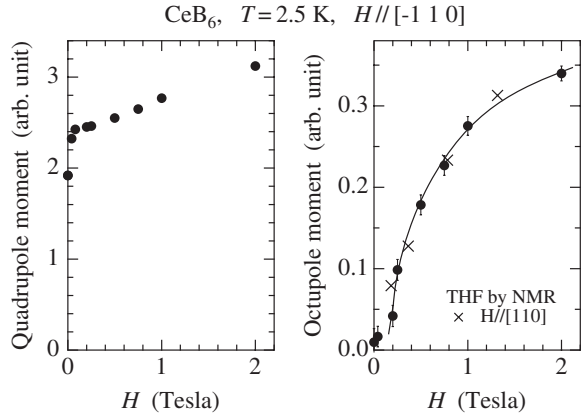

FIG. 4. Magnetic-field dependences of the AFQ and AFO moments deduced from the symmetric $E1$ and asymmetric $E2$ intensities in Fig. 2. The solid line is a guide for the eye. The crosses represent the THF as deduced from NMR.

ideal situation. Using the wave functions obtained from a realistic mean-field model [23], we can calculate the Z factors for each rank and polarization channel. First, all of the Z factors for the $\pi\pi'$ channel vanish except for $Z^{(4)}_{E2,\pi\pi'}$, making the measurement and analysis straightforward. Vanishing of the signal for the $\pi\pi'$ channel was checked by a polarization analysis using a Mo-(200) crystal analyzer at $H = +2$ T, though the data in this Letter were taken without analyzing the polarization. Second, $Z^{(2)}_{E1,\pi\sigma'}$ and $Z^{(3)}_{E2,\pi\sigma'}$ take their maximum at $H \parallel [\bar{1}10]$, giving rise to the strongest interference.

In summary, we have demonstrated that even and odd rank multipoles can be extracted effectively by measuring the asymmetrical intensity of RXD with respect to the field reversal, originating from the interference between the $E1$ and $E2$ resonances. In the present case for CeB_6 in $H \parallel [\bar{1}10]$, this method was quite effective to extract the field dependences of AFQ and AFO moments. The result for the octupole showed a good agreement with that of THF at the boron site deduced from NMR. Our observation directly shows that the octupole moment is, indeed, induced in the $4f$ orbital itself as well as the quadrupole moment, providing evidence for the theory of field-induced multipoles in CeB_6. We expect that the field-reversal method used in the present study can be widely applied to other multipole ordering systems such as NpO_2, $Ce_xLa_{1-x}B_6$, $SmRu_4P_{12}$ [24], and so on.

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