Magnetic-Field-Induced 4f-Octupole in CeB₆ Probed by Resonant X-ray Diffraction

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CeB₆, a typical Γ₅-quartet system, exhibits a mysterious antiferroquadrupolar ordered phase in magnetic fields, which is considered as originating from the Tₓᵧz-type magnetic octupole moment induced by the field. By resonant x-ray diffraction in magnetic fields, we have verified that the Tₓᵧz-type octupole is indeed induced in the 4f-orbital of Ce with a propagation vector (1/2, 1/2, 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 O₂ᵧ-type quadrupole. The field-reversal method used in the present study opens up the possibility of being widely applied to other multipole ordering systems such as NpO₂, CeₓLa₁₋ₓB₆, SmRu₄P₁₂, and so on.

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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 magnetic dipole moment, 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 orderings can also take place as in NpO₂ and CeₓLa₁₋ₓB₆ (x ≤ 0.8) 1,2,3,4,5. 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 PrRu₄P₁₂, a 4f-hexadecapole order is combined with a Fermi-surface nesting, causing a metal-insulator transition 6. In PrOs₄Sb₁₂, 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 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 3. 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 DyₓB₄C₁₂ 3. On the other hand, with respect to an antiferrooctupole (AFO) order, there has been only one report on Ce₀.₇La₀.₃B₆ 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 6. Azimuthal dependence only is not sufficient to separate contributions from different rank tensors to an E2 signal.

In this Letter, we report an effective method that can distinguish between 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 affects the macroscopic properties, it is of fundamental importance to trace what kind of multipole is induced in magnetic fields.

A compound we study is CeB₆, a typical Γ₅-quartet system with a simple cubic structure. The Γ₅ has 15 degrees of freedom in total, 3 dipoles, 5 quadrupoles, and 7 octupoles 11. At zero field, CeB₆ exhibits an O₂ᵧ-type AFQ order at Tᵥ=3.3 K followed by an antiferromagnetic (AFM) order at Tᵥ=2.3 K 12, 13, 14. In magnetic fields, Tᵥ 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 Tₓᵧz-type 11. Splitting of the Boron-NMR line in the AFQ phase can be a 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 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, reflect-
The splitting can also be explained by 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

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

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

$$Z_{E1} = \sum_{n} e^{i\kappa \mathbf{R}_n} \sum_{q} A_K T_{q}^{(K)}(5d) X_{q}^{(K)}(-1)^q \quad (2)$$

$$Z_{E2} = \sum_{n} e^{i\kappa \mathbf{R}_n} \sum_{q} B_K T_{q}^{(K)}(4f) H_{q}^{(K)}(-1)^q. \quad (3)$$

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, $\mathbf{R}_n$ is a position vector of the nth Ce ion in a unit cell, and $\kappa$ is a scattering vector. $(T_q^{(K)})$ 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 $\Delta_{E2}$) 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 such 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 tensor (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 $Z^* + iZ^a$, where $Z^*(Z^a)$ represents the symmetric/asymmetric part corresponding to the even(odd) rank term. It is noted that the odd rank term is imaginary. The energy and field dependent intensity $I(E, H)$ can be calculated by $|F_{\text{reso}}(E, H)|^2$, and the symmetric and asymmetric part 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

$$I^s(E, H) = \{(Z_{E1}^* + Z_{E1}^{a})^2\} \{f_{E1}^{s^*} + f_{E1}^{a}\}^2 + \{(Z_{E2}^* + Z_{E2}^{a})^2\} \{f_{E2}^{s^*} + f_{E2}^{a}\}^2$$

$$+2(Z_{E1} Z_{E2}^{*} Z_{E2}^{a} Z_{E1}^{*} f_{E1}^{s} f_{E2}^{a} \text{Re}\{f_{E1}^{a} f_{E2}^{s}\} \quad (4)$$

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

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$$I^s(E, H) = \{(Z_{E1}^* + Z_{E1}^{a})^2\} \{f_{E1}^{s^*} + f_{E1}^{a}\}^2 + \{(Z_{E2}^* + Z_{E2}^{a})^2\} \{f_{E2}^{s^*} + f_{E2}^{a}\}^2$$

$$+2(Z_{E1} Z_{E2}^{*} Z_{E2}^{a} Z_{E1}^{*} f_{E1}^{s} f_{E2}^{a} \text{Re}\{f_{E1}^{a} f_{E2}^{s}\} \quad (4)$$

$$I^a(E, H) = 2(Z_{E1} Z_{E2}^{*} - Z_{E1}^{a} Z_{E2}^{a} f_{E1}^{s} f_{E2}^{a} \text{Im}\{f_{E1}^{a} f_{E2}^{s}\}. \quad (5)$$
In Fig. 2 we show the field dependence of the integrated intensity for a rocking scan at each resonance energy. The symmetric and asymmetric components 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. (1) and (3), the field dependence of the multipole tensors can be extracted. Of course, to determine all 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 $H \parallel [1 1 0]$, however, some factors can be neglected and the situation become quite simple and suited for a demonstration.

The sharp anomaly in intensity around 0.1 T corresponds to the one reported in [19]. This is a phase transition from the $(O_{yz})$-OP at zero field, with $(O_{yz})$ and $(O_{xx})$ domains equally populated, to the $(\alpha O_{yz} + \beta O_{xx} + \gamma O_{xy})$-OP, where $(\alpha, \beta, \gamma)$ is the unit vector of the field direction. This has also been observed by non-resonant 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 $\pm 2$ 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. (1) and (3) was assumed as a Lorentzian, where the real and imaginary parts of $f_{E1}^s f_{E2}^a$ are connected by the Kramers-Kronig relation. Absorption effect and a Gaussian resolution of 2 eV were also taken into account in the fit. Although there are two contributions from $Z_{E1}^s$ and $Z_{E1}^a$ to $I(E = \Delta_{E1})$, $Z_{E1}^s$, 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 $(\alpha O_{yz} + \beta O_{xx} + \gamma O_{xy})$, indicating 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 $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$, 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 $I^s(E = \Delta_{E1})$, $Z_{E1}^s$, reflecting the AFQ moment of the 5d orbital, is obtained. This is proportional to that of the 4f orbital, which is $(O_{yz} - O_{xx})$ for $H \parallel [1 1 0]$ from the structure-factor calculation. Next, since $Z_{E1}^a$ in Eq. (3) can be neglected, we can deduce $Z_{E2}^a$ by dividing $I^s(E = \Delta_{E2})$ by $Z_{E1}$. As described above, the dipole contribution to $Z_{E2}^s$ may also be neglected, the obtained result is considered as reflecting only the 4f-octupole. From the structure-factor calculation, $Z_{E2}^s$ is proportional to $(T_{xyz} + 0.02 T_{xyz})$ for $H \parallel [1 1 0]$, where $(T_{xyz})$ is dominant. These results are plotted in Fig. 4. $Z_{E2}^a$, reflecting the 4f-quadrupole and hexadecapole with the same symmetry of $T_{yz}^2 - T_{yx}^2$, can also be deduced after some data treatments, but this results in the same field dependence as that of $Z_{E1}^s$ as...
The crosses represent the THF as deduced from NMR. 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 $Z_{E2}^{(2)}$ is dominated by the octupole contribution.

One of the reasons we could obtain this elegant result is that the scattering geometry for $H \parallel [\bar{1} 1 0]$, this method was quite effective to take their maximum at $H = \pm 2$ T, though the data in this paper were taken without analyzing the polarization. Secondly, $Z_{E1,\pi\sigma'}^{(2)}$ and $Z_{E2,\pi\sigma'}^{(3)}$ take their maximum at $H \parallel [\bar{1} 1 0]$, giving rise to the strongest interference.

To summarize, 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 $H \parallel [\bar{1} 1 0]$, this method was quite effective to extract the field dependences of AFQ and AFO moments. The result for 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 an 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$_2$La$_{1-x}$B$_6$, SmRu$_4$P$_{12}$ [24], and so on.

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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.
[20] Y. Tanaka, K. Katsumata, S. Shimomura, and Y. Onuki, J. Phys. Soc. Jpn. 74, 2201 (2005).

[21] M. Takigawa, Ph.D. thesis, University of Tokyo, 1982.

[22] J. Rossat-Mignot, in Methods of Experimental Physics, edited by K. Skold and D. L. Price (Academic Press, New York, 1987) Vol. 23C, p. 69.

[23] M. Sera and S. Kobayashi, J. Phys. Soc. Jpn. 68, 1664 (1999).

[24] M. Yoshizawa, P. Sun, M. Nakamura, Y. Nakanishi, C. Sekine, I. Shirotani, D. Kikuchi, H. Sugawara, and H. Sato, J. Phys. Soc. Jpn. 77, Suppl. A, 67 (2008).