Antiferro-quadrupole Ordering of CeB\textsubscript{6} Studied by Resonant X-ray Scattering

Hironori Nakao, \(^\ast\) Ko-ichi Magishi,\(^1\) Yusuke Wakabayashi,\(^2\) Youichi Murakami, Kuniyuki Koyama,\(^1\) Kazuma Hirota,\(^3\) Yasuo Endoh,\(^4\) and Satoru Kunii\(^3\)

Photon Factory, Institute of Materials Structure Science, High Energy Accelerator Research Organization (KEK), Tsukuba 305-0801, Japan

\(^1\) Faculty of Integrated Arts and Sciences, The University of Tokushima

\(^2\) Department of Physics, Keio University, Yokohama 223-8522, Japan

\(^3\) Department of Physics, Tohoku University, Sendai 980-8578, Japan

\(^4\) Institute for Materials Research, Tohoku University, Sendai 980-8577, Japan

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Under zero magnetic field, a quadrupolar order parameter at \(q_Q = (\frac{1}{2}, \frac{1}{2}, \frac{1}{2})\) in a typical antiferro-quadrupole (AFQ) ordering compound CeB\textsubscript{6} has been observed for the first time by means of a resonant X-ray scattering (RXS) technique. The RXS is observed at the \(2p \rightarrow 5d\) dipole transition energy of the Ce \(L_3\)-edge. Using this RXS technique to observe the pure order parameter of the AFQ state, the magnetic phase diagram of Phase II is first determined.

**KEYWORDS**: CeB\textsubscript{6}, antiferro-quadrupole ordering, orbital ordering, resonant X-ray scattering, magnetic phase diagram

For both \(d\)- and \(f\)-electron systems, various phase transitions involving the orbital degree of freedom are attracting much interest. The orbital degree of freedom is usually coupled with atomic displacements by the Jahn-Teller effect. For example, 3\(d\) electrons are spread in space so that the orbital ordering is definitely accompanied with lattice distortion. In the \(f\)-electron system, however, orbital ordering without atomic displacement owing to electron-electron interaction exists, which is called antiferro-quadrupole (AFQ) ordering.

CeB\textsubscript{6} has been considered a typical compound for AFQ ordering.\(^1\)\textsuperscript{–10}\ CeB\textsubscript{6} has a cubic CsCl-type structure with Ce and B\textsubscript{6} octahedra as shown in Fig. 1. The space group is \(Pm\bar{3}m\) and the lattice constant is \(a = 4.14\ \text{Å}\.\textsuperscript{1}\) The ground state of the Ce\textsuperscript{3+} multiplet is a \(\Gamma_8\) quartet of the spin doublet (Kramers doublet) and the orbital doublet.\(^2\) The specific heat measurement indicates the anomaly of a sharp peak at \(T_N \sim 2.3\ \text{K}\) and a broad satellite peak at \(T_Q \sim 3.2\ \text{K}\).\(^3\) When a magnetic field is applied, \(T_Q\) shifts to a higher temperature with a rise in the peak height and \(T_N\) decreases rapidly. This unusual behavior of \(T_Q\) has attracted much attention. The magnetic scattering of neutron experiments proved that the phase below \(T_N\) (Phase III) is an antiferromagnetic state. In the phase at \(T_N < T < T_Q\) (Phase II), on the other hand, there is no magnetic ordering although \(T_Q\) is strongly affected by the magnetic field.\(^4\) Because the entropy calculated from the specific heat reaches \(R \ln 2\) at \(T_N\),\(^3\) the Kramers degeneracy was expected to lift below \(T_N\). Based on these experimental results, the AFQ transition is expected at \(T_Q\), although the AFQ
order parameter has never been observed under zero magnetic field. This is a famous hidden orbital ordering of the $f$-electron.

A magnetic field was applied to confirm the orbital ordering in Phase II. The field-induced moment was observed by neutron scattering$^{4}$ and NMR.$^{5}$ The neutron experiment observed the order parameter at $q_Q = (\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ indicating a NaCl-type AFQ ordering as shown in Fig. 1, while the results of the NMR measurements indicated a complicated triple-$q$ structure. Recently, however, theories including the influence of octapoles have clarified that the antiferromagnetic structure of $q_Q = (\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ can account for the NMR data.$^{6}$ In ultrasonic measurements, the softening of elastic constants was observed toward $T_Q$, which implied the AFQ ordering of $\Gamma_5$ symmetry.$^{7}$ The mysterious behavior of Phase II under the magnetic field was theoretically explained by the effect of the octupole-octupole interaction$^{6}$ and the fluctuation of the quadrupole moment.$^{8}$ All the results suggest the existence of the $O_{xy}$-type AFQ orbital ordering in Phase II, but the AFQ order parameter $q_Q$ under zero magnetic field has not been observed up to now.

Recently, the resonant X-ray scattering (RXS) technique to observe orbital ordered states has been developed for the 3$d$-electron system.$^{11,12}$ When the orbital of 3$d$-electrons is ordered, the energy level of the 4$p$-orbital splits owing to some interactions. This 4$p$-level splitting is the origin of the RXS.$^{12}$ Two mechanisms for the 4$p$-level splitting are theoretically proposed, however, the mechanisms are a controversial problem.$^{13}$ In this 3$d$-electron system, the orbital ordering can also be discussed on the basis of the state of the lattice distortion studied by structural analysis.$^{14}$ In the 4$f$-electron system, on the other hand, the RXS is the only technique for measuring the order parameter of AFQ without magnetic ordering under zero magnetic field. For the $L_3$-edge of the Ce ion, the energy level splitting of the 5$d$-orbital is expected to induce the RXS. The 5$d$-level splitting is caused by the Coulomb interaction between 4$f$- and 5$d$-orbitals rather than by the lattice distortion, because the localized 4$f$-electron has the weaker coupling with the lattice. Actually, no superlattice peak due to lattice distortion$^{15}$ has been observed below $T_Q$ in CeB$_6$ up to now. In DyB$_2$C$_2$ of the 4$f$-electron system, Hirota et al. successfully measured an RXS signal.
of the AFQ ordering for the first time.\(^\text{16}\) In order to develop the RXS technique to observe the orbital ordering in \(f\)-electron systems, a study on AFQ ordering in CeB\(_6\) is very important. In this letter, we present the AFQ order parameter in CeB\(_6\) which has been observed for the first time by using the RXS technique under zero magnetic field and a magnetic field up to 2 T.

A single crystal of CeB\(_6\) was fabricated by the floating zone method under pressurized high-purity Ar gas.\(^\text{9}\) The (1 1 1) surface, \(\sim 3 \times 1.5\) mm\(^2\), was cut and polished with fine emery paper. X-ray scattering experiments were carried out at the beam lines (BL) 4C and 16A2 of the Photon Factory in KEK. At BL-16A2, the incident beam was monochromatized by Si(111) double crystals; the second crystal was used for horizontal sagittal focusing. The beam was vertically focused using a mirror. The incident X-ray energy is about 5.72 keV of a Ce L\(_3\)-edge and the energy resolution is about 1 eV. A four-circle diffractometer equipped with a He-flow cryostat was used. The flow of He gas in the sample space prevented the sample surface from heating up due to X-ray irradiation. The temperature can be decreased to 2.5 K by He pumping, and the magnetic field can be applied up to \(H = 2\) T using a superconducting magnet. The polarization vector \(\sigma\) of the incident X-ray was parallel to [11 \(-\bar{2}\)] of the crystal structure and the magnetic field was also applied along the [11 \(-\bar{2}\)] in this experiment.

The RXS of the order parameter at \(q_Q = (\frac{1}{2}, \frac{1}{2}, \frac{1}{2})\) due to AFQ ordering has been searched under zero magnetic field. The energy dependence of scattering intensities at \((\frac{1}{2}, \frac{1}{2}, \frac{1}{2})\) and at \((0.49, 0.49, 0.49)\) (open circles) with \(H = 0\) T and \(T = 2.7\) K. The difference of intensities between \((\frac{1}{2}, \frac{1}{2}, \frac{1}{2})\) and \((0.49, 0.49, 0.49)\) (filled triangles). Inset: Temperature dependence of (hhh) scans at 5.722 keV and at \(H = 0\) T.

The RXS of the order parameter at \(q_Q = (\frac{1}{2}, \frac{1}{2}, \frac{1}{2})\) due to AFQ ordering has been searched under zero magnetic field. The energy dependence of scattering intensities at \((\frac{1}{2}, \frac{1}{2}, \frac{1}{2})\) is measured when \(H = 0\) T and \(T = 2.7\) K, as shown in Fig. 2. The intensity at \((0.49, 0.49, 0.49)\) is mainly
attributed to the fluorescence of the Ce ion so that we regard the intensity as the background. The
difference between the two intensities is also shown in Fig. 2. The weak signal of RXS is observed
at the \(2p \rightarrow 5d\) dipole transition energy of 5.722 keV which is denoted by an arrow. The \((hhh)\)
scans of the reciprocal lattice space at 5.722 keV are shown in the inset of Fig. 2. The half-width at
half-maximum of the peak at \(T = 3.02\) K \((<T_Q)\) is \(0.00053\ \AA^{-1}\) which is resolution-limited in this
experimental configuration; namely, this phase is a long-range ordered state. The dependence of the
intensity on the energy and \(q\)-space is strong evidence that this peak intensity is attributable to
the AFQ ordering in CeB\(_6\). The signal of RXS disappears at \(T = 3.20\) K \((>T_Q)\), as shown in the
inset. Consequently, the temperature dependence of the AFQ order parameter is clearly observed.

![Fig. 3. Temperature dependence of \((hhh)\) scans at \(E = 5.722\) keV and \(H = 1.9\) T.](image)

Next, we investigate the AFQ ordering in a magnetic field using this RXS technique. Figure 3
shows the temperature dependence of the RXS of \((1/2,1/2,1/2)\) at \(E = 5.722\) keV and \(H = 1.9\) T. The
RXS intensity is much larger than that of the RXS under zero magnetic field. The peak profiles
can be fitted by Gaussian curves and the peak widths are also resolution-limited. The dependence of the
RXS integrated intensities on the temperature and field is summarized in Fig. 4. As the
magnetic field is increased, the RXS intensity becomes larger and the transition temperature \(T_Q\)
shifts to higher ones. The intensities of RXS at low temperatures grow with increasing field owing
to the development of the order parameter of the AFQ state. These temperature dependences of the
intensities are fitted well by \(I_{(1/2,1/2,1/2)} \propto (\frac{T_Q-T}{T_Q})^{2\beta}\) with the critical exponent \(\beta = 0.37\)
which was determined by the neutron scattering experiment. The solid lines in Fig. 4 indicate this
function. All the data can be fitted by this function with the same \(\beta\) within experimental error.
Based on this fitting, the \(H - T\) phase diagram is determined, as shown in the inset of Fig. 4. This
phase diagram is in good agreement with previous result of neutron diffraction. The increase in
\(T_Q\), which is an unusual behavior of CeB\(_6\), is clearly shown in the phase diagram. All the peak
This work Ref.[4] & Ref.[2]

Phase I
Phase II

Fig. 4. Temperature dependence of RXS intensities of CeB$_6$ with various magnetic fields, $H \parallel [11\bar{2}]$. The solid lines are results of fitting with the critical index $\beta = 0.37$. The transition temperatures $T_Q$ are indicated by thick vertical lines. The baselines are shifted for clarity.

Inset: $H - T$ phase diagram for the present result and the result of the neutron experiment with the magnetic field $H \parallel [111]$ (Ref.[4]).

widths below $T_Q$ are resolution limited and have no temperature dependence. The short-range ordered state could not be observed at $T > T_Q$ owing to a weak signal although the short-range ordering is expected theoretically.\(^8\) Thus, by using the RXS technique at the Ce $L_3$-edge $2p \rightarrow 5d$ dipole transition energy, the order parameter of AFQ has been measured and the phase diagram has also been determined. It is noted that the RXS technique is the only experimental technique for observing the order parameter of AFQ under zero magnetic field.

When a magnetic field is applied, X-ray scattering, as well as neutron scattering, can be used to detect magnetic scattering of the field-induced moment. Therefore we should pay attention to the origin of the observed intensity. Under zero magnetic field, on the other hand, the intensity of RXS corresponds not to magnetic scattering, but to the pure AFQ order parameter. The scattering intensity does not change much when the field is applied. Therefore, it is expected that the RXS under magnetic field also corresponds to the pure order parameter of AFQ ordering and has no component of magnetic scattering.

On the basis of the azimuthal angle dependence of RXS, the wave function of the ordered orbital can be determined quantitatively, which has been demonstrated in the case of YTiO$_3$.\(^{17}\) We attempted to measure the azimuthal angle dependence of RXS under zero magnetic field. The intensity was so weak in CeB$_6$ that a quantitative discussion could not be made. However, it is possible to determine the wave function of the ordered orbital in the AFQ state based on the
azimuthal angle dependence of RXS. Moreover, there is a possibility of determining the various types of the induced quadrupole ordered state depending on the applied field directions, which have been predicted by some theories.\(^6\) This RXS at the dipole transition energy is represented by a tensor of the atomic scattering factor, which only reveals the symmetry of the quadrupole ordered state. On the basis of RXS at the dipole transition, therefore, we unfortunately can not observe octapole. The RXS observed here is considered to reflect the energy level split of the Ce 5\(d\)-orbital due to the Coulomb interaction between 4\(f\) and 5\(d\)-orbitals, however, the scattering mechanism is still a controversial problem. In fact, we also must consider an anisotropic potential of the core 2\(p\)-hole. Development of a theory concerned with the RXS mechanism in the \(f\)-electron system is strongly desired.

We have succeeded in measuring the order parameter \(q_Q = (\frac{1}{2}, \frac{1}{2}, \frac{1}{2})\) under zero magnetic field in a typical AFQ-ordered system, CeB\(_6\), for the first time. The RXS is observed at the 2\(p\) \(\rightarrow\) 5\(d\) dipole transition energy of the Ce L\(_3\)-edge owing to the energy level split of the Ce 5\(d\)-orbital. Only the RXS technique can be used to observe the order parameter including information on Q of AFQ ordering under zero magnetic field, as opposed to neutron scattering observing the field-induced moment. Using this observation of the pure order parameter of AFQ, the magnetic phase diagram is elucidated. This success with the typical AFQ compound, CeB\(_6\), will be crucial in the study of AFQ materials.

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