Detection of Neutron Scattering from Phase IV of Ce$_{0.7}$La$_{0.3}$B$_6$: A Confirmation of the Octupole Order

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We have performed a single crystal neutron scattering experiment on Ce$_{0.7}$La$_{0.3}$B$_6$ to microscopically investigate the order parameter of phase IV. Below the phase transition temperature 1.5 K of phase IV, weak but distinct superlattice reflections at the scattering vector $\kappa = \left(\frac{1}{3}, \frac{1}{3}, \frac{1}{3}\right)$ ($h, l = \text{odd number}$) have been observed for the first time by neutron scattering. The intensity of the superlattice reflections is stronger for high scattering vectors, which is quite different from the usual magnetic form factor of magnetic dipoles. This result directly evidences that the order parameter of phase IV has a complex magnetization density, consistent with the recent experimental and theoretical prediction in which the order parameter is the magnetic octupoles $T^3$ with $\Gamma_5$ symmetry of the point group $O_h$. Neutron scattering experiments using short wavelength neutrons, as done in this study, could become a general method to study the high-rank multipoles in $f$ electron systems.

KEYWORDS: Ce$_x$La$_{1-x}$B$_6$, phase IV, neutron scattering, octupole order

The importance of high-rank multipolar degrees of freedom of $f$ electrons in strongly correlated electron systems has recently been widely recognized. A typical dense Kondo compound CeB$_6$ with a simple cubic crystal structure of space group $Pm3m$ is a well-known example where the importance was clarified experimentally and theoretically. It shows the following two successive phase transitions: The first is from the paramagnetic phase (phase I) to the antiferro-quadrupolar ordering phase characterized by the wave vector $\mathbf{k}_Q = \left[\frac{1}{3}, \frac{1}{3}, \frac{1}{3}\right]$ at 3.3 K (phase II), followed by the second transition to the antiferromagnetic ordering phase with a complex magnetic structure characterized by the four nonequivalent wave vectors at 2.3 K (phase III), where the fifteen multipoles in the $\Gamma_8$ quartet crystal-field ground state of CeB$_6$ play an important role for these orderings. By doping La into the Ce site in this system, a new phase called phase IV appears below $T_{IV} = 1.7$ K and 1.5 K in Ce$_x$La$_{1-x}$B$_6$ for $x = 0.75$ and 0.70, respectively. From the initial discovery of phase IV, its characteristic magnetic phase diagram and anomalous bulk properties, which show the isotropic cusp of magnetization at $T_{IV}$ and the strong elastic softening of $c_{44}$ within phase IV, suggested that the ordering of phase IV must be different from any quadrupolar ordering. Since the $\Gamma_8$ quartet has three types of octupoles – $T_{xyz}$, $T^2$, and $T^3$ – in addition to dipoles and quadrupoles, it was argued that the magnetic octupoles are a possible candidate for the order parameter. Following these studies, the magnetization under uniaxial pressure, thermal expansion, and elastic constant measurements supported that the order parameter of phase IV is $T^3$ octupoles with $\Gamma_5$ symmetry of the point group $O_h$. It is consistent with the existence of internal magnetic fields detected by NMR and $\mu$SR as well as a theoretical model. Furthermore, evidence of the antiferro-octupolar ordering of $T^3$ with the same wave vector as $\mathbf{k}_Q$ has recently been reported by the resonant X-ray scattering experiment and its detailed analysis, although further studies are necessary for understanding the overall nature of phase IV in Ce$_x$La$_{1-x}$B$_6$.

In principle, such time-reversal-symmetry-breaking high-rank multipoles can be detected by neutron scattering, because a neutron interacts with electrons through magnetic interactions. Moreover, this probe has the advantage of being able to get direct information about the magnetization density of high-rank multipoles from the magnetic form factor. Notwithstanding this expectation, no significant magnetic Bragg peaks were observed for phase IV within experimental accuracy in our previous neutron scattering experiments below $|\mathbf{Q}| = \frac{2\pi \kappa}{\lambda} = 0.4 \text{Å}^{-1}$, where $\mathbf{k}$, $\theta$, and $\lambda$ are the scattering vector, Bragg angle, and neutron wavelength, respectively. Although the contribution from magnetic octupoles to the neutron scattering cross section may be small, it must be finite and the scattering intensity in the high $\mathbf{k}$ vector region is expected to be stronger than that in the low $\mathbf{k}$ vector, because magnetic octupoles must have a complex magnetization density with no spatially uniform magnetization. Furthermore, a recent theoretical calculation of the magnetic form factor of octupoles predicts a detectable scattering intensity magnitude.

In this letter, we report the recent results of the neutron scattering experiment on a Ce$_{0.7}$La$_{0.3}$B$_6$ single crystal, focusing attention on superlattice reflections in the high scattering vector region. We have succeeded in detecting weak but distinct superlattice reflections from...
phase IV by neutron scattering for the first time. The \[\kappa\] dependence of the magnetic form factor in the superlattice spots directly evidences that the order parameter of phase IV has a complex structure of magnetization density, consistent with the theoretical and experimental prediction that the order parameter is the magnetic octupoles \[T^{\beta}\] with \[\Gamma_5\] symmetry of \[O_h\].

A large single crystal of \[\text{Ce}_0.7\text{La}_{0.3}\text{B}_6\] was grown by the floating zone method, using 99.52\% enriched \[^{11}\text{B}\] to avoid the large neutron absorption due to \[^{10}\text{B}\]. The bulk properties of the single crystal were checked by electrical resistivity and magnetization measurements. The sample is cylindrical in shape with a diameter and length of 4.4 mm and 14 mm, respectively. The cylinder axis is nearly parallel to the [010] direction. The neutron scattering experiment was performed on the thermal neutron triple-axis spectrometer TOPAN (6G) at the JRR-3M reactor in the Japan Atomic Energy Agency. The sample was mounted in the mixing chamber of a \[^3\text{He}-^4\text{He}\] dilution refrigerator with a superconducting magnet.

Magnetic fields were applied along the [49x-950]normal to the \((\text{Magnetic fields were applied along the } [\bar{4}3\text{M reactor in the Japan Atomic Energy Agency.})\) 

The neutron scattering experiment was performed on the thermal neutron triple-axis spectrometer TOPAN (6G) at the JRR-3M reactor in the Japan Atomic Energy Agency. The sample was mounted in the mixing chamber of a \[^3\text{He}-^4\text{He}\] dilution refrigerator with a superconducting magnet. Magnetic fields were applied along the [1,1,0] direction, normal to the \((h,h,l)\) scattering plane. Incident neutrons with the short wavelength \[\lambda = 1.4133\text{A}\] were selected by a pyrolytic graphite (PG) monochromator in order to search for superlattice reflections in the high scattering vector region. The triple-axis mode was used with the collimation open-60'-60'-60' and double PG filters to get a better signal-to-noise ratio. In this experimental setup, the mosaicity of the sample is 0.36\° full width at half maximum (FWHM), reflecting the good quality of the single crystal.

For determining of the magnetic form factor, some corrections are needed. The Lorentz factor and absorption factor corrections were made for the observed nuclear and superlattice reflections. The former was represented by \[1/\sin 2\theta\] in the present geometry of scans. The latter was numerically calculated by the Fortran program by taking the approximate shape of the sample into account. The change in the intensity due to the absorption correction is less than 16\%. To obtain the absolute value of the magnetic form factor, information about the normalization factor between the integrated intensity of fundamental nuclear Bragg reflections and the intensity calculated from the nuclear structure factors is also needed. For calculating the nuclear structure factors, the most reliable site parameter of B determined by the previous powder neutron experiment on \[\text{Ce}_{0.75}\text{La}_{0.25}\text{B}_6\] was used. However, the integrated intensity of several nuclear Bragg reflections is not proportional to the calculated value, especially for strong Bragg reflections. This deviation may be caused by the unavoidable extinction effects,\textsuperscript{23} which strongly influence the Bragg intensity in experiments using a large single crystal with a small mosaicity as used in this study. It is difficult to correct for the influence of the extinction effects on the nuclear Bragg intensity in this case. Thus, the normalization factor was estimated by using the intensity of three relatively weak Bragg reflections \((2,2,0), (1,1,0),\) and \((0,0,1)\).

At the lowest temperature 0.25 K under a zero magnetic field in phase IV, we have observed weak superlattice reflections characterized by the wave vector \([1\frac{1}{2},2\frac{1}{2},1\frac{1}{2}]\) for the first time. This wave vector is the same as determined by the recent resonant X-ray scattering experiment.\textsuperscript{16} Figure 1 shows an example of the scattering patterns of rocking curves at the scattering vector \(\mathbf{\kappa} = (\frac{5}{2},\frac{5}{2},\frac{5}{2})\) in phase I (at temperature \(T = 2\ \text{K}\) and magnetic field \(B = 0\ \text{T}\)), phase III \((T = 0.25\ \text{K}, B = 1\ \text{T})\), and phase IV \((T = 0.25\ \text{K}, B = 0\ \text{T})\) in Ce\textsubscript{0.7},La\textsubscript{0.3}B\textsubscript{6}. The magnetic field is applied along the [1,1,0] direction.

![Fig. 1. (Color online) Scattering patterns of rocking curves at the scattering vector $\mathbf{\kappa} = (\frac{5}{2},\frac{5}{2},\frac{5}{2})$ in phase I (at temperature $T = 2$ K and magnetic field $B = 0$ T), phase III ($T = 0.25$ K, $B = 1$ T), and phase IV ($T = 0.25$ K, $B = 0$ T) in Ce$_{0.7}$La$_{0.3}$B$_6$. The magnetic field is applied along the [1,1,0] direction.](image1.png)

![Fig. 2. (Color online) Difference diffraction patterns between 0.25 K and 2 K under a zero magnetic field at $\kappa = (\frac{5}{2},\frac{5}{2},\frac{5}{2})$ along the [1,1,1] direction in Ce$_{0.7}$La$_{0.3}$B$_6$. The lines are Gaussian fits.](image2.png)
Fig. 3. (Color online) (a) Temperature dependence of the intensity at the peak positions of $\kappa = (\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$, $(\frac{1}{2}, 0, 0)$, and $(\frac{1}{2}, 0, \frac{1}{2})$ in a zero magnetic field. (b) Magnetic field dependence along the $[\bar{1}, 1, 0]$ direction of the intensity at the peak position of $\kappa = (\frac{1}{2}, 0, \frac{1}{2})$ at 0.25 K, where the background intensity is subtracted. The arrows indicate the phase boundary of phase IV reported by the bulk measurements.

The width of the Gaussian profile function is fixed to that under a zero magnetic field, the peaks at $\kappa = (\frac{1}{2}, 0, \frac{1}{2})$ at 0.25 K, where the background intensity is subtracted. The arrows indicate the phase boundary of phase IV reported by the bulk measurements.

Fig. 4. (Color online) Magnetic form factor at the superlattice spots along the $[1,1,1]$ (open circles) and $[1,1,\bar{1}]$ (filled circles) directions in phase IV of Ce$_{0.7}$La$_{0.3}$B$_6$.

The expected value of $2Q_{\perp}\mu_B = -\kappa \times (M(\kappa) \times \kappa)$.

The expectation value of $2Q_{\perp}$ is the magnetic form factor. Since the magnetization density of octupoles is completely different from that of dipoles, as seen in eq. (2), their magnetic form factors show a qualitatively different behavior in the $\kappa$ dependence. In the dipolar case, the form factor decreases with increasing $\kappa$, such as that reported in the pure system CeB$_6$. On the other hand, in the octupolar case, the form factor is zero at $\kappa = 0$ and has a maximum at a finite $\kappa$, reflecting its complex magnetization density with no spatially uniform magnetization. The characteristic behavior of the form factor of octupoles is given by the detailed theoretical calculation of $2|\lambda Q_{\perp}|^2$, taking the orbital contribution of the second term of eq. (1) correctly, in which the atomic wave function diagonal for the magnetic octupole $T^3$ in the $\Gamma_8$ quartet is assumed. Therefore, we can distinguish whether the observed superlattice reflections originate from dipoles or octupoles by the $\kappa$ dependence of the magnetic form factor.

Figure 4 shows the magnetic form factor at the superlattice spots along the $[1,1,1]$ and $[1,1,\bar{1}]$ directions obtained by using the integrated intensity of the observed superlattice reflections and by making the corrections. The absolute value of the form factor is slightly less than 0.1$\mu_B$. This magnitude especially at the smallest scattering vector $\kappa = (\frac{1}{2}, 0, \frac{1}{2})$ with $\frac{\Delta Q_{\perp}}{Q_{\perp}} = 0.1A^{-1}$, which is expected to be the largest scattering intensity in the
usual magnetic neutron scattering, is quite small; it is comparable to the magnitude of tiny magnetic dipole moments reported in some heavy electron systems. This smallness must be the reason why the high-rank multipoles in f electron systems. Further neutron scattering measurements, including experiments under uniaxial stress, are planned to clarify the detailed nature of the order parameter of phase IV.

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