Magnetic Anisotropy of the Antiferroquadrupole Phase in $Ce_{0.50}La_{0.50}B_6$

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Magnetic phase diagrams for antiferroquadrupole (AFQ) phase II and antiferromagnetic (AFM) phase III in $Ce_{0.50}La_{0.50}B_6$ with a Γ_8 ground state have been investigated by ultrasonic measurements. The hybrid magnet (Gama) in the National Institute for Materials Science was employed for high-field measurements up to 30 T and a ^{3}He-^{4}He dilution refrigerator was used for low-temperature experiments down to 20 mK. The phase boundary from paramagnetic phase I to AFQ phase II under [001] magnetic fields closes at $H_{\text{I-II}} \sim 29$ T, while the boundary is still open under fields along the [110] and [111] directions even up to 30 T. This anisotropic character of phase II in fields is consistent with the theoretical calculation based on the O_{xy}-type AFQ ordering. We also found that AFM phase III reduces considerably in fields turning from the [001] to [110] and [111] directions.

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The spin and orbital degrees of freedom of $4f$ electron in rare earth compounds brings about multipole orderings in addition to conventional magnetic dipole orderings at low temperatures. The Ce-based cubic compound CeB_6 with a Γ_8 quartet being mapped to SU(4) symmetry for the ground state, in particular, has currently received a lot of interest because of a rich variety of phenomena relating to multipole orderings. The separation of the Γ_8 ground state from a Γ_7 excited doublet at 540 K in CeB_6 [1,2] provides an ideal electron system, which is dominated by the pure Γ_8 quartet with 15 degrees of freedom of SU(4) as $\Gamma_8 \otimes \Gamma_8 = \Gamma_1 \oplus \Gamma_2 \oplus \Gamma_3 \oplus 2\Gamma_4 \oplus 2\Gamma_5$. Three magnetic dipoles of J_x, J_y, J_z with Γ_4 symmetry are relevant for antiferromagnetic (AFM) ordering in phase III below $T_N = 2.3$ K of CeB_6. There are five electric quadrupoles of O_2^0, O_2^2 with Γ_3 symmetry and O_{yz}, O_{zx}, O_{xy} with Γ_5. The intersite interaction of O_{yz}, O_{zx}, O_{xy} is relevant for the antiferroquadrupole (AFQ) ordering with a propagation vector $\boldsymbol{k} = [1/2, 1/2, 1/2]$ in phase II below $T_Q = 3.3$ K of CeB_6 [3,4]. Seven magnetic octupoles consist of T_{xyz} with Γ_2 symmetry, $T_x^\alpha, T_y^\alpha, T_z^\alpha$ with Γ_4, and $T_x^\beta, T_y^\beta, T_z^\beta$ with Γ_5. The octupole T_{xyz}, in particular, plays an important role to stabilize AFQ phase II of CeB_6 under magnetic fields [4].

The transition temperature $T_Q = 3.3$ K at zero field from paramagnetic phase I to AFQ phase II in CeB_6 shifts to higher temperatures with increasing field as $T_Q = 8.5$ K at $H = 15$ T [3]. Recent high-field magnetic measurements with a metal film cantilever magnetometer revealed that the I-II phase transition temperature further increases to $T_Q = 9.5$ K at 30 T [5]. A model calculation based on the Hamiltonian of the Ruderman-Kittel-Kasuya-Yoshida (RKKY)-type interaction for the O_{xy}-type quadrupole and field-induced octupole T_{xyz} has successfully reproduced this increasing of T_Q with increasing field in CeB_6 [6,7]. It has also been pointed out that the fluctuation of the multipole degrees of freedom of the Γ_8 quartet plays a role in giving rise to the increase of T_Q with increasing field. Because of the symmetry breaking character of the AFQ ordering in phase II, the I-II phase boundary should definitely exist in magnetic field. Presumably, the I-II phase boundary in CeB_6 is expected to show a closed loop in high magnetic fields. Recently, Shiina has shown an extended model calculation for the magnetic anisotropy of the AFQ phase in CeB_6. His calculation has shown that the I-II phase boundary may close at a high field of ~70 T along the [001] direction and may not close even in fields of 70 T along the [110] or [111] directions [7]. Because of the difficulty of high-field experiments, the overall feature about AFQ phase II of CeB_6 in fields has not been settled yet. The reduction of the intersite interactions in the diluted system $Ce_xLa_{1-x}B_6$ may provide a chance to detect whether the I-II phase boundary close or not with increasing field. The specific heat measurements on $x = 0.4$–0.36 in fields up to 15 T have shown a tendency to close the I-II phase boundary [8] that seems to be favorable for the theoretical anticipation by Shiina [7].

The decreasing x from pure CeB_6 ($x = 1.0$) in the diluted $Ce_xLa_{1-x}B_6$ system reduces the intersite quadrupole interaction for T_Q of AFQ phase II as well as the magnetic interaction for T_N of AFM phase III. The former quadrupole interaction decreases much faster than the latter magnetic interaction with decreasing x. The compound $x = 0.75$ exhibits an ordered phase IV at $T_C = 1.6$ K and successively changes into AFM phase III at $T_N = 1.1$ K [9–11]. In magnetic fields phase IV closes to the tetracritical point where the I-II-III-IV phases coexist.

In diluted compounds of $x = 0.70$ and 0.65 phase IV is stable down to 20 mK showing no sign of the transition to phase III [12]. The ordered phase IV is characterized by huge softening of the transverse C_{44} mode [9] and magnetic isotropy [10]. Recently, our group has found the transition from a cubic lattice to a trigonal one in phase IV with a spontaneous distortion $\langle \varepsilon_{yz} \rangle = \langle \varepsilon_{zx} \rangle = \langle \varepsilon_{xy} \rangle \neq 0$. We have proposed the ferroquadrupole ordering accompanied by trigonal distortion in phase IV [13]. The octupole ordering $T_x^\beta, T_y^\beta, T_z^\beta$ with Γ_5 symmetry in phase IV has also been proposed to explain the trigonal strain, which is proportional to the quadrupole, as the secondary order parameter [14].

In more diluted compounds $x = 0.60$ and 0.50, the Γ_8 ground state falls into the nonmagnetic state due to the Kondo screening effect showing no distinct transition down to $T = 0$ K [12,15,16]. The broad rounded anomaly around 1.0 K in specific heat in the compounds $x = 0.60$ and 0.50 is distinguished from sharp λ peaks at the I-IV phase transition points in $x = 0.70$ and 0.75 [15]. Furthermore, the low-temperature limit of the soft C_{44} in $x = 0.60$ and 0.50 is shallower than that in phase IV of $x = 0.70$ and 0.75 [12]. The low-temperature nonmagnetic state in $x = 0.60$ and 0.50 easily transforms into the ordered AFQ phase II or AFM phase III in low-magnetic fields above $H \sim 2$ T.

In the present Letter we report on the first observation of the upper critical field of phase II in $x = 0.50$, being responsible for the theoretical analysis of the intersite quadrupole interaction not only in $x = 0.50$ but also in pure CeB_6. Furthermore, we report on a magnetic anisotropy of phase III at low temperatures. We have performed the ultrasonic measurements on the compound $x = 0.50$ to examine the magnetic phase diagram at high magnetic fields up to 30 T and at low temperatures down to 20 mK. Single crystals of $Ce_{0.50}La_{0.50}B_6$ for the present experiments were grown by a floating zone method. The hybrid magnet (Gama) consisting of the superconducting magnet and the water-cooled Cu magnet in the Tsukuba Magnet Laboratory at the National Institute for Materials Science was used for the present high-field ultrasonic measurements up to 30 T with a ^{4}He cryostat. The temperature in high magnetic fields was measured by a calibrated thermometer of Cernox™ CX-1030AA (Lake Shore Cryotronics, Inc.), which is highly efficient against field-induced error [17]. The sensor in the present experiment indicates 1.8 K at 1.5 K and 30 T, which error reduces considerably in higher temperatures and below 20 T. A ^{3}He-^{4}He dilution refrigerator down to 20 mK with a top-loading probe combined to a superconducting magnet up to 18 T at Niigata University has been used for the low-temperature ultrasonic measurements. The temperature in the dilution refrigerator was measured by calibrated ruthenium oxide thermometers equipped at the side of a sample in the magnetic field center and the mixing chamber in the field cancellation region. The ultrasonic pulse wave was generated and detected by piezoelectric plates $LiNbO_3$ with thickness 40 μm bonded on the plane parallel surfaces of the sample. The high electromechanical coupling coefficient $k = 0.4$–0.5 in $LiNbO_3$ was crucially important for low-input power ultrasonic experiments in the dilution refrigerator down to 20 mK.

Because the elastic constant corresponds to the quadrupole susceptibility, the ultrasonic measurement is a sensitive probe to detect the quadrupole phase transition of $Ce_{0.50}La_{0.50}B_6$ in fields. In Fig. 1 we show the temperature dependence of the elastic constant C_{11} measured by the longitudinal ultrasonic wave propagating along the fourfold [001] axis. The magnetic fields up to 30 T were applied parallel to the propagation direction of [001]. The bending point indicating the I-II phase transition shifts to lower temperatures with increasing field from 15 T up to 25 T. The temperature dependence under 30 T, however, does not show any sign of the I-II phase transition above 1.8 K. This result clearly shows the I-II phase boundary closes at a critical field below 30 T. The inset of Fig. 1 shows $\Delta C_{11}/C_{11}$ as a function of applied magnetic fields. At 1.5 and 3 K we have observed the I-II phase transition in low fields and successively the II-I phase transition in high fields. These transition points are shown by arrows in the inset of Fig. 1.

Next we survey the I-II phase transition points in fields along the threefold [111] axis and the twofold [110] axis, where phase II is expected to be more stable than that along [001]. In Fig. 2(a), we show the temperature dependence of $C_{L[111]} = C_B + 4C_{44}/3$ in applied magnetic fields from 10 to 30 T along the [111] axis parallel to

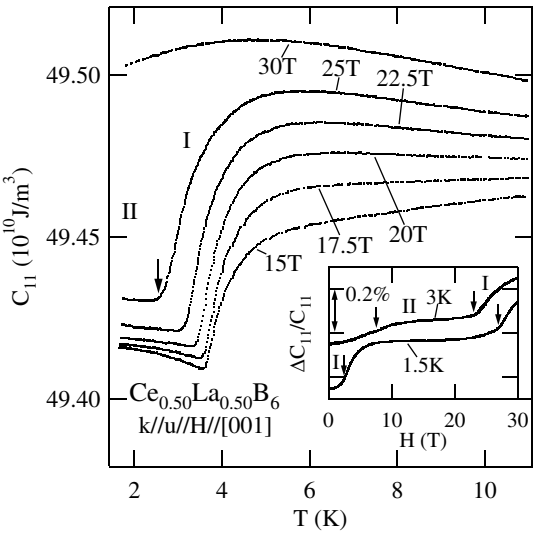

FIG. 1. Temperature dependence of the elastic constant C_{11} in $Ce_{0.50}La_{0.50}B_6$ in high magnetic fields along the [001] direction. The inset shows field dependence of $\Delta C_{11}/C_{11}$ at various temperatures.

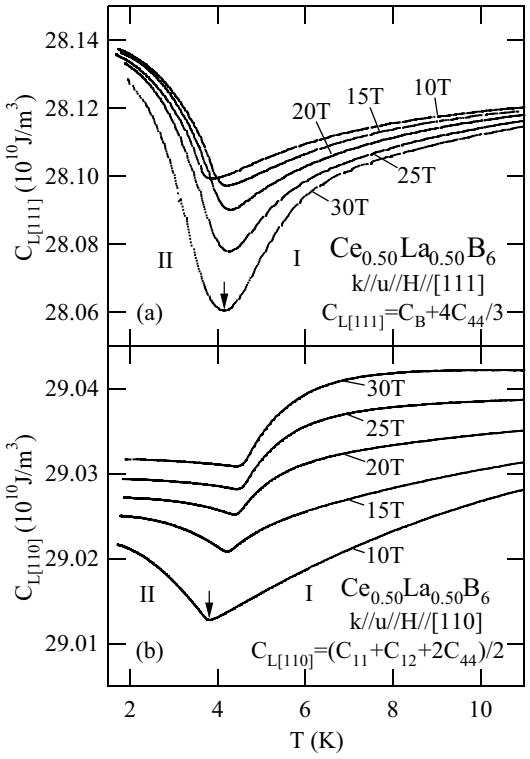

FIG. 2. (a) Temperature dependence of the elastic constant $C_{L[111]} = C_B + 4C_{44}/3$ of $Ce_{0.50}La_{0.50}B_6$ in high magnetic fields along the [111] direction. (b) Temperature dependence of the elastic constant $C_{L[110]} = (C_{11} + C_{12} + 2C_{44})/2$ of $Ce_{0.50}La_{0.50}B_6$ in high magnetic fields along the [110] direction.

the propagation direction of the longitudinal ultrasonic wave. The I-II phase transition temperature T_Q indicated by the minimum points shifts to higher temperatures with increasing field from 10 to 20 T. And above 20 T up to 30 T the T_Q turns to slightly decrease with increasing field.

In Fig. 2(b), we show the temperature dependence of $C_{L[110]} = (C_{11} + C_{12} + 2C_{44})/2$ in applied magnetic fields along the [110] axis parallel to the propagation direction of the longitudinal ultrasonic wave. The bending point exhibiting the I-II phase transition shifts to higher temperatures with increasing field up to 25 T. The transition temperature to AFQ phase II from phase I at 30 T is almost equal to that at 25 T.

In Fig. 3 we show the field dependence of C_{44}, $(C_{11} - C_{12})/2$, and $C_{L[111]} = C_B + 4C_{44}/3$ at low temperatures in fields along the [001], [110], and [111] directions, respectively. The three elastic constants show the I-III phase transition with hysteresis at $H \sim 1.8$ T. The C_{44} in $H\|[001]$ and $C_{L[111]}$ in $H\|[111]$ clearly show anomalies of the III-II phase transition at $H = 4.2$ T ($T = 380$ mK) and 2.9 T ($T = 29$ mK), respectively. The $(C_{11} - C_{12})/2$ mode does not show an appreciable anomaly indicating the III-II phase transition in $H\|[110]$. This result probably means that the III-II phase transition point exists near the I-III phase transition point. The hysteresis behaviors near the I-III phase transition in Fig. 3 indicate that the I-III phase transition is a first order phase transition. The hysteresis behavior below $H = 1.8$ T along the [111] direction may mean a magnetic induced short-range ordering occurs in low fields at low temperatures.

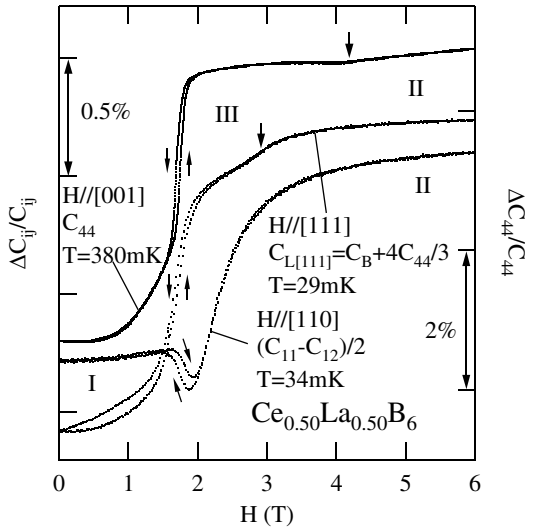

FIG. 3. Temperature dependence of the elastic constants C_{44}, $(C_{11} - C_{12})/2$, and $C_{L[111]} = C_B + 4C_{44}/3$ of $Ce_{0.50}La_{0.50}B_6$ at low temperatures in applied magnetic fields along the [001], [110], and [111] directions, respectively.

Figure 4 shows the magnetic phase diagrams of $Ce_{0.50}La_{0.50}B_6$ in three applied magnetic fields along the [001], [111], and [110] directions. The solid symbols (circle, triangle, and square) indicate the phase transition points obtained by the present ultrasonic experiments. The open symbols (circle, triangle, and square) display the previous results of the ultrasonic and specific heat measurements [18]. The I-II phase transition point T_Q increases with increasing field up to 15 T. A tendency of the magnetic anisotropy $T_{Q[001]} < T_{Q[111]} \sim T_{Q[110]}$ has already been observed in relatively low field below 15 T. As the magnetic fields along [001] increase above 15 T, the I-II phase transition point $T_{Q[001]}$ decreases considerably and forms a closed loop with a critical field $H_{I\text{-}II} \sim 29$ T at absolute zero. In fields along [111] and [110], however, $T_{Q[111]}$ decreases and $T_{Q[110]}$ increases slightly with increasing field above 20 T. The I-II phase boundaries along [111] and [110] do not show a closed loop even at 30 T. An appreciable difference in $T_{Q[111]} = 4.1$ K and $T_{Q[110]} = 4.5$ K at 30 T may promise the magnetic anisotropy of $T_{Q[111]} < T_{Q[110]}$ in high magnetic fields above 15 T. The magnetic phase diagrams having a large anisotropy of $T_{Q[001]} \ll T_{Q[111]} \sim T_{Q[110]}$ in high magnetic fields is almost duplicated by the theoretical calculation by Shiina in Ref. [7]. As was pointed out by Shiina *et al.*, the quite anisotropic Zeeman splitting of the Γ_8

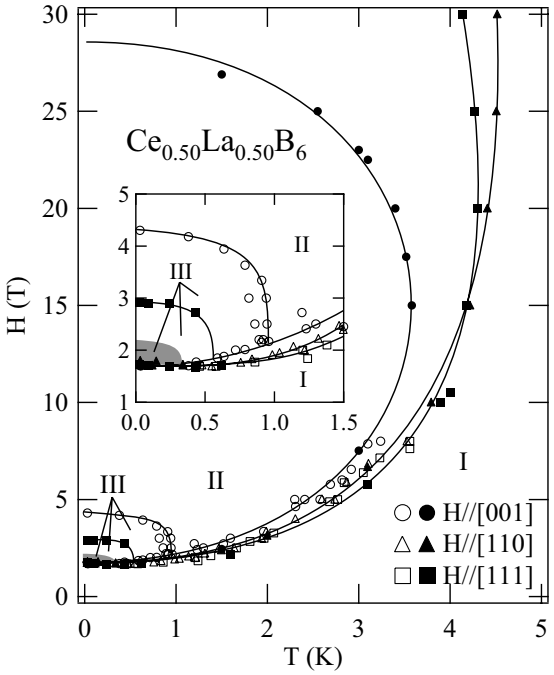

FIG. 4. Magnetic phase diagram of $Ce_{0.50}La_{0.50}B_6$ in the applied magnetic field along the [001], [110], and [111] directions. The inset shows the low-temperature phase diagram of AFM phase III under fields along [001], [110], and [111].

quartet depending on the field directions accounts for the considerable anisotropy of $T_{Q[001]} \ll T_{Q[111]} \sim T_{Q[110]}$ in high fields [19]. The theoretical calculation, however, cannot reproduce a small anisotropy of the experimental result $T_{Q[111]} < T_{Q[110]}$. One of the reasons is that the calculation did not take into account the magnetic induced dipole, although the quadrupoles O_{yz}, O_{zx}, O_{xy}, and octupole T_{xyz} were considered. The experimental determination of the magnetic anisotropy of AFQ phase II is very useful for the estimation of the RKKY-type intersite interaction in the system.

As one can see in the inset of Fig. 4, AFM phase III located inside AFQ phase II also shows anisotropic behavior in fields. At absolute zero phase III changes into phase II above the critical field of $H_{III\text{-}II} = 4.3$ T in fields along the [001] direction. When the field is turned to the [111] direction, phase III shrinks considerably being the critical field of $H_{III\text{-}II} = 2.9$ T for absolute zero. In the fields along the [110] direction, however, AFM phase III remains in the restricted region only, which is shown by the gray area in the inset. The magnetic anisotropy of phase III is supposed to be attributed to the complex magnetic structure and competition with multipole interaction [20,21]. On the other hand, the anisotropy of the I-III phase boundary at low temperatures is very small. This fact suggests the Kondo screening effect depends hardly on magnetic directions.

In conclusion, we have successfully observed the magnetic anisotropy of AFQ phase II in $Ce_{0.50}La_{0.50}B_6$ by using the hybrid magnet (Gama) up to 30 T. The I-II phase boundary of $T_{Q[001]}$ in fields along the [001] direction shows a closed loop with the critical field $H_{I\text{-}II} \sim 29$ T, which agrees with the phase boundary of the symmetry breaking character in Landau theory of phase transition. The anisotropy $T_{Q[111]} < T_{Q[110]}$ in high magnetic fields above 15 T is of importance for the estimation of the intersite multipole interactions in the system. We have also found AFM phase III is stable in fields along the [001] direction and shrinks considerably in fields along [110], in particular. The high-field measurements with a pulse magnetic field above 30 T is required to observe a closed loop for the I-II phase boundary along the [110] or [111] direction.

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