Extension of the temperature-magnetic field phase diagram of CeB_6

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(Received 11 August 2003; published 20 February 2004)

We have measured the magnetic field dependence of the paramagnetic to the field-induced high-temperature antiferroquadrupolar magnetically ordered phase transition in CeB_6 from 0 to 60 T using a variety of techniques. It is found that the field-dependent phase separation line becomes reentrant above 35 T and below 10 K. Measurements of resonant ultrasound, specific heat, and neutron diffraction on samples from the same growth batch show all of the known phase transitions plus a new phase appearing at $T=1.6$ K in zero magnetic field.

DOI: 10.1103/PhysRevB.69.054415 PACS number(s): 75.20.Hr, 61.12.Ld, 62.20.Dc, 71.27.+a

I. INTRODUCTION

The nature of cooperative ordering in highly correlated electron systems continues to be a central topic of fundamental interest. In the past decade cerium hexaboride (CeB_6) and related materials have been the focus of many studies of their electronic, thermal, and magnetic properties to investigate the delicate balance between the Kondo-lattice ground state of these highly correlated electron systems and various states with long-range magnetic order.[1] CeB_6 is a prototype system because all the interesting properties arise from a single $4f$ electron on the Ce ion that hybridizes with the conduction electrons, giving rise to heavy fermion (HF) behavior.

Cerium hexaboride is one of several rare-earth hexaborides that crystallize in the primitive cubic structure with the rare-earth ions at the cube center and boron octahedra at the cube corners. The cubic crystal field due to the six boron atoms in CeB_6 splits the single-electron $4f$ six-fold-degenerate $^2F_{5/2}$ level into a two-fold-degenerate Γ_7 and a four-fold-degenerate Γ_8 level.[2] It has been shown that in CeB_6 the Γ_8 is the lowest-energy state, and the splitting between the Γ_7 and Γ_8 levels is on the order of 530 K.[3] The Γ_8 symmetry of the f electron on Ce allows the existence of not only a magnetic dipole moment, but also higher-order moments, including an orbital electric quadrupole moment. Three different phases so far have been identified in this material. Phase I occurs at high temperatures ($\geqslant 10$ K), where CeB_6 is paramagnetic and exhibits the Kondo effect (electrical resistivity increasing logarithmically with decreasing temperature).[4] In an applied field an ordered state identified as antiferroquadrupolar (AFQ) order develops below $T_q=3.3$ K (phase II), while conventional dipolar antiferromagnetic order develops below $T_N=2.3$ K (phase III).[5] As a function of applied magnetic field, phase III has been reported to exhibit three different orderings of the dipole moments, with phase boundaries that come together at 2.3 K in zero field,[6] while the phase boundary for the AFQ order has recently been found to increase with increasing field with no indication of reentrant behavior up to 30 T (see Fig. 1).[7] In this paper we present several types of measurements on high-quality single crystals of CeB_6. First, we have extended the phase boundary between phases I and II to 60 T and observe that, above 35 T, phase I becomes reentrant, in agreement with expectations of theory.[8] Second, we have verified from resonant ultrasound (RUS) and specific heat measurements that on ^{11}B-enriched samples a weak second-order phase transition occurs at zero field between phases I and II, while a sharp second-order phase transition occurs between phases II and III as a function of temperature. Both transitions occur at the same temperatures as in natural B isotope abundance samples.[9] Third, from neutron diffraction measurements in zero applied magnetic field, we have decreased the maximum possible magnetic dipole moment that exists in zero applied magnetic field on the Ce sites in phase II by a factor of 2.5 from the previously established limit.[6] Fourth, we have identified a new zero-field second-order phase transition to an unknown magnetic state at 1.6 K, inside the accepted phase III regime.

II. EXPERIMENTAL AND SAMPLE DETAILS

All of the measurements were performed on single crystals synthesized by the solution method from an aluminum

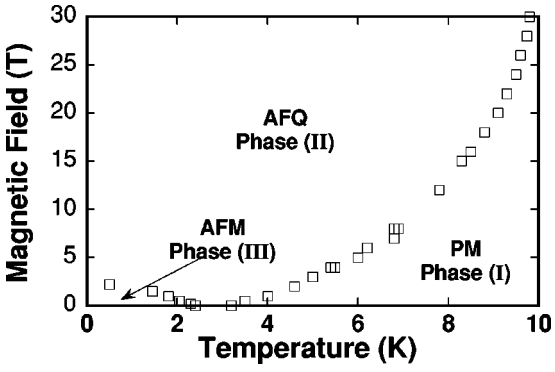

FIG. 1. Phase diagram for CeB_6 determined previously, showing three main phases. At zero field there are two magnetic ordering temperatures: the quadrupolar ordering at $T_q=3.3$ K and the Néel temperature $T_N=2.3$ K.

flux. Hexaboride single crystals grown by this technique have been shown to be of high chemical and structural quality.[10] The single crystals were made with ultrahigh-purity (99.9999%) isotopically enriched (99%) ^{11}B. For the high-field phase boundary determination we have made measurements with the magnetic field applied along the [100] and [110] directions using two different techniques. First, temperature-dependent cantilever magnetometer measurements with $\mathbf{B}\|[100]$ of the sample magnetization between 25 T and 45 T were made in steady fields using the hybrid superconducting-plus-resistive magnet at the National High Magnetic Field Laboratory (NHMFL) in Tallahassee, FL. This method of measurement previously has been described in Ref. 7. Second, we made constant temperature susceptibility measurements with $\mathbf{B}\|[100]$ in pulsed fields to 60 T at the NHMFL, Los Alamos. For these latter measurements the sample was placed in a balanced pickup coil to measure the change in susceptibility of the sample as a function of field at constant temperature. Third, we measured the magnetization with $\mathbf{B}\|[110]$ from zero to 32 T in a resistive magnetic at the NHMFL, Tallahassee. Neutron diffraction measurements between 1.4 K and 4.5 K were performed at the NIST Center for Neutron Research. The sample was mounted in the $[hhl]$ scattering plane with no applied field ($<10^{-4}$ T). A pyrolytic graphite monochromator and filter were employed at neutron wavelengths of 2.359 Å for BT-2 and 2.461 Å on BT-7, with relaxed angular collimations to optimize the observed intensities. The specific heat was measured using a pulse relaxation method on a small single crystal. Measurements of the elastic moduli were performed with a commercial RUS spectrometer.[11]

III. RESULTS AND DISCUSSION

Uimin[12] has described the shape and anisotropy of T_q vs H as arising from competing AFQ patterns near the ordering temperature. These fluctuations are suppressed by an applied magnetic field. Uimin's model predicts three important characteristics of the AFQ-PM (paramagnetic) phase diagram: (1) that T_q vs H increases linearly at low applied fields, (2) that the AFQ-PM phase line is anisotropic in the T-H plane, and (3) that T_q vs H decreases and goes to zero at sufficiently high fields. Based on previously published data Uimin estimated the lower limit field for the reentrance of T_q vs H as approximately 25–30 T, yielding an $H(T_q=0)$ approaching 80 T. The measurements reported here do show reentrance above 30 T (Fig. 2), and if a quadratic fit to the data were to persist (inset of Fig. 2), the projected $H(T_q=0)$ is at 80 T. Uimin points out that his estimate of $H(T_q=0)$ does not take into account the Kondo effect, but ignoring the Kondo effect is a valid approximation at fields $H \gg 2$ T where the f electrons are localized and the Kondo interaction is therefore weak.

The data for $\mathbf{B}\|[110]$ along with data for $\mathbf{B}\|[100]$ are shown in Fig. 3. It can be seen that there is some slight anisotropy in the magnetization versus field, but changing to $\mathbf{B}\|[110]$ does not appear to cause much of a change in the overall shape of the curve that would cause the phase boundary to go to zero field at much lower fields as predicted by Uimin.[12]

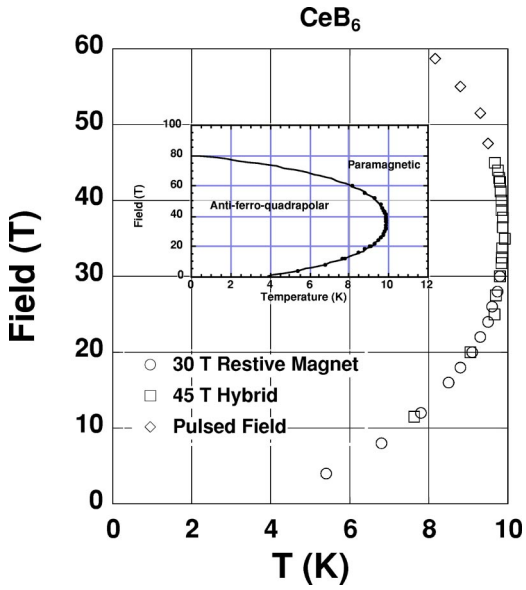

FIG. 2. Quadrupolar ordering temperature (T_q) vs field from previously published results (Ref. 1) plotted with the current data that now extends to 60 T. Inset: quadratic fit to the data suggesting the zero-temperature transition would occur near 80 T.

The ordering in phase II previously has been studied in the presence of applied magnetic fields by neutron diffraction. Quadrupolar order is not observed directly with neutrons, but a magnetic field induces magnetic dipole moments on the periodic structure of ordered electric quadrupole moments.[13] The corresponding wave vector $\mathbf{k}_0 = [1/2,1/2,1/2]$ was observed in neutron diffraction,[9] and the ordering in phase II was proposed to be that of electric quadrupole moments, requiring a splitting of the fourfold-degenerate Γ_8 ground state into two doublets. Several models have been given for this splitting, including a dynamic Jahn-Teller effect involving acoustic phonons or a

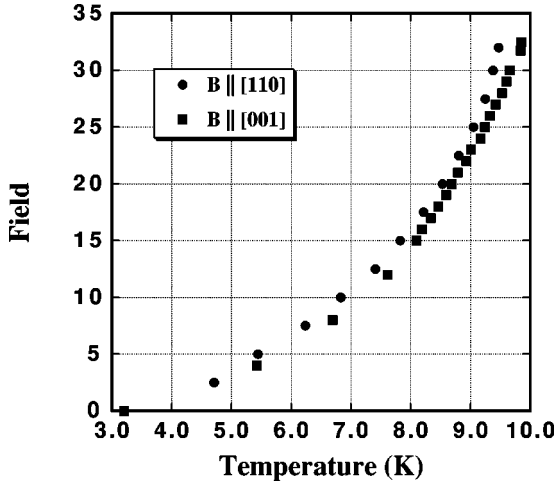

FIG. 3. Quadrupolar ordering temperature (T_q) vs field for two different crystallographic directions with respect to the direction of the applied magnetic field.

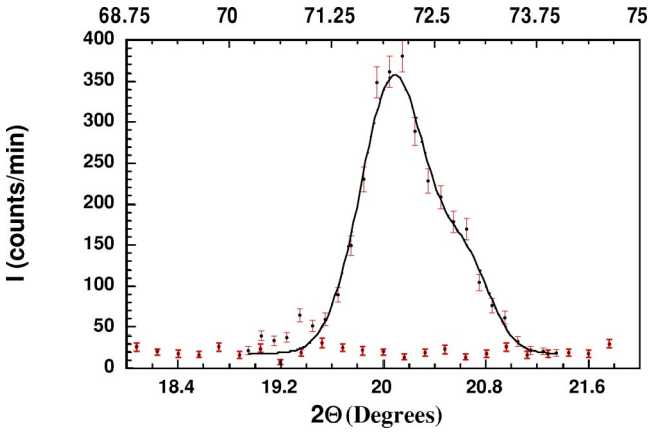

FIG. 4. Direct comparison of the (1/4,1/4,1/2) antiferromagnetic peak taken at 1.6 K (upper scale) with the absence of scattering (lower scale) at the (1/2,1/2,1/2) AFQ position at 2.8 K.

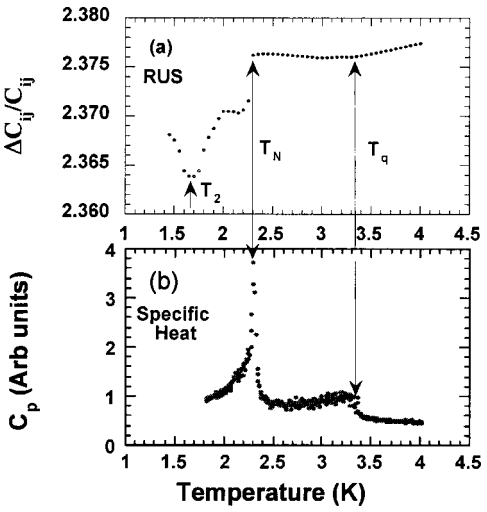

FIG. 5. (a) Relative change in the elastic constants C_{ij} of a single crystal of cubic CeB_6 as measured by RUS as a function of temperature. (b) Temperature dependence of the heat capacity of CeB_6. The phase I to phase II transition (3.3 K), although weak, occurs at zero field, and the phase II to phase III transition (2.3 K) is extremely sharp and second order.

hybridization-mediated anisotropic coupling of the $4f$ wave functions to p-like boron or $5d$-type cerium wave functions.[7] In an early paper Ohkawa[14] proposed that indirect exchange interactions between pairs of Ce atoms would produce a splitting of the fourfold-degenerate level into (4×4) 16 levels, split into a group of two triplets and a group consisting of a singlet plus a nine fold-degenerate level. More recently, an alternate interpretation of the neutron scattering results was given by Uimin[12] in which the low-temperature frequency shift of the $\Gamma_7-\Gamma_8$ splitting was interpreted as arising from collective modes caused by the orbital degrees of freedom. Most recently there have been a multitude of theoretical papers by Shiina and co-workers about the structure of phase II in CeB_6.[15] This group was the first to propose a consistent explanation for the apparent discrepancy between neutron and NMR results in phase II. It should be noted that muon spin rotation measurements in zero applied magnetic field yield a different magnetic structure for CeB_6 for both phase II and III,[16] but these measurements do show that the exchange coupling between Ce atoms must be antiferromagnetic.

To investigate the nature of the zero-field ordering and to ensure that the phase II transitions we were observing were the same as previously reported, we have performed zero-field neutron diffraction measurements between 1.4 K and 4.5 K. Magnetic dipole moments ($M1$) and electric quadrupole moments ($E2$) have the same parity symmetry, but have opposite time reversal symmetry ($M1$, odd, and $E2$, even). Thus the application of an external magnetic field is required to break the time reversal symmetry of $M1$ and allow the magnetic dipole moments to coexist with the electric quadrupole moments. Figure 4 shows a comparison of the antiferromagnetic peak observed at the (1/4,1/4,1/2) position at 1.6 K. The asymmetry of the scattering originates from the mosaic of the crystal. The ordered antiferromagnetic moment we observe is $\langle m\rangle=0.26(4)\mu_B$, in good agreement with the literature. Also shown in the figure is the scattering at the AFQ position (1/2,1/2,1/2). No scattering in zero field at this position was detectable at 1.4 K, 1.6 K, 2.8 K, or 3.3 K, and the measurements place an upper limit of $0.03\mu_B$ for any induced dipole moment associated with the AFQ order. Note in particular that the data taken at 2.8 K are well within the phase II region, and the absence of a peak shows that there is no significant zero-field magnetic ordering due to coupling with quadrupolar moments, in contrast to the ordering that is readily observed in the phase II regime for fields of 1 T and above.[9] A measurement of the total magnetic structure in zero field to below 1.6 K recently has been reported with no change in magnetic structure occurring from above to below 1.6 K in phase III.[17] In Ref. 17 the magnetic order from 700 mK to 2.3 K in zero field was measured. The intensity of the (1/4,1/4,1/2) and (1/4,1/4,0) peaks changes smoothly to the lowest temperatures measured, and they conclude that there is no change in the magnetic structure at zero field as a function of temperature in phase III. Thus, the 1.6-K zero-field transition seen in the RUS measurements arises from something other than a change in magnetic order.

In order to verify that a phase transition occurs in our samples from phase I to phase II and that a further transition to phase III exists at zero field, both RUS and specific heat measurements were made at the NHMFL (Los Alamos), again in fields $<10^{-4}$ T. The RUS measurements gave signals proportional to the elastic response of a single crystal of CeB_6 from 1.2 K to 4.2 K, with emphasis on the region near the phase transitions at 3.3 K and 2.3 K. With a resolution of 1 part in 10^6, we observe two changes in the elastic tensor C_{ij} near the AFQ (T_q), and the AFM (T_{AF}) phase transitions. These changes are shown in Fig. 5(a), where the transition T_q at 3.3 K is observed as a change in slope in the temperature-dependent data, and T_N at 2.3 K shows a discontinuity with no hysteresis. These data indicate that the 3.3 K transition (T_q) is weakly second order, while the AFM transition (T_N) is a sharp second-order transition. A second zero-field transition T_2 is observed in phase III near 1.6 K. The nature and magnetic structure of the phase below 1.6 K are not known, but the fact that a transition exists is clearly

evident in the RUS measurements.

In addition to the RUS results, temperature-dependent specific heat results at zero field are shown in Fig. 5(b). Again, the T_q transition is seen to be weakly second order, and T_N is sharp. To verify the thermodynamic order of T_q and T_N, specific heat measurements were made using a pulse-relaxation technique for both increasing and decreasing temperature. The results shown in Fig. 5(b) clearly demonstrate the nature of the transitions with no hysteresis in either, indicating that the T_N transition is also second order. Further measurements in applied fields up to 15 T showed that both transitions followed the published phase diagram, but we were unable to make measurements at sufficiently low temperatures to observe the new zero-field transition seen in the RUS data. All of our measured data on RUS and C_p are in excellent agreement with previously published data on natural B isotope abundance samples.[9]

IV. CONCLUSIONS

From high-field magnetic measurements the T_q phase diagram of CeB_6 is seen to reverse direction in temperature with increasing field, and then the paramagnet phase becomes reentrant as a function of field and temperature. All of the present data, taken together, show that phase II in CeB_6 exists at zero field, but does not become magnetically ordered until application of an external magnetic field breaks the time-reversal symmetry between the dipole and quadrupole moments. We have observed that this magnetically ordered field-induced phase can be destroyed by fields only exceeding 35 T. Based on these results, any theory that predicts the destruction of phase II below 30 T does not include either all of the effects or it includes incorrect mechanisms. However, two of the theories presented to date, both of which are predicated on indirect exchange, predict destruction of the AFQ phase at fields$>$30 T and cannot be ruled out. Finally, when the RKKY interaction between the $4f$ electron spins overcomes the thermal effects, internal magnetic fields are produced that break time-reversal symmetry and allow spontaneous ordering of the magnetic moments in phase III.

ACKNOWLEDGMENTS

A portion of this work was performed at the National High Magnetic Field Laboratory, which is supported by NSF Cooperative Agreement No. DMR-9527035 and by the State of Florida. Two of the authors, R.G.G. and D.P.Y., wish to thank A. R. P. Rau and Dana Browne for several helpful conversations. Support is acknowledged from NSF Grant No. DMR 0203214 by Z.F. and DOE Grant DE-FG02-01ER45860 by R.G.G.

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