

# Magnetic-field dependence of the paramagnetic to the high-temperature magnetically ordered phase transition in $\text{CeB}_6$

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We have measured the magnetic-field dependence of the paramagnetic to high-temperature magnetically ordered phase transition  $T_Q(H)$  in  $\text{CeB}_6$  from 2 to 30 T using cantilever magnetometry. It is found that the phase-separation temperature continuously increases in field with an increasingly positive slope. In addition, we find that measurements in strong magnetic-field gradients have no effect on the phase transition.

## I. INTRODUCTION

The dense Kondo system  $\text{CeB}_6$  ( $T_K \sim 1$  K) exhibits a three-part phase diagram (see Fig. 1). This paper reports new high-field measurements of the phase I to phase II transition temperature in the  $H$ - $T$  plane  $T_Q(H)$ . 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. In the past decade there have been many studies of the electronic, thermal, and magnetic properties of  $\text{CeB}_6$  because of interest in the low-temperature heavy fermion (HF) ground state.<sup>1</sup> All of the magnetic properties arise from the single  $4f$  electron on the Ce atom that hybridizes with the conduction electrons to give rise to the HF behavior.

The largest factor influencing the energy levels of the  $4f$  electron on the Ce atom in  $\text{CeB}_6$  is the spin-orbit interaction. This interaction splits the 14-fold degenerate  $4f$  level into a 6-fold degenerate,  $^2F_{5/2}$ , and an 8-fold degenerate  $^2F_{7/2}$ , level. The  $^2F_{5/2}$  level lies lowest in energy and is separated from the  $^2F_{7/2}$  level by an energy much greater than 500 K. Thus only the  $J=5/2$  state is populated at room temperature and below. In the absence of any other effects the magnetic sublevels would correspond to  $J = \pm 1/2, \pm 3/2, \text{ and } \pm 5/2$  with a Lande  $g$  factor for this level of  $6/7$ .

Point ion crystal-field theory<sup>2</sup> predicts that the cubic crystal field due to the six borons in  $\text{CeB}_6$  further splits the Ce 6-fold degenerate  $^2F_{5/2}$  level into a 2-fold degenerate  $\Gamma_7$  and a 4-fold  $\Gamma_8$  level. There have been different interpretations of data with differing conclusions about the energy ordering of these two levels,<sup>3-6</sup> but it is now generally perceived that in  $\text{CeB}_6$  the  $\Gamma_8$  is the lowest-energy state, and the splitting between the  $\Gamma_7$  and the  $\Gamma_8$  levels is on the order of 530 K.<sup>7</sup> The  $\Gamma_8$  symmetry of the  $f$  electron on Ce allows not only a magnetic dipole moment, but in addition, an orbital electric and magnetic quadrupole moment. In zero applied magnetic field several different orderings of these moments have been proposed to occur.

The overall results of the previously published magnetic field-temperature phase diagram of  $\text{CeB}_6$  is shown in Fig. 1.<sup>8</sup> At high temperatures the material is paramagnetic (Phase I)

with  $2.34\mu_B$  per Ce atom. In zero applied field, as the temperature is decreased, there is a transformation into the first ordered state at 3.5 K (Phase II), then at 2.2 K the Ce dipole moments align antiferromagnetically (Phase III). There are several substructures within Phase III, but we will not be concerned with the structure of Phase III other than to point out that at all applied magnetic fields above about 2.2 T, it does not exist.

The ordering in Phase II was studied by neutron diffraction and proposed to be an ordering of quadrupole moments.<sup>8</sup> Antiferro quadrupolar ordering has been observed in other materials, for example TmTe.<sup>9</sup> In TmTe this AFQ ordering is destroyed by applied magnetic fields of higher than 6 T. As can be seen from the published phase diagram for  $\text{CeB}_6$ , the

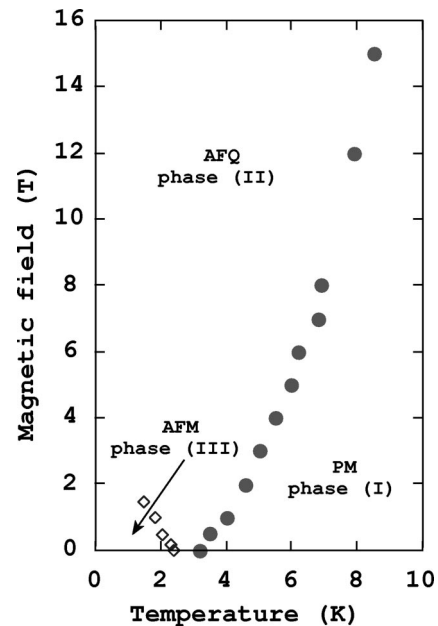


FIG. 1. The magnetic phase diagram of  $\text{CeB}_6$  exhibits three main phases at zero field separated by two magnetic ordering temperatures: the quadrupolar ordering temperature  $T_Q=3.2$  K and the Néel temperature  $T_N=2.4$  K.<sup>8</sup> Phases I through III are labeled paramagnetic, antiferroquadrupolar (AFQ), and antiferromagnetic (AFM), respectively.

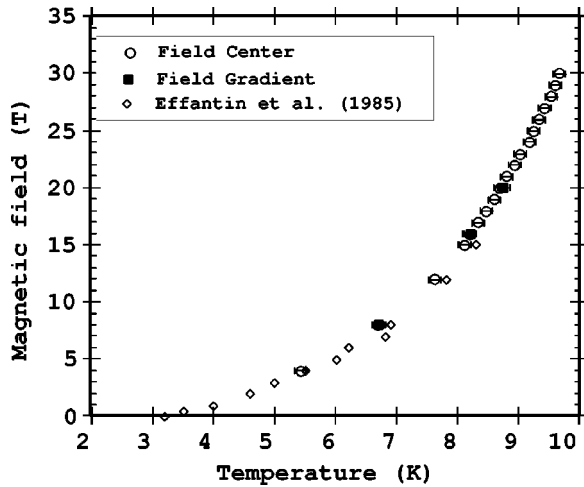


FIG. 2. The quadrupolar transition temperature  $T_Q(H)$  is shown as a function of magnetic field. New data are compared with previously published data.

state is not destroyed by the application of magnetic fields up to 15 T. In this AFQ model it is the coupling between the orbital quadrupole and spin dipole moments that allows the phase transition to be observed with magnetic torque measurements in uniform fields.

## II. MEASUREMENTS

The magnetic measurements were carried out with a metal film cantilever magnetometer, composed of two metal plates (one fixed and the other flexible) that senses forces and torques capacitively. A single crystal of  $\text{CeB}_6$  is attached to the flexible plate with Apiezon  $N$  grease. When the sample/cantilever is positioned at field center, the sample experiences a torque proportional to its magnetization. Most of the measurements reported here were made at field center. However, three data points were taken with the sample in a field gradient (0.2 T/cm), where the sample experiences a force proportional to its magnetization. The data is summarized in Fig. 2.

The sample's magnetization was measured at fixed fields as a function of temperature (as shown in Fig. 3). To ensure proper determination of temperature a Lake Shore Cernox<sup>TM</sup> CX 1030 series resistive thermometer was thermally anchored to the flexible plate of the cantilever with Cry-Con grease,<sup>10</sup> and corrections were made for the magnetic-field dependence of the Cernox<sup>TM</sup> thermometer. Details of how such corrections should be made can be found in a paper by Brandt *et al.*<sup>11</sup>

## III. DISCUSSION

Because of the antiferromagnetic ordering with wave vector  $k_0 = [1/2, 1/2, 1/2]$  observed in neutron diffraction,<sup>8</sup> the ordering in Phase II was proposed to be that of quadrupole moments, requiring a splitting of the fourfold degenerate  $\Gamma_8$  ground state into two doublets. Several models have been given for this splitting. Either a dynamic Jahn-Teller effect involving acoustic phonons, or a hybridization-mediated anisotropic coupling of the  $4f$  wave functions to the  $p$ -like boron or  $5d$ -type cerium wave functions were suggested as

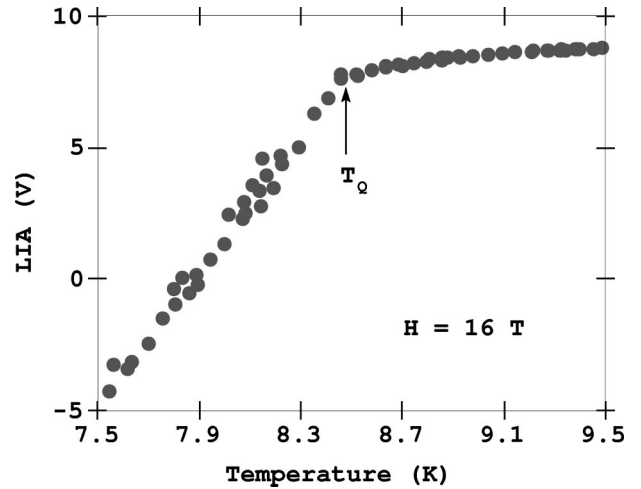


FIG. 3. This is an example of raw data taken at an applied magnetic field of 16 T. The temperature was ramped slowly through the quadrupolar transition shown as  $T_Q$  on the plot. The change in slope of the capacitance versus temperature curve is taken as  $T_Q$ .

possibilities in Ref. 7. An alternative interpretation of these neutron scattering results has been given by Uimin in Ref. 12. Uimin interprets the low-temperature frequency shift of the  $\Gamma_7$ - $\Gamma_8$  as arising from collective modes of spin fluctuations caused by the orbital degrees of freedom.

In an early paper Ohkawa<sup>13</sup> proposed that indirect exchange interactions between pairs of Ce atoms would produce a splitting of the fourfold degenerate level into  $(4 \times 4)$  sixteen levels split into a group of two triplets and a group consisting of a singlet plus a ninefold degenerate level with Phase II representing an ordering of the orbital moments. Calculations in Ref. 13 based on this model predict that the critical field that destroys Phase II will be in excess of 30–50 T.

Building on Ohkawa's work, Shiina *et al.*<sup>14</sup> have constructed a mean-field theory for Ohkawa's Ruderman-Kittel-Kasuya-Yosida model and calculated the phase diagram. They argue that the increase of  $T_Q(H)$  at low fields is due mainly to field-induced dipolar and octupolar moments. Also, they suggest an improvement to the model by introducing asymmetry into the interaction between dipolar and octupolar moments, which leads to induced staggered dipolar moments and accounts for the distinction of Phase II into a low-field phase and a high-field phase suggested by Nakamura *et al.*<sup>15</sup> However, detailed measurements on the symmetry of the order parameter are required to see what applicability Shiina *et al.*'s model has to  $\text{CeB}_6$ .

Uimin<sup>16,17</sup> described the shape  $T_Q(H)$  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-paramagnetic phase diagram: (1) that  $T_Q(H)$  increases linearly at low-applied fields, (2) that the AFQ-paramagnetic phase line is anisotropic in the  $H$ - $T$  plane, and (3) that  $T_Q(H)$  decreases and goes to zero at sufficiently high fields. Based on data available at the time,<sup>18</sup> Uimin estimated the lower limit field for the re-entrance of  $T_Q(H)$  as approximately 25–30 T yielding an  $H(T_Q=0)$  approaching 80 T.<sup>17</sup> The measurements reported here do not show re-entrance up to 30 T. Uimin points out that his estimate of  $H(T_Q=0)$

does not take into account the Kondo effect, however, the measurements are carried out at higher energies than the Kondo energy (on the order of 2 K).

Uimin's theoretical treatment also found a significant dependence of  $T_Q(H)$  on the orientation of the applied field. In the [111],  $T_Q(H)$  does not decrease for arbitrarily high fields. Our measurements were made with the sample in the [100]. However, no experiment has shown any significant orientation dependence in the  $T_Q(H)$  phase line, which Uimin attributes to the unusual anisotropy of the Zeeman energy.

More recently, Kasuya<sup>19</sup> has considered a paired dynamic Jahn-Teller distortion with no quadrupolar ordering causing an increased Ce-Ce antiferromagnetic (AFM) coupling that is enhanced by increasing the applied magnetic field. In Ref. 19 the critical field at which this enhanced AFM ordering is destroyed also is predicted to be greater than 30 T.

It should be noted that muon spin rotation measurements in zero applied magnetic field yield a different magnetic structure for CeB<sub>6</sub> for both Phases II and III.<sup>20,21</sup> A detailed measurement of the variation of the magnetic order parameter as a function of temperature is needed.

#### IV. CONCLUSIONS

Our measurements of the phase boundary between Phase I and Phase II, along with previously published points, are shown in Fig. 2. As can be seen, the present measurements below 15 T are in good agreement with published values and double the measured field range. The slope of the phase boundary continues to increase with applied field and be-

comes nearly independent of temperature above 25 T. There is no indication that the phase is being destroyed with field up to 30 T. In addition to measurements in uniform fields, we have included several points that were taken in the presence of a strong magnetic-field gradient  $dH/dz$ , where both  $H$  and  $z$  are along the [100] axis of the sample. If Phase II includes antiferro ordering of magnetic quadrupole moments, then the application of a field gradient should exert a force on the moments causing them to align and destroy the phase. As can be seen, the magnetic-field gradient has no effect on the transition temperature (see Fig. 2).

In conclusion, it is seen that any theory that predicts the destruction of Phase II below 30 T does not include either all of the effects, or includes incorrect mechanisms. Two theories presented to date,<sup>13,19</sup> both of which are predicated on indirect exchange, predict destruction of the phase at fields  $>30$  T, and cannot be ruled out. Additional measurements would aid in distinguishing between competing theories of the magnetically ordered phase. Clearly, the phase diagram  $T_Q(H)$  needs to be measured to high fields. Also, measurements on the alloy series Ce<sub>x</sub>La<sub>1-x</sub>B<sub>6</sub> will assist in understanding the splitting of the  $\Gamma_8$  level as the Ce concentration increases.

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<sup>1</sup>P. Schlottmann, Phys. Rep. **181**, 1 (1989).

<sup>2</sup>W. Low, in *Solid State Physics, Supplement 2*, edited by F. Seitz and D. Turnbull (Academic Press, New York, 1960).

<sup>3</sup>K.N. Lee and B. Bell, Phys. Rev. B **6**, 1032 (1972).

<sup>4</sup>Y. Aoki and T. Kasuya, Solid State Commun. **36**, 317 (1980).

<sup>5</sup>K. Hanzawa, A. Yanase, and T. Kasuya, Solid State Commun. **36**, 317 (1981).

<sup>6</sup>K. Hanzawa, in *Proceedings of the International Symposium on High Field Magnetism*, edited by M. Date (North-Holland, Amsterdam, 1982).

<sup>7</sup>E. Zirngiebl, B. Hillebrands, S. Blumenrder, G. Gntherodt, M. Loewenhaupt, J.M. Carpenter, K. Winzer, and Z. Fisk, Phys. Rev. B **30**, 4052 (1984).

<sup>8</sup>J.M. Effantin, J. Rossat-Mignod, P. Burllet, H. Bartholin, S. Kunii, and T. Kasuya, J. Magn. Magn. Mater. **47-48**, 145 (1985).

<sup>9</sup>T. Matsumura, S. Nakamura, T. Goto, H. Shida, and T. Suzuki, Physica B **223-224**, 385 (1996).

<sup>10</sup>Lake Shore Cryotronics, Westerville, OH 43082-8888.

<sup>11</sup>B.L. Brandt, D.W. Liu, and L.G. Rubin, Rev. Sci. Instrum. **70**, 104 (1999).

<sup>12</sup>G. Uimin, Phys. Lett. A **215**, 97 (1996).

<sup>13</sup>F.J. Ohkawa, J. Phys. Soc. Jpn. **52**, 3897 (1983).

<sup>14</sup>R. Shiina, H. Shiba, and P. Thalmeier, J. Phys. Soc. Jpn. **66**, 1741 (1997).

<sup>15</sup>S. Nakamura, T. Goto, and S. Kunii, J. Phys. Soc. Jpn. **64**, 3941 (1995).

<sup>16</sup>G. Uimin, Y. Kuramoto, and N. Fukushima, Solid State Commun. **97**, 595 (1996).

<sup>17</sup>G. Uimin, Phys. Rev. B **55**, 8267 (1997).

<sup>18</sup>M. Torikachvili and A. Lacerda (unpublished).

<sup>19</sup>T. Kasuya, J. Phys. Soc. Jpn. **60**, 33 (1998).

<sup>20</sup>R. Feyerherm, A. Amato, F.N. Gynax, A. Schenck, Y. Onuki, and N. Sato, Physica B **194-196**, 357 (1994).

<sup>21</sup>R. Feyerherm, A. Amato, F.N. Gyax, A. Schenck, Y. Onuki, and N. Sato, J. Magn. Magn. Mater. **140-144**, 1175 (1995).