

## Fluctuation study of the specific heat of $\text{Mg}^{11}\text{B}_2$

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The specific heat of polycrystalline  $\text{Mg}^{11}\text{B}_2$  has been measured with high-resolution ac calorimetry from 5 to 45 K at constant magnetic fields. The excess specific heat above  $T_c$  is discussed in terms of Gaussian fluctuations and suggests that  $\text{Mg}^{11}\text{B}_2$  is a bulk superconductor with Ginzburg-Landau coherence length  $\xi_0 = 26 \text{ \AA}$ . The transition-width broadening in field is treated in terms of lowest-Landau-level (LLL) fluctuations. That analysis requires that  $\xi_0 = 20 \text{ \AA}$ . The underestimate of the coherence length in field, along with deviations from three-dimensional LLL predictions, suggests that there is an influence from the anisotropy of  $B_{c2}$  between the  $c$  axis and  $a$ - $b$  plane.

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Experimental observations of thermodynamic fluctuations in the specific heat have been limited in low- $T_c$  superconductors because the long coherence lengths make the excess specific heat very small compared to the mean-field term.<sup>1</sup> By contrast, the high transition temperatures and small coherence lengths of cuprate superconductors lead to significant fluctuation effects.<sup>2</sup> In the recently discovered superconductor  $\text{Mg}^{11}\text{B}_2$ ,<sup>3</sup> the coherence length and superconducting transition temperature lie between these extremes, suggesting that fluctuation effects will be observable and lead to further information on the superconducting coherence length. Indeed, the excess magnetoconductance of  $\text{Mg}^{11}\text{B}_2$  was reported recently and discussed in terms of fluctuation effects.<sup>4</sup> Here we report the specific heat of  $\text{Mg}^{11}\text{B}_2$  from 5 K to 45 K at several magnetic fields. Using high-resolution ac calorimetry, we could study the superconducting transition region in detail. At zero field, the excess specific heat is treated in terms of three-dimensional (3D) Gaussian fluctuations and in field, the broadening and shift of the transition is analyzed in terms of lowest-Landau-level (LLL) fluctuations.

Polycrystalline  $\text{Mg}^{11}\text{B}_2$  was prepared at  $T=950^\circ\text{C}$  and  $p=3 \text{ GPa}$  from a stoichiometric mixture of Mg and  $^{11}\text{B}$  isotope using a high-pressure synthesis method. Since the sample was synthesized at high pressure, there has been no additional annealing. Details of the synthesis can be found elsewhere.<sup>5,6</sup>

Measurements of the heat capacity were based on an acalorimetric technique.<sup>7</sup> A long cylindrical sample was cut into a disk by a diamond saw and then was sanded to a thin rectangular shape whose dimensions are approximately  $1.1 \times 1.5 \times 0.1 \text{ mm}^3$ ; its mass is  $375 \mu\text{g}$ . The front face of the prepared sample was coated with colloidal graphite suspension (DAG) thinned with isopropyl alcohol to prevent a possible change of the optical absorption properties of the sample with temperature. The sample was weakly coupled to the heat bath through helium gas and suspending thermocouple wires. As a heating source, we used square-wave modulated laser pulse. The oscillating heat input incurred a steady temperature offset (or dc offset) from the heat bath

with an oscillating temperature superposed. The ac part was kept less than 1/10 of the dc offset and was then converted to heat capacity by the relationship  $C \propto 1/T_{ac}$ . The heat capacity obtained was converted to a specific heat by using a literature value above the superconducting temperature.<sup>8</sup> The frequency of the periodic heating was chosen so that the ac temperature was inversely proportional to the frequency and, therefore, to the heat capacity; 23 Hz was used in this experiment. The ac and dc temperatures were measured by type-E thermocouples, which were varnished on the back face of the sample using a minute amount of GE7031 diluted with a solvent of methanol and toluene. The GE varnish typically amounts to less than 1% of the sample mass. Since the field induced error of type-E thermocouples is less than 1% at 40 K in 8 T, we will neglect the field dependence of the addenda contribution (DAG, GE varnish, and type-E thermocouple) and treat the field dependence as due only to the sample.

The inset to Fig. 1 shows the temperature dependence of the specific heat at 0 and 7 T from 5 to 45 K. The main graph is a plot of  $\Delta C_{\text{expt}}$  vs temperature at zero field. Here  $\Delta C_{\text{expt}}$  is the measured difference between the mixed- and normal-state specific heats. A 7-T data set was used as a reference state above 20 K because it shows no observable transition in that range. The subtraction was executed without any smoothing of the 7-T data. The dash-dotted line is a BCS fit with the ratio of  $\Delta C_{\text{expt}} / \gamma_n T_c$  being variable.<sup>9</sup> The normal electronic coefficient  $\gamma_n$  was set to be  $2.6 \text{ mJ/mol K}$  from the literature<sup>8</sup> and  $T_c$  of 38.4 K was determined from scaling discussed below. The best fit showed that the ratio is 0.7, which is much smaller than the weak-coupling BCS value of 1.43. Since the ratio is generally larger for strong-coupling superconductors, the small value does not tell us anything about its coupling strength. Recently, there has been a plethora of experimental and theoretical evidence which supports two-gap features in  $\text{MgB}_2$ , which can explain the non-BCS jump magnitude with some success.<sup>10-14</sup> However, we cannot rule out such other scenarios as an anisotropic gap structure.<sup>15,16</sup> For a system in which fluctuation effects are

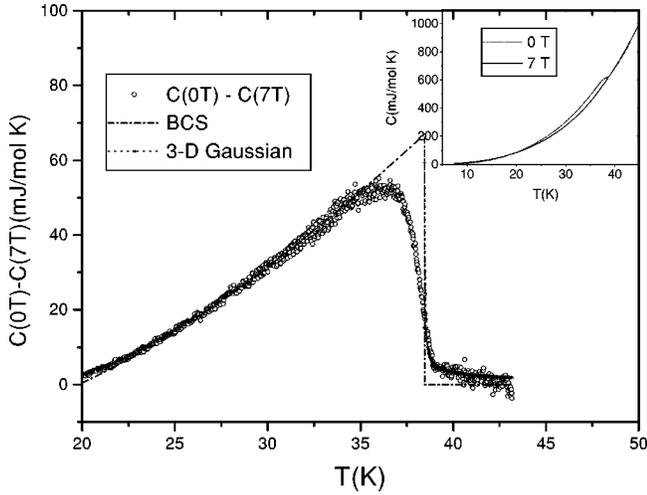


FIG. 1. Temperature dependence of  $\Delta C$  at zero field. The dash-dotted line is a BCS fit with  $\Delta C_{\text{expt}} / \gamma_n T_c = 0.7$ . The star represents a 3D Gaussian fluctuation model above  $T_c$  of 38.4 K. Inset: The temperature dependence of the specific heat at 0 and 7 T from 5 to 45 K.

pronounced, the experimentally determined transition temperature is lower than the mean-field critical temperature ( $T_c^{mf}$ ) because fluctuations drive the system into the normal state even below  $T_c^{mf}$ . It is unlikely, however, that this can explain the large deviation from the BCS value.

Above the transition temperature, there is an excess specific heat tail apparent in Fig. 1. Thouless<sup>17</sup> and subsequently Aslamazov and Larkin<sup>18</sup> showed that Gaussian fluctuations arise above  $T_c$  and predicted that  $C_{fl} = C^+ t^{-(2-d/2)}$  with  $C^+ = (k_B/8\pi) \xi_{GL}(0)^{-3}$ , where  $t = T/T_c - 1$ ,  $d$  is the dimensionality, and  $\xi_{GL}(0)$  the  $T=0$  K Ginzburg-Landau coherence length. Figure 2 shows the temperature dependence of the excess specific heat on a log-log scale. The data follow a power law with an exponent of  $-0.5$  and  $C^+$

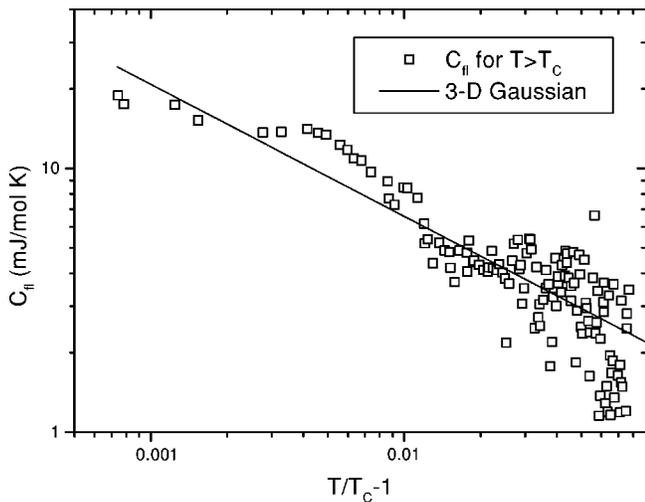


FIG. 2. The excess specific heat  $C_{fl} = \Delta C_{\text{expt}}(0)$  for  $T > T_c$  is plotted against reduced temperature  $t = T/T_c - 1$  on a log-log scale. The solid line describes Gaussian fluctuations for a bulk superconductor with a GL coherence length of 26 Å.

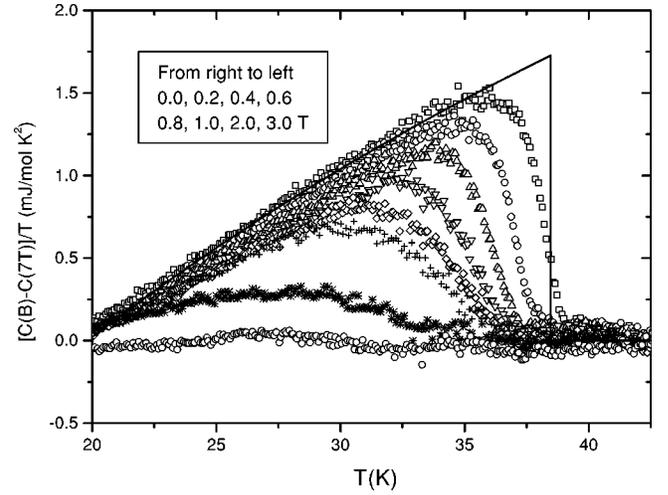


FIG. 3.  $\Delta C/T$  is plotted against temperature in  $B=0, 0.2, 0.4, 0.6, 0.8, 1.0, 2.0,$  and  $3.0$  T. Data were taken with increasing temperature after field cooling. The solid line represents a BCS fit.

$= 0.66$  mJ/mol K. The exponent indicates that  $\text{Mg}^{11}\text{B}_2$  is a 3D superconductor and the substitution of  $C^+$  into the above formula gives  $\xi_{GL}(0) = 26 \pm 1$  Å.

When a magnetic field is applied, the specific heat broadens. Figure 3 shows the temperature dependence of  $\Delta C/T$  at several magnetic fields. The ratio of the transition temperature shift to the transition width broadening in field is unique in that it is not as large as in low- $T_c$  superconductors or as small as in high- $T_c$  materials. Its intermediate behavior is related to the fact that the coherence length and the superconducting transition temperature of  $\text{Mg}^{11}\text{B}_2$  are intermediate between low- $T_c$  and high- $T_c$  superconductors. Lee and Shenoy<sup>19</sup> studied fluctuation phenomena in the presence of a magnetic field, arguing that bulk superconductors exhibit a field-induced effective change to one-dimensional behavior in the vicinity of the transition temperature  $T_c(B)$ . In a uniform magnetic field, the fluctuating Cooper pairs move in quantized Landau orbits and, close to upper critical field ( $B_{c2}$ ), the lowest Landau level dominates the contribution to the excess specific heat. So a bulk superconductor behaves like an array of one-dimensional rods parallel to the field. Thouless<sup>20</sup> extended the idea above and below  $T_c$  and suggested a scaling parameter for the fluctuation specific heat that is valid throughout the transition region:

$$\frac{\Delta C_{\text{expt}}}{\Delta C_{\text{mft}}} = g\left(\frac{t}{\tau}\right), \quad (1)$$

where  $t$  is the reduced temperature and  $\tau$  is a field-dependent dimensionless parameter that describes the superconducting transition width. The functional form  $g(y)$  is model dependent. When a Hartree-like approximation<sup>21</sup> is used to examine the fluctuation effects of the quartic term in the free energy functional, it results in a simple form

$$g(y) = [1 + x(y)]^{-1}, \quad (2)$$

$$y = x^{2/3}(1 - 2/x), \quad (3)$$

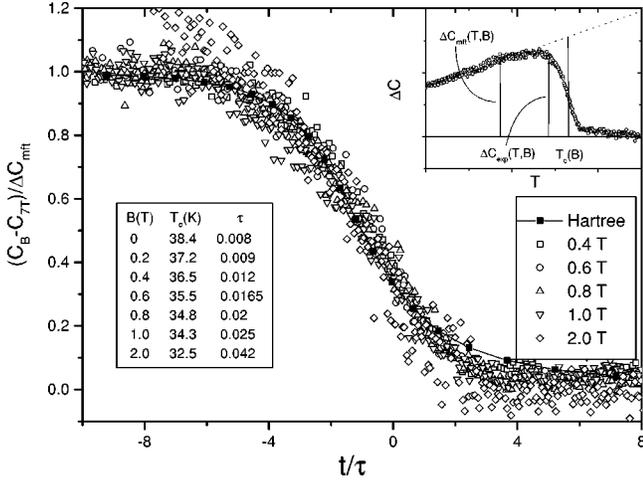


FIG. 4.  $\Delta C_{\text{expt}}/\Delta C_{mft}$  vs  $t/\tau$  is shown, where  $\Delta C_{\text{expt}} = C(B) - C(7T)$  and  $\Delta C_{mft}$  are defined in the inset. Here  $t$  is reduced temperature and  $\tau$  is a field-dependent dimensionless broadening parameter. Solid squares are from a Hartree-like approximation. Other field data were scaled so that they were collapsed onto the Hartree result. The obtained parameters ( $T_c$ ,  $\tau$ ) are tabulated inside the figure at each magnetic field. The inset sketches the definition of  $\Delta C_{mft}(T, B)$  (Ref. 22).

where  $y = t/\tau(B)$ .

In Fig. 4, the ratio of  $\Delta C_{\text{expt}}/\Delta C_{mft}$  in the transition region was plotted as  $t/\tau(B)$ , where  $\Delta C_{\text{expt}}(B) = C(B) - C(7T)$  and  $\Delta C_{mft}$  was determined as in the classic work by Farrant and Gough<sup>22</sup> by fitting the low-temperature side of  $\Delta C_{\text{expt}}(B)$  as in Figs. 1 and 3 and extrapolating linearly above  $T_c(B)$ . A sketch is shown in the inset of Fig. 4. The scaling parameters  $\tau(B)$  and  $T_c$  were chosen to make the data collapse onto the Hartree-like approximation (solid squares). The values of  $\tau(B)$  and  $T_c$  are listed in Fig. 4. The temperature dependence of the upper critical field  $T_c(B)$  is plotted in Fig. 5 and shows positive curvature close to  $T_c(B=0)$ . A simple empirical formula<sup>23</sup>  $B_{c2}(T) = B_{c2}(0)[1 - (T/T_c)^2][1 - a(T/T_c)^2]$  was used to describe the curvature, in which  $a$  is a fitting parameter that is 0 and 0.3 for the two-fluid model and for the Werthamer-Helfand-Hohenberg (WHH) model,<sup>24</sup> respectively. The best fit, solid line in Fig. 5, was produced with  $B_{c2}(0) = 15.4$  T and  $a = 0.8$ . Positive curvature near  $T_c(B=0)$  was also observed in nonmagnetic rare-earth nickel borocarbides  $RNi_2B_2C$  ( $R = \text{Lu, Y}$ ) and could be explained by the dispersion of the Fermi velocity using an effective two-band model.<sup>25</sup>

The broadening parameter  $\tau(B)$  consists of a field-dependent part ( $\tau_B$ ) and a field-independent part ( $\tau_{in}$ ). We postulate that they are independent of each other and add in quadrature, such that the total broadening is  $\tau^2 = \tau_{in}^2 + \tau_B^2$ . The field-independent part was obtained in zero field and accounts for sample inhomogeneity and zero-field fluctuation effects while the field-dependent part is due solely to field-induced fluctuations. The field dependence of the broadening parameter is given by<sup>20</sup>

$$\tau_B = \left( \frac{B}{B_W} \right)^{1/\alpha}, \quad (4)$$

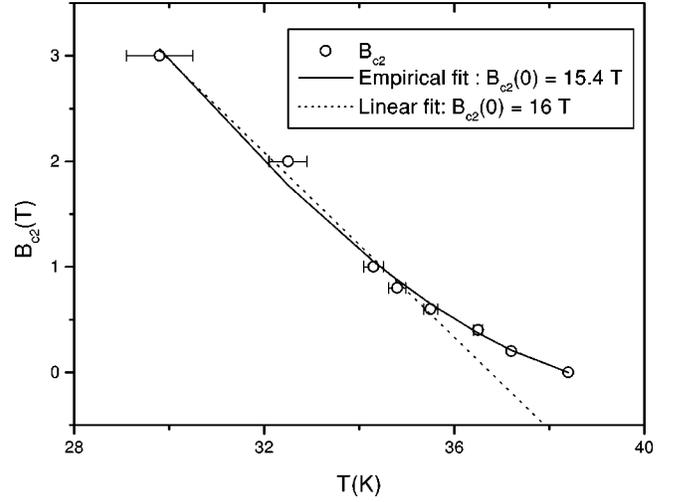


FIG. 5. The temperature dependence of the upper critical field  $B_{c2}(T)$  is shown. The solid line is a simple empirical formula  $B_{c2}(0)[1 - (T/T_c)^2][1 - a(T/T_c)^2]$ , with  $a=0.8$  and  $B_{c2}(0) = 15.4$  T. The dotted line is a linear fit with  $B_{c2}(0) = 16$  T and  $dB_{c2}/dT = -0.44$  T/K.

$$B_W = \left( \frac{\Delta C}{k_B/8\pi\xi_0^3} \right) B_S, \quad (5)$$

where  $\alpha = 2 - (d-2)/2$  ( $\alpha = 3/2$  for a bulk superconductor) and  $B_S = -T_c(dB_{c2}/dT)_{T_c}$  in the mean-field scheme. The exponent  $d-2$  indicates a dimensional crossover from  $d$ -dimension to  $d-2$ -dimension behavior. The shift field  $B_S$  is a characteristic field that sets the scale of the shift of the transition temperature while  $B_W$  sets the scale of the width broadening of the transition region. In a standard superconductor, the ratio  $B_W/B_S$  is very large ( $\sim 10^4$ ), and the transition is shifted much more rapidly in field than it is broadened. In high-temperature superconductors, such as YBCO, the broadening is as large as the shift ( $B_S \sim B_W$ ), which is an indication that a mean-field approach based on a perturbation expansion might not be proper and that fluctuations should be treated in the context of critical phenomena. In Mg<sup>11</sup>B<sub>2</sub>, the ratio is in the order of  $10^2$ , which is in between those two extremes. This feature seems consistent with other properties that show aspects of both conventional and high- $T_c$  superconductors. In order to study the anomalous broadening in field, we plot  $\tau_B$  vs  $(B/\Delta C)$  on a log-log scale in Fig. 6. The slope represents the exponent ( $1/\alpha$ ) while the coefficient of the slope  $\beta$  is related to the Ginzburg-Landau (GL) coherence length through  $\beta = (k_B/8\pi\xi_0^3 B_S)^{1/\alpha}$ . The lowest-Landau-level approximation is shown as a solid line having a slope of  $2/3$  and coefficient  $2.7$  (A/m K)<sup>2/3</sup>. From the coefficient of the fit, the Ginzburg-Landau coherence length is estimated to be  $20$  Å. In the above analysis, the shift field  $B_S$  of  $16$  T was obtained by fitting the linear region of  $B_{c2}$  (see Fig. 5).

Before making any further conclusions, we discuss some of the assumptions that we made in the analysis. In the zero-field analysis, sample inhomogeneity has been neglected. Boron 11 isotope Mg<sup>11</sup>B<sub>2</sub> has a  $T_c$  of  $39$  K while the excess

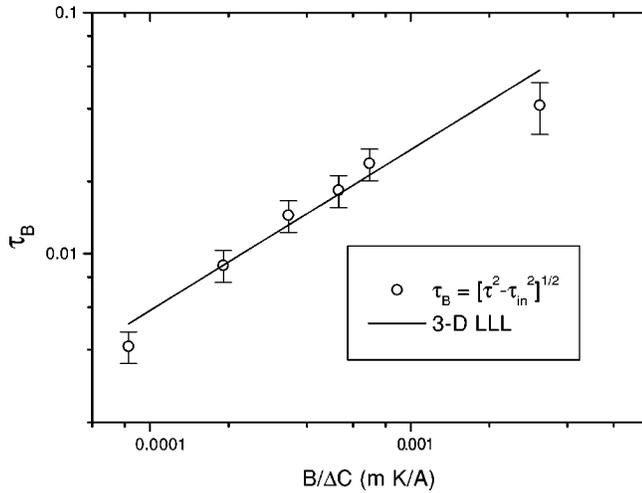


FIG. 6. Field-broadened dimensionless parameter  $\tau_B$  is plotted against  $B/\Delta C$  on a log-log scale. The parameter was obtained by using  $\tau_B = (\tau^2 - \tau_{in}^2)^{1/2}$  and  $\Delta C$  is a mean-field discontinuity at  $T_c$ . The solid line represents a lowest-Landau-level (LLL) fluctuation:  $\tau_B = \beta(B/\Delta C)^{1/\alpha}$  with  $\alpha=3/2$  and  $\beta=2.7$  (A/m K) $^{2/3}$ .

specific heat extends well above 40 K. We might expect inhomogeneity effects to complicate the fluctuation analysis below the transition temperature but above  $T_c$ , where our analysis is concerned, the effect will be negligible. However, when nonzero field is applied, sample inhomogeneity must be considered because the analysis is of the field-dependent behavior of the transition region. Sample inhomogeneity could produce an additional broadening through the Ginzburg-Landau parameter  $\kappa$  and, hence,  $H_{c2}$ . Information on  $H_{c2}$  slopes at different parts of the sample with different  $T_c$ 's would be needed to account for the additional broadening correctly. To be more precise, the  $H_{c2}$  slope in the  $T_c$

=39 K part of the sample and that in the, e.g.,  $T_c=38$  K part would be needed. In our in-field analysis, we assumed that the slopes of  $H_{c2}$  at different parts of the sample are same or, if they are different, the difference is small, which leads to field independent inhomogeneity effect. It is necessary to study high-quality single crystals with different  $T_c$ 's to better understand sample inhomogeneity effects on transition-width broadening.

In summary, the zero-field specific heat was discussed in the context of BCS theory plus 3D Gaussian fluctuations. The analysis indicates that  $\text{Mg}^{11}\text{B}_2$  is a bulk superconductor and its coherence length is about 26 Å. In-field specific heat was treated in terms of lowest-Landau-level fluctuations. That analysis requires that  $\xi_0=20$  Å. The in-field analysis could be complicated due to the effect of anisotropy in a polycrystalline sample. The anisotropy of  $B_{c2}$  between ab-plane and c-axis directions can lead to a field dependent broadening due to the  $T_c$  distribution arising from the randomly oriented grains of the present sample. This in turn leads to an underestimation of the G-L coherence length. In order to understand the influence of anisotropy, we can assume that the transition broadening arises solely from  $B_{c2}$  anisotropy and calculate the required anisotropy in our experimental temperature range. The reported anisotropy value of  $\sim 3$  from single-crystal measurements<sup>26-28</sup> is much smaller than the ratio 6 required to explain the broadening. From this consideration, we conclude that the anisotropy alone cannot explain the whole broadening and therefore that fluctuation effects should be considered in explaining the anomalous broadening.

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