Specific Heat of $Mg^{11}B_2$: Evidence for a Second Energy Gap

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Measurements of the specific heat of $Mg^{11}B_2$ from 1 to 50 K, in magnetic fields to 9 T, give the Debye temperature, $\Theta = 1050$ K, the coefficient of the normal-state electron contribution, $\gamma_n = 2.6\ \mathrm{mJ\,mol^{-1}\,K^{-2}}$, and a discontinuity in the zero-field specific heat of $133\ \mathrm{mJ\,mol^{-1}\,K^{-1}}$ at $T_c = 38.7$ K. The estimated value of the electron-phonon coupling parameter, $\lambda = 0.62$, could account for the observed T_c only if the important phonon frequencies are unusually high relative to Θ. At low T, there is a strongly field-dependent feature that suggests the existence of a second energy gap, about 4 times smaller than the major gap.

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The superconductivity of MgB_2, with $T_c = 39$ K [1] and an isotope effect [2–4] consistent with the phonon-mediated electron pairing of the BCS theory [5], has reopened the question of the maximum T_c that can be produced by that mechanism [6,7]. It also raises a new question: What is the mechanism of the superconductivity of MgB_2? In this Letter, we report measurements of the heat capacity (C) of $Mg^{11}B_2$ that give information relevant to the latter question: Comparison of the coefficient (γ_n) of the normal-state electron contribution to C with band-structure calculations [8–10] gives an estimate of the electron-phonon coupling parameter (λ). The value of λ suggests moderately strong coupling, but whether it can account for the high value of T_c on the basis of phonon coupling alone depends on the values of other parameters that are not yet determined. The superconducting-state electron contribution to C (C_{es}) deviates from the BCS expression in a way that has no parallel among known superconductors. It suggests the presence of a second, smaller gap in the electron density of states (EDOS), which may be related to the high value of T_c.

The $Mg^{11}B_2$ sample was a powder, prepared by reacting ^{11}B powder and Mg metal in a capped BN crucible at 850 °C under a 50-bar argon atmosphere for 1.5 h. Thermal contact to the powder was achieved by mixing it with a small amount of GE7031 varnish in a thin-walled copper cup. These extra contributions to the addenda limited the precision of the data by reducing the contribution of the sample to between 10% to 75% of the total measured heat capacity. However, the alternate method of providing thermal contact, sintering the powder, can have adverse effects on the sample [11] and may in some cases account for differences between the results reported here and those obtained in other measurements. The measurements of C were made by a modified heat-pulse technique, 1–32 K, and by a continuous-heating technique, 29–50 K. Measurements in magnetic field (H) were made on the field-cooled (FC) sample after applying the field at $T \geq 60$ K. For $H = 1$ T, for which the field penetration is about 50% of that in the normal state, measurements made after applying the field at 1 K were indistinguishable from the FC results, suggesting that equilibrium flux distributions were attained.

Below 2 K, there is an H-dependent hyperfine contribution to C. There are also several H-independent features in C, including an "upturn" below 2 K, that are probably associated with small amounts of impurity phases. Partly for that reason, most of the interpretation of the results is based on an analysis of the differences, $C(H) - C(9\ \mathrm{T})$, in which the H-independent extraneous contributions and most of the contributions of the addenda, including the varnish, cancel. $C(H) - C(9\ \mathrm{T})$ was calculated after the data were corrected for the hyperfine contributions and a small H-dependent part of the heat capacity of the sample holder. Since C is the sum of an H-dependent electron contribution (C_e) and an H-independent lattice contribution (C_l), an analysis of $C(H) - C(9\ \mathrm{T})$ also has the advantage that C_l cancels, leaving $C_e(H)$, the contribution of greater interest. In the normal state $C_e(H) = \gamma_n T$, independent of H; in the mixed state $C_e(H)$ includes a T-proportional term, $\gamma(H)T$, and H-dependent terms; and in the superconducting state, $C_e(0) = C_{es}$.

The upper critical field (H_{c2}) of MgB_2 is approximately linear in T with $H_{c2}(0) \sim 16$ T [12]. This is reasonably consistent with the C measurements, for which the onset of the transition to the mixed state, at $H = H_{c2}(T)$, is marked by the deviations of $C(H) - C(9\ \mathrm{T})$ from zero [see Fig. 1(a)]. It leads to the expectation that for 9 T the sample would be in the normal state for $T \geq 20$ K. The data actually plotted in Fig. 1(a) are $[C(H) - C(9\ \mathrm{T})]/T$, but with the scale shifted by $\gamma(9\ \mathrm{T})$. (They are essentially point-to-point differences, with no smoothing of the 9-T data, which increases the scatter.) The values of $\gamma(H)$ have been determined by fitting the low-T, mixed-, and superconducting-state data with $[C(H) - C(9\ \mathrm{T})] = [\gamma(H) - \gamma(9\ \mathrm{T})]T + a\exp(-b/T)$, where a and b are H dependent. Consistent with the $H = 0$ data, $\gamma(0)$ was taken as zero, fixing the values of $\gamma(H)$ for all H. Figure 2 shows $\gamma(H)$ vs H, and the extrapolation to $H_{c2}(0) = 16$ T to obtain $\gamma_n = 2.6\ \mathrm{mJ\,mol^{-1}\,K^{-2}}$.

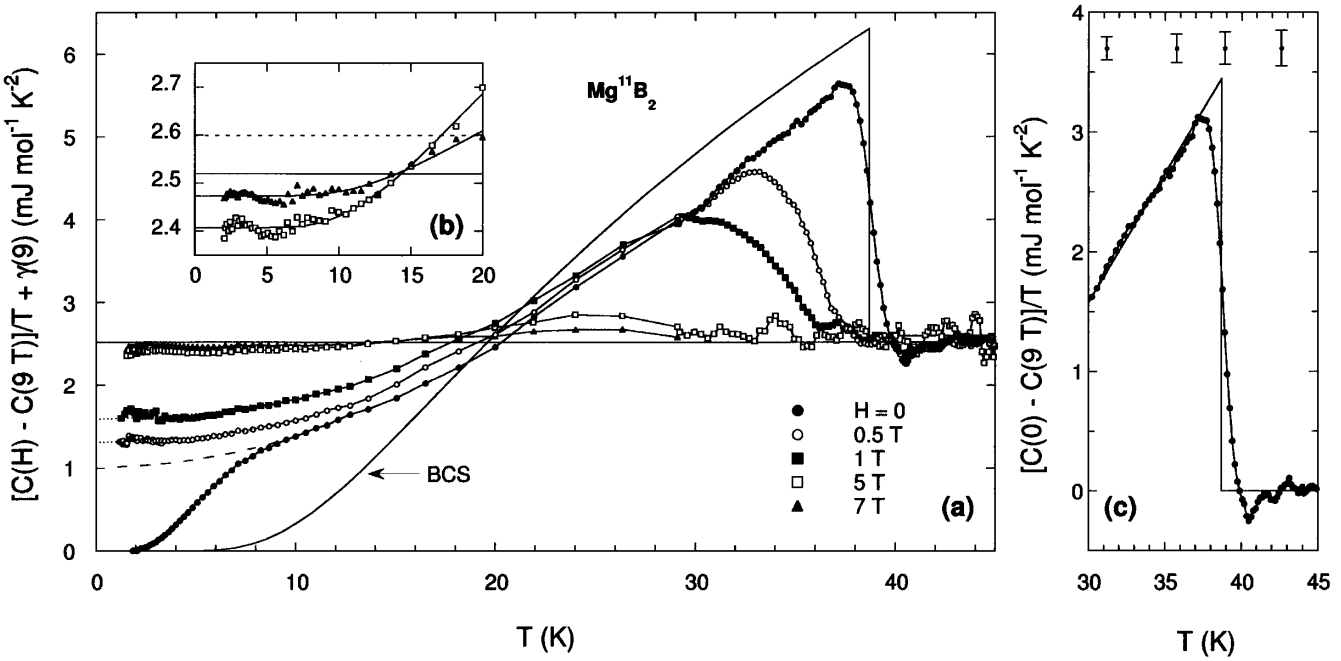

FIG. 1. (a) $[C(H) - C(9\ \mathrm{T})]/T$. In (a) and (b) the scale has been shifted by $\gamma(9\ \mathrm{T})$ to give an approximation to $C_e(H)/T$ (see text). In (a) the dashed curve is a polynomial extrapolation of the 12–20 K, $H = 0$ data to $T = 0$; the horizontal line represents $\gamma(9\ \mathrm{T})$. In (b) the low-T, 5-T, and 7-T data are shown on an expanded scale with solid curves representing fits described in the text; the horizontal solid and dashed lines represent $\gamma(9\ \mathrm{T})$ and γ_n, respectively. In (c) the solid lines represent an entropy-conserving construction. The error bars are $\pm 0.1\%$ of the total measured heat capacity.

Although the extrapolation is somewhat arbitrary, the very small differences between $\gamma(5\ \mathrm{T})$, $\gamma(7\ \mathrm{T})$, and $\gamma(9\ \mathrm{T})$ suggest that it gives γ_n to within $\sim 0.1\ \mathrm{mJ\,mol^{-1}\,K^{-2}}$. If the sample were normal at all temperatures in 9 T the quantity shown in Fig. 1(a) would be exactly $C_e(H)/T$. That is not the case, but the differences are small, as shown by the small differences between $C(5\ \mathrm{T})$, $C(7\ \mathrm{T})$, and $C(9\ \mathrm{T})$. Quantitatively, $C_e(H)/T$ is underestimated by the amount $\gamma_n - C_e(9\ \mathrm{T})/T$. For $T \leq 10$ K, $\gamma_n - C_e(9\ \mathrm{T})/T \approx \gamma_n - \gamma(9\ \mathrm{T}) \approx 0.08\ \mathrm{mJ\,mol^{-1}\,K^{-2}}$; for $10 \leq T \leq 20$ K, where there must be a small broad anomaly in $C(9\ \mathrm{T})$, the underestimate is smaller and T dependent.

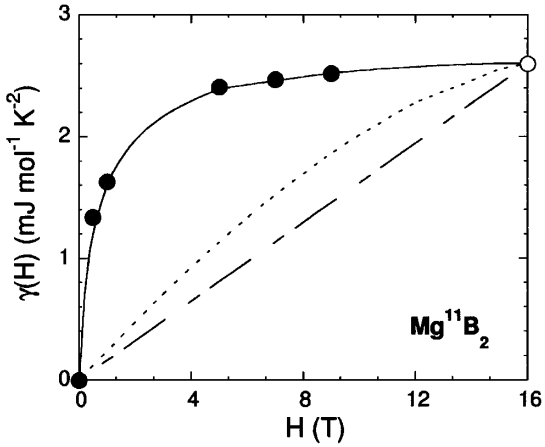

FIG. 2. γ as a function of H. The solid curve is a guide to the eye and an extrapolation to $H_{c2}(0)$. The dashed curve is a "fit" with an H_{c2} anisotropy of 10.

The transition to the superconducting state, shown in Fig. 1(c), with an entropy-conserving construction that gives $T_c = 38.7$ K and $\Delta C(T_c) = 133\ \mathrm{mJ\,mol^{-1}\,K^{-1}}$, is relatively sharp, with a width ~ 2 K. In this temperature interval the sample is in the normal state for $H = 9$ T, and addition of $\gamma_n = 2.6\ \mathrm{mJ\,mol^{-1}\,K^{-2}}$ to the quantity plotted would give $C_e(H)$ through the transition. The effect of H in broadening the transition (to the mixed state), as expected for measurements on a powder with an anisotropic H_{c2} [9,13], is evident in Fig. 1(a).

The thermodynamic consistency of the data, including, in particular, the very unusual T dependence of $C_{es}(0)$, can be tested by calculating the difference in entropy (S) between 0 and T_c for different fields. The result of such a test is shown in Fig. 3(a) where the entropies obtained by integrating the plotted points are compared with $\gamma(9\ \mathrm{T})T$, which represents the 9 T data. At 40 K, the entropies for all H are within $\pm 2\%$ of the same value. The result of a second integration of the entropies to obtain free energies and the thermodynamic critical field (H_c) is shown in Fig. 3(b).

Fitting the 20–50 K, 9-T data with $\gamma_n T + B_3 T^3 + B_5 T^5$ gave $B_3 = 5.1 \times 10^{-3}\ \mathrm{mJ\,mol^{-1}\,K^{-4}}$ and $B_5 = 2.5 \times 10^{-6}\ \mathrm{mJ\,mol^{-1}\,K^{-6}}$. The Debye temperature (Θ), calculated following the usual convention of using the value of B_3 per g atom, $\Theta^3 = (12/5)\pi^4 R(3/B_3)$, is 1050 ± 50 K.

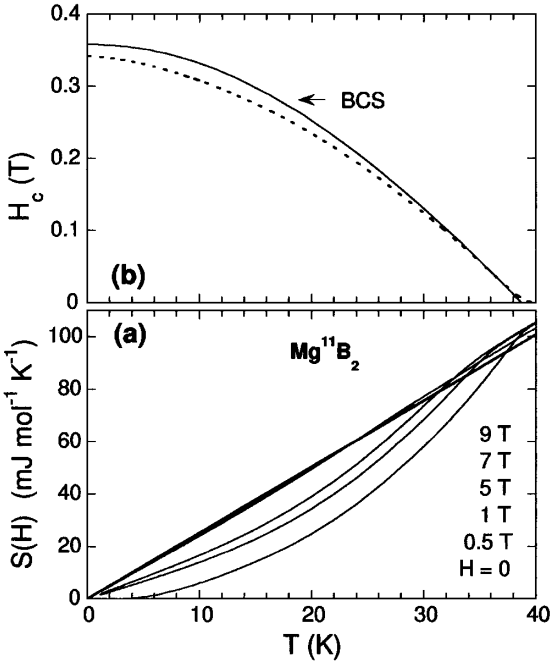

FIG. 3. (a) Entropies as functions of T for different H, with H increasing from the lowest to highest curve. (b) Thermodynamic critical field, compared with a BCS curve for the derived values γ_n and T_c.

Figure 1(a) includes a comparison of the experimental C_{es} with that for a BCS superconductor with $\gamma_n = 2.6\ \mathrm{mJ\,mol^{-1}\,K^{-2}}$ and $T_c = 38.7$ K. For $T \geq 27$ K, C_{es} is approximately parallel to the BCS curve; at lower T it rises above the BCS curve and then decreases to zero as $a\exp(-b/T)$, but with values of a and b very different from those of the BCS superconductor. This behavior is conspicuously different from that of any other superconductor. Qualitatively, it gives the appearance of a transition to the superconducting state in two stages, associated with two energy gaps: the first, a partial transition that leaves a "residual" γ (the extrapolation of C_{es} to $T = 0$ from above 12 K gives $\sim 1\ \mathrm{mJ\,mol^{-1}\,K^{-2}}$); the second, which completes the transition and is associated with a second, smaller energy gap. Taking the exponential decrease in C_{es} as a manifestation of a BCS-like transition, and comparing the parameters a ($67\ \mathrm{mJ\,mol^{-1}\,K^{-1}}$) and b (15.8 K) with BCS theory, gives $T_c = 11$ K, the gap parameter $\Delta(0) = 1.765 k_B T_c = 1.7$ meV, and $\gamma = 0.74\ \mathrm{mJ\,mol^{-1}\,K^{-2}}$. This interpretation of C_{es} is qualitatively consistent with band-structure calculations that give different gaps, with amplitudes differing by a factor of ~ 3, on two parts of the Fermi surface [14]. In general, coupling between the two parts ensures that the two gaps open at a common T_c and have a similar T dependence, but at low T C_{es} is determined by the small gap [15]. The major features of C_{es} can be understood in terms of the existence of two gaps [15], but in this case the strengths of the electron-phonon coupling between, and on, the two parts give the small gap a non-BCS T dependence [14], which may affect the observed feature in C_{es} in the 8–12 K region. The existence of two gaps on the Fermi surface is also consistent with scanning tunneling spectroscopy, which has shown both a flat-bottomed BCS-like gap at low T, but with a small amplitude, ~ 2 meV, corresponding to a BCS T_c of ~ 13 K [16], and a V-shaped gap with an amplitude of ~ 5.2 meV, corresponding to a BCS T_c of 35 K [17], more compatible with the observed T_c. Despite the difficulty of explaining why different groups measure different gaps (see also Refs. [18,19]), it is striking how well these two gaps would account for C_{es}: At low T, where the thermal excitations are too weak to overcome the larger gap, the exponential behavior of C_{es} is consistent with the smaller gap; the opening of both gaps at T_c explains the large $\Delta C(T_c)$. Between 20 K and T_c, C_{es}/T is more linear in T than the BCS curve [see Fig. 1(a)]. This approximate T^2 term is reminiscent of the C_{es} of some heavy-fermion superconductors [20], which has been associated with electron-pairing mechanisms that might produce a V-shaped gap. (Comparison of these empirical results is worth notice even though it is only the low-T C_{es} that is generally associated with the V shape, and the T^2 dependence extending to T_c in the heavy-fermion case is not theoretically understood.)

Anisotropy in H_{c2} cannot explain the dramatic increase in $\gamma(H)$ at low H shown in Fig. 2. The dashed curve is a calculation using the effective-mass model with an anisotropy of 10, which is already greater than reported values [9,13], but $\gamma(H)$ cannot be fitted with *any* value of the anisotropy. The rapid increase in $\gamma(H)$ at low H is a consequence of the small magnitude of the second gap and the associated small condensation energy.

An average over the Fermi surface of the electron-phonon coupling parameter can be estimated by comparing γ_n with band-structure calculations of the "bare" EDOS at the Fermi surface ($N(0)$) using the relation $\gamma_n = (1/3)\pi^2 k_B^2 N(0)(1 + \lambda)$. $N(0)$ has been reported as 0.68, 0.71, and 0.72 states $\mathrm{eV^{-1}}$ unit $\mathrm{cell^{-1}}$ (Refs. [8–10], respectively) giving $\lambda = 0.58$, 0.51, and 0.49. Theoretically calculated values of λ are 0.71 [8], and ~ 1 [10]. T_c is related to λ, Θ, and the electron-electron repulsion (μ^*) by [6]

$$T_c = (\Theta/1.45) \times \exp\{-1.04(1 + \lambda)/[\lambda - \mu^*(1 + 0.62\lambda)]\}, \quad (1)$$

with μ^* frequently taken to be ~ 0.1 [6,7]. With $\lambda = 0.58$, the highest of the values obtained from γ_n and $N(0)$, and $\Theta = 1050$ K, Eq. (1) gives $T_c = 18$ K, too low by a factor of more than 2. For these values of λ and Θ, $T_c = 39$ K would require $\mu^* = 0.0130$, an unusually low value. However, in this expression Θ represents a relatively crude estimate of the phonon frequencies that are important in the electron pairing. As derived from the coefficient of the T^3 term in C_l, Θ is really a measure of the frequencies of the low-frequency acoustic phonons, which may not be particularly relevant to the pairing of

the electrons. In the Debye model, Θ is also the cutoff frequency, but real phonon spectra often extend to significantly higher frequencies. In another version of the theory [7], $\Theta/1.45$ is replaced by $\omega_{\log}/1.20$, where $\omega_{\log}$ is a moment of the phonon frequencies in which they are weighted by the electron-phonon matrix elements. More detailed calculations that take into account relevant features of the phonon spectrum and electron-phonon scattering may give a value of the preexponential factor in Eq. (1) that accounts for the observed T_c with a physically plausible value of μ^*, but until they are available, the question of whether the electron pairing in MgB_2 is phonon mediated would seem to remain open.

The parameters $[H_c(0)]^2/\gamma_n T_c^2$ and $\Delta C(T_c)/\gamma_n T_c$ measure the strength of the electron pairing [21]. In the BCS, weak-coupling limit, their values are 5.95 and 1.43, respectively. There are a number of "strong-coupled" superconductors for which these parameters are greater than the BCS values, but relatively few for which they are smaller [21]. For $Mg^{11}B_2$ they are unusually small, 5.46 and 1.32. Such small values can arise from gap anisotropy (see, e.g., Ref. [21]) and from multigap structure [15].

In general, there are more differences than similarities among the specific-heat measurements on MgB_2 [2,22–25], but in one case [22] major features of the results, obtained on a sintered sample of commercial material by a different experimental technique, are qualitatively similar to those reported here. The similarities attest the qualitative validity of these features; the differences can be understood in terms of sample dependence, but they do lead to somewhat different conclusions in several significant respects. Measurements in 14 and 16 T gave the same C, and $\gamma_n = 2.7\ \mathrm{mJ\,mol^{-1}\,K^{-2}}$ was obtained without any extrapolation [22], but since the data included an unknown contribution from paramagnetic impurities, the uncertainty in γ_n may be comparable to that in the estimate reported here. The tests of thermodynamic consistency are similar in the two cases, but limited by contributions of the paramagnetic impurities of Ref. [22], and by the precision of the data here. The anomaly at T_c has the same entropy but is broader and lower, which led to a substantial underestimate of $\Delta C(T_c)$ [22]. C_{es} shows the same sharp drop below 10 K [22], but the limiting $T \rightarrow 0$ dependence was obscured by the contribution of the paramagnetic centers, and was taken as approximately T^2 [22], which would be expected for line nodes, rather than the exponential dependence reported here, which corresponds to a finite gap over the whole of the Fermi surface. [In comparing Fig. 1(a) with Fig. 9 in Ref. [22], it should be noted that the two BCS curves are different: the one in Fig. 1(a) is consistent with γ_n and T_c, and has the same entropy at T_c as the experimental data; that in Ref. [22] was drawn to fit the smaller $\Delta C(T_c)$.]

Several other values of $\Delta C(T_c)$, all for sintered samples, and most lower than that reported here, have been given in other reports [2,23–25]. Values of γ_n that range from 1.1 to 5.5 $\mathrm{mJ\,mol^{-1}\,K^{-2}}$, based on different [23,25] or unspecified [2] analysis of experimental data have also been reported, but the very similar values reported here and in Ref. [22] are supported by the thermodynamic consistency of the data.

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Note added.—Photoemission spectroscopy has given additional evidence of two gaps, with gap parameters 1.7 and 5.6 meV [26]. Additional specific-heat results, similar to those described here, have been reported [27].

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