Order Parameter of MgB$_2$: A Fully Gapped Superconductor

H. D. Yang,[1] J.-Y. Lin,[2] H. H. Li,[1] F. H. Hsu,[1] C. J. Liu,[3] S.-C. Li,[4] R.-C. Yu,[4] and C.-Q. Jin[4]

[1]*Department of Physics, National Sun Yat-Sen University, Kaohsiung 804, Taiwan, Republic of China*

[2]*Institute of Physics, National Chiao Tung University, Hsinchu 300, Taiwan, Republic of China*

[3]*Department of Physics, National Changhua University of Education, Changhua 500, Taiwan, Republic of China*

[4]*Institute of Physics, Center for Condensed Matter Physics and Beijing High Pressure Research Center,*
Chinese Academy of Science, P.O. Box 603, Beijing 1000080, People's Republic of China

We have measured the low-temperature specific heat $C(T)$ for polycrystalline MgB$_2$ prepared by high pressure synthesis. $C(T)$ below 10 K vanishes exponentially, which unambiguously indicates a fully opened superconducting energy gap. However, this gap is found to be too small to account for T_c of MgB$_2$. Together with the small specific heat jump $\Delta C/\gamma_n T_c = 1.09$, scenarios such as anisotropic s-wave or multicomponent order parameter are called for. The magnetic field dependence of $\gamma(H)$ is neither linear for a fully gapped s-wave superconductor nor $H^{1/2}$ for nodal order parameter. It seems that this intriguing behavior of $\gamma(H)$ is associated with the intrinsic electronic properties other than flux pinning.

The recently discovered superconductivity in MgB$_2$ has simulated new excitement in condensed matter physics [1]. MgB$_2$ possesses the highest $T_c \approx 39$ K among intermetallic compounds, and the strong isotope effect on T_c clearly suggests an electron-phonon interaction [2]. Therefore, it is thought that T_c of MgB$_2$ probably represents the upper limit of the phonon-mediated superconductivity [3]. However, to reach any conclusion, one requires better understanding of the superconducting properties of MgB$_2$. Up to now, there have been several fundamental questions to be answered. For example, is MgB$_2$ a fully gapped superconductor? If it is, is it a conventional s-wave superconductor? In principle, the tunneling experiments can answer part of these questions. Nevertheless, the existing tunneling data are not consistent with each other, partly due to junction interface problems. On the contrary, the specific heat (C) measurements probe the bulk nature of the designated properties. If an exponentially vanishing electronic specific heat in the superconducting state C_{es} is observed, a full superconducting gap Δ can be unequivocally established. Furthermore, the magnetic field H dependence of C_{es} would provide the information about the quasiparticle excitation associated with the vortex state, since MgB$_2$ is a type-II superconductor. Therefore, specific heat has been a powerful tool to investigate superconductivity among other methods. In the case of MgB$_2$, however, the present existing specific heat studies are not quite consistent with each other both qualitatively and quantitatively.

In this Letter, to shed light on this issue, we have carefully conducted the low-temperature specific heat measurements on high quality polycrystalline MgB$_2$ prepared by high pressure synthesis. *The data clearly manifest a superconducting gap with no node at $H = 0$. However, the same data show equally clearly that MgB$_2$ may not be a simple s-wave conventional superconductor.*

The polycrystalline MgB$_2$ sample was prepared by high pressure synthesis with pyrophyllite as the pressure trans-

mitting medium at 3.0 GPa and 1000 °C for 15 min. Details of the synthesis were describe elsewhere [4]. The x-ray diffraction pattern showed a nearly single phase of MgB$_2$. In spite of the tiny amount of other phases such as MgO and B$_2$O, the overall phase purity is better than that of the commercial alpha powder when the comparison was done. The superconductivity was first verified by SQUID magnetization and resistivity measurements. Both found the superconductivity onset around 39 K and the transition width less than 1 K. The resistivity at $T = 40$ K is about 1 $\mu\Omega$ cm. The low resistivity, sharp transition, and the large specific jump ΔC at T_c all indicate the high quality of the sample. $C(T)$ was measured from 0.6 to 50 K in the magnetic fields up to 8 T, with a ^{3}He thermal relaxation calorimeter in which $C = (\Delta P/\Delta T)\tau$, where ΔT is the temperature change associated with the change of the heat power ΔP and τ is the thermal relaxation time constant. The error of the measurements in the temperature range is about 1% through the whole temperature range. However, the electronic specific heat is better determined at low temperatures since at high temperatures a large phonon specific heat has to be subtracted. Details of the measurements and system calibrations can be found in [5–7].

Figure 1(a) shows the raw data of $C(T)$ of MgB$_2$ both at $H = 0$ and 8 T. A clear anomaly around 39 K demonstrates bulk superconductivity in the sample. Better information of the anomalous specific heat jump at T_c can be deduced from the difference between the superconducting state and the normal state specific heat $\Delta C = C_{es} - C_{en}$. Since $T_c \approx 20$ K at $H = 8$ [8], ΔC above 20 K can be obtained by $C(H = 0) - C(H = 8$ T$)$. (The polynomial expression was used for $C(H = 8$ T$)$ during the subtraction.) The resulting zero field $\Delta C/T$ is shown in Fig. 1(b). The dimensionless specific jump $\Delta C/\gamma_n T_c = 1.09$ at $H = 0$, where $T_c = 39$ K and $\gamma_n = 2.7$ mJ/mol K^2 [9], is only 15% smaller than that in [10] and significantly larger than most of those in [2,9,11,12]. However, it
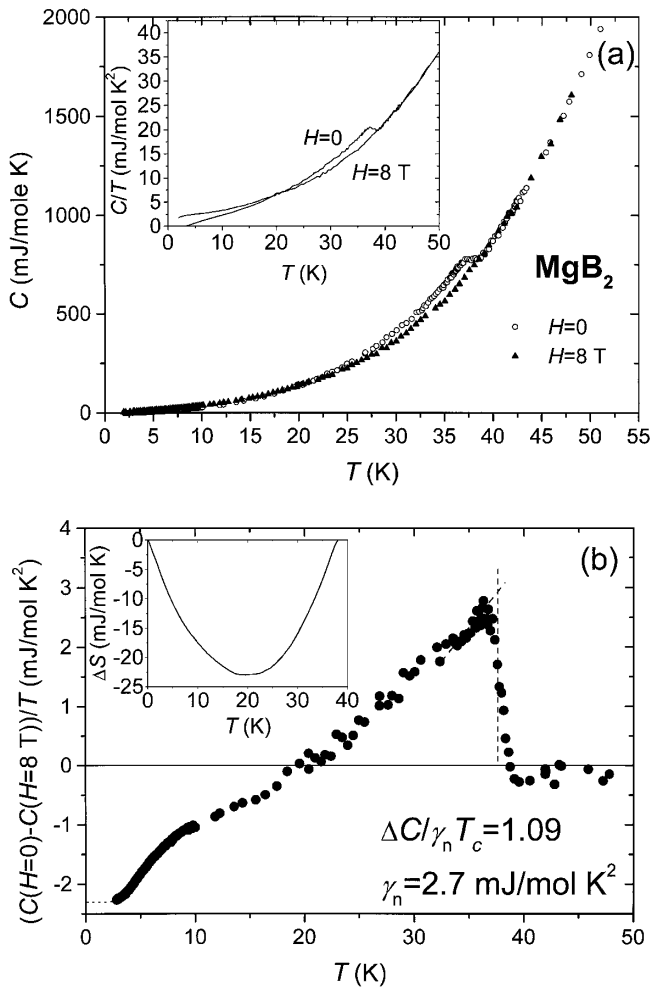
FIG. 1. (a) $C(T)$ of MgB_2 both at $H = 0$ and 8 T. The anomaly around 39 K manifests the bulk superconductivity. C/T vs T was plotted in the inset to show the thermodynamic consistency. (b) $\Delta C[= C(H = 0) - C(H = 8 \text{ T})]/T$ vs T. The dashed lines are determined by the conservation of entropy around the anomaly and used to estimate $\Delta C/T_c$. The dotted line at low temperature is an exponential extrapolation of data between 3 and 5 K. Inset: Entropy difference ΔS by integration of $\Delta C/T$ according to the data or the extended dot line.

FIG. 2. Evolution of $\Delta C = C(H) - C(H = 8 \text{ T})$ in magnetic fields.

magnetic fields up to at least 6 T, though only $\Delta C(T,H)$ up to 2 T is presented in Fig. 2 for clarity.

The low temperature data below 10 K reveal even more intriguing pictures. C/T vs T^2 below 10 K for $H = 0$ to 8 T is shown in Fig. 3. For zero field data at very low temperatures, a remnant cannot be excluded, probably due to small magnetic contribution or a few percents of normal state portion. Other than that, C increases very fast with T. In magnetic fields, C/T vs T is nearly a straight line at high temperatures. With increasing H, the intersection γ increases and the slope remains the same. All these results are expected, assuming an increase in the quasiparticle contribution associated with the vortices. In the mixed state ($H > H_{c1}$), the linear-T quasiparticle contribution due to the presence of the vortices would dominate the contribution in the Meissner state (e.g., the exponential

is still small compared to the weak limit BCS value 1.43. This result may imply that MgB_2 is not a simple strong-coupling BCS superconductor as one naively expects from its high T_c. Moreover, ΔC becomes zero at about $T_c/2$ as suggested in Fig. 1(b). A similar crossing temperature was also observed in [9,10]. For an isotropic s-wave superconductor with the coupling constant $\lambda > 1$, the crossing temperature should have happened above 0.6 T_c [13]. A curious dip of $\Delta C/T$ to a small negative value just above T_c was observed. Interestingly, a similar dip with almost the same magnitude was also shown in [10]. This dip could be due to fluctuations and may deserve further investigation. Evolution of $\Delta C/T$ in the magnetic fields is shown in Fig. 2. It is seen that the bulk superconductivity continues to exist in
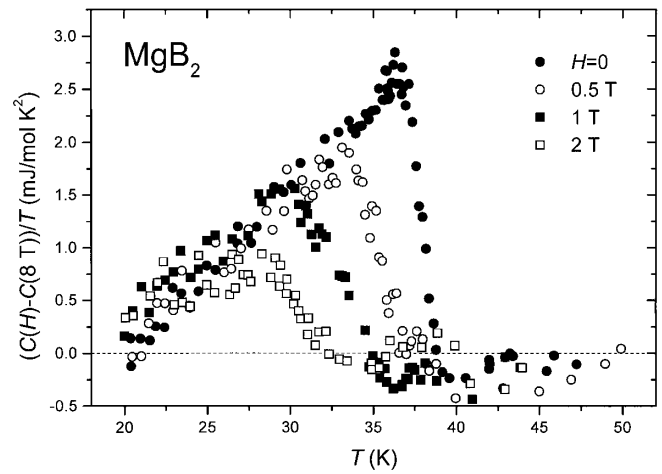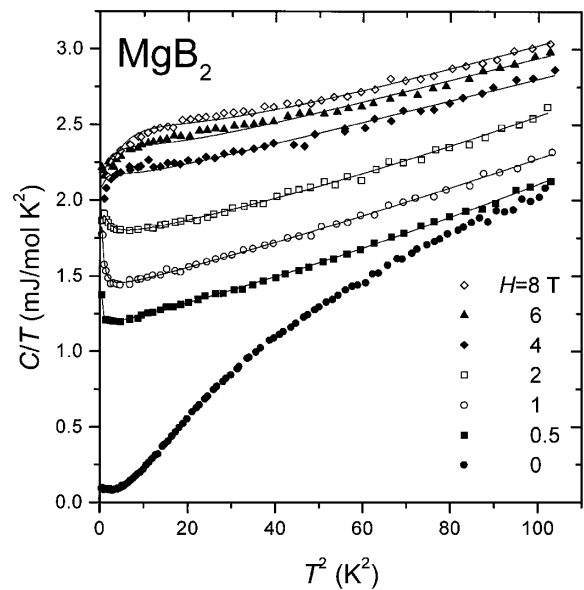
FIG. 3. $C(T,H)/T$ vs T^2 below 10 K. The solid lines demonstrate the quality of the fit.

temperature dependence for a gapped superconductor). A more quantitative description for the data in magnetic fields can be given by $C(T,H) = \gamma(H)T + C_{\text{lattice}}(T) + nC_{\text{Schottky}}(g\mu H/k_B T)$, where the second term is a two-level Schottky anomaly $C_{\text{Schottky}}(x) = x^2 e^x / (1 + e^x)^2$. $C_{\text{lattice}}(T) = \beta T^3 + \delta T^5$ represents the phonon contribution. The T^5 term due to the phonon dispersion is usually negligible at low temperatures, though inclusion of this term sometimes improves the quality of fit. The fits were carried out for data below 10 K at each H by the above formula. Phenomenologically, the satisfactory descriptions for data were obtained, as exemplified by the solid lines in Fig. 3. By this method, $\gamma(H)$, n, and C_{lattice} can be obtained. The corresponding Debye temperature is $\Theta_D = 910$ K which is close to that reported in [9,10]. The fits yield very similar C_{lattice} for each H as expected. The value of n does not vary with H very much, either. The averaged $n = 7.2 \times 10^{-5}$ mol^{-1}, which is much smaller than that in [9], again indicates the good quality of the sample, and makes the determination of $\gamma(H)$ more reliable. In principle, one would be concerned with the expression of C_{Schottky} which is, strictly speaking, only suitable for spin-$\frac{1}{2}$ paramagnetic centers. The existence of a small amount of Fe ions in MgB$_2$ was proposed [9]. Not knowing which oxide Fe forms, the spin of Fe ions cannot be exactly determined. However, due to the small value of n, the resultant $\gamma(H)$ is not expected to change drastically if another spin is chosen.

The electronic specific heat in the superconducting state at H is $C_{\text{es}}(T) = C(T,H) - C_{\text{lattice}}(T)$. $C_{\text{es}}(T)$ vs T_c/T for $H = 0$ was plotted in Fig. 4. The results unambiguously sh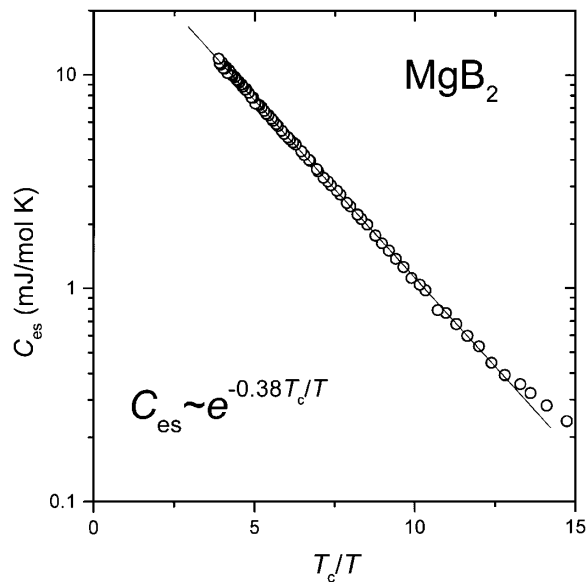ow that $C_{\text{es}}(T)$ vanishes exponentially at low temperatures. In Fig. 4, no attempt was made to correct the remnant. The fit from 3 to 10 K reveals $C_{\text{es}}(T) \propto \exp(-0.38T_c/T)$ which is demonstrated by the solid straight line in Fig. 4. This behavior of $C_{\text{es}}(T)$ clearly manifests the existence of an energy gap with no node. An exponential $C_{\text{es}}(T)$ was also reported in [10]. Deviations at very low temperatures are presumably due to the remnant.

With an apparent gap at low temperatures, MgB$_2$ may still not be so simple as an isotropic s-wave superconductor. For the expression of $C_{\text{es}}(T) \propto \exp(-aT_c/T)$, the weak-coupling BCS theory predicts that the value of a should be between 1.44 and 1.62 for the reduced temperature (T/T_c) range investigated in this Letter [14]. Obviously, the observed value of a is four times smaller. One of the main points of this Letter is to establish the fact that *indeed a fully opened gap was observed at low temperatures, but this gap is too small to account for the high T_c of MgB$_2$*. It is possible to reconcile this difficulty, at least qualitatively, by the scenario of either the anisotropic or multicomonent order parameter for MgB$_2$. In both scenarios, the large gap(s) would be responsible for the T_c, while the low-energy excitation would be most influenced by the small gap. These scenarios are consistent with the theoretical considerations [15,16] and the results from the photoemission spectroscopy [17]. Since the sample in this study is polycrystalline, the present data are not likely to distinguish either of these scenarios. It is now clear that the small $\Delta C/\gamma_n T_c = 1.09$ is probably intrinsic in order to be in accord with the observation of a small gap at low temperatures. Previously, the small $\Delta C/\gamma_n T_c$ of Mo was considered a manifestation of gap anisotropy [18]. In the multigap (say, two-gap) scenario, both the large and small gap should open at T_c. If the small gap were BCS-like and opened at $T \approx 10$ K, C_{es} should have deviated from the exponential behavior above 5 or 6 K. Furthermore, no corresponding anomaly was observed around this temperature both in this work and in [9], though a possible signature was suggested in [10].

The magnetic field dependence of $\gamma(H)$ is even more puzzling. For a gapped superconductor, $\gamma(H)$ is expected to be proportional to H [19]. Apparently, $\gamma(H)$ is not linear in H as seen in Fig. 5. For nodal superconductivity, $\gamma(H) \propto H^{1/2}$ is predicted [20], and was verified by several studies in cuprates [5,6,21–23]. Fitted to the power law, $\gamma(H) \propto H^{0.23}$ can be found as shown by the dashed line in Fig. 5. Therefore, this nonlinearity in $\gamma(H)$ may be due to origin(s) other than the nodes of the order parameter. Phenomenologically, the small power is caused by the rapid increase in $\gamma(H)$ at low fields, and is likely to be related to the small gap mentioned in the previous paragraph. This possibility is suggested by the poor description of high field data in Fig. 5 by the power law. Since this curious behavior was observed in hot-pressed polycrystalline sample here and the powder sample in [10] or the sintered one from the commercial powder in [9], it is

FIG. 4. $C_{\text{es}} = C - C_{\text{lattice}}$ of MgB$_2$ in the superconducting state is plotted on a logarithmic scale vs T_c/T. The exponential dependence on $1/T$ is evident. The straight line is the fit from 3 to 10 K.
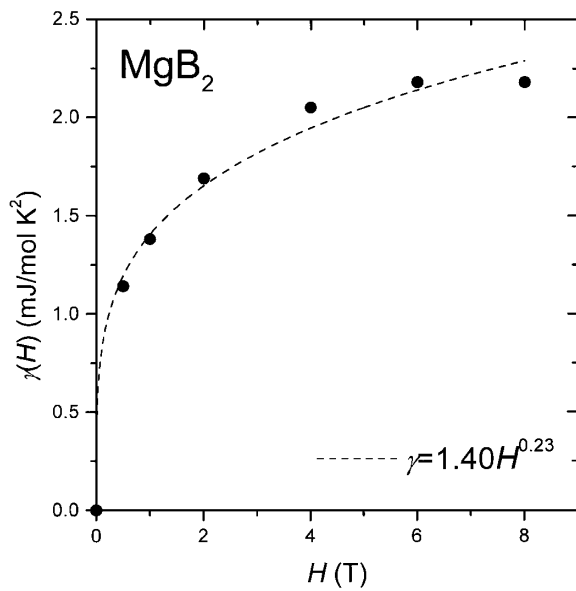
FIG. 5. The magnetic field dependence of $\gamma(H)$. The dashed line is a fit to the power law.

not likely to originate from the pinning mechanism. More likely, in addition to the possible cause of a small gap, it is associated with the quasiparticle states in the cores or the unusual magnetoresistance reported in [8]. Extrapolating $\gamma(H)$ by this power law fit, $\gamma(H) = 2.6$ mJ/mol K^2 at $H = 14$ T, which is consistent with γ_n in [9]. Other than in MgB$_2$, it is noted that a nonlinear $\gamma(H)$ in H was also observed in the s-wave superconductors such as NbSe$_2$ [24]. Therefore, the thermodynamics of the mixed state in the gapped superconductors apparently is not well understood and might provoke new interest on this issue.

To conclude, we have presented convincing evidence for a fully opened gap in MgB$_2$. The low temperature C_{es} in this work is qualitatively similar to that in [9,10]. However, it is quantitatively consistent with an exponential behavior as reported in [10] rather than the T^2 dependence in [9]. The gap deduced from the exponential T dependence is too small, together with the small $\Delta C/\gamma_n T_c$ to account for $T_c = 39$ K in the isotropic s-wave model. Other scenarios such as anisotropic or multicomponent order parameter are called for to reconcile. Isotropic or not, the nonlinear H dependence of $\gamma(H)$ cannot be easily explained. The present study suggests that MgB$_2$ is not a simple conventional superconductor. To understand the origin of its high T_c, more work on the fundamental properties, especially on the complexity of order parameter, is indispensable.

[1] J. Nagamatsu, N. Nakagawa, T. Muranaka, Y. Zenitani, and J. Akimitsu, Nature (London) **410**, 63 (2001).
[2] S. L. Bud'ko, G. Lapertot, C. Petrovic, C. E. Cunningham, N. Anderson, and P. C. Canfield, Phys. Rev. Lett. **86**, 1877 (2001).
[3] W. L. McMillan, Phys. Rev. **167**, 331 (1968).
[4] S. C. Li, J. L. Zhu, R. C. Yu, F. Y. Li, Z. X. Liu, and Changqin Jin, Chin. Phys. **10**, 338 (2001).
[5] S. J. Chen, C. F. Chang, H. L. Tsay, H. D. Yang, and J.-Y. Lin, Phys. Rev. B **58**, R14 753 (1998).
[6] C. F. Chang, J.-Y. Lin, and H. D. Yang, Phys. Rev. B **61**, 14 350 (2000).
[7] C. F. Chang, J.-Y. Lin, and H. D. Yang, Phys. Rev. Lett. **84**, 5612 (2000).
[8] D. K. Finnemore, J. E. Ostenson, S. L. Bud'ko, G. Lapertot, and P. C. Canfield, Phys. Rev. Lett. **86**, 2420 (2001).
[9] Y. Wang, T. Plackowski, and A. Junod, cond-mat/0103181.
[10] F. Bouquet, R. A. Fisher, N. E. Philips, D. G. Hinks, and J. D. Jorgensen, Phys. Rev. Lett. (to be published).
[11] R. K. Kremer, B. J. Gibson, and K. Ahn, cond-mat/0102432.
[12] Ch. Wälti, E. Felder, C. Degen, G. Wigger, R. Monnier, B. Delley, and H. R. Ott, cond-mat/0102522.
[13] A. Mirmelstein, A. Junod, E. Walker, B. Ravaz, J.-Y. Genoud, and G. Triscone, J. Supercond. **10**, 527 (1997).
[14] G. Gladstone, M. A. Jensen, and J. R. Schrieffer, in *Superconductivity,* edited by R. D. Parks (Marcel Dekker, New York, 1969), Vol. 2.
[15] S. Haas and K. Maki, cond-mat/0104207.
[16] A. Y. Liu, I. I. Mazin, and J. Kortus, cond-mat/0103570.
[17] S. Tsuda, T. Tokoya, T. Kiss, T. Takano, K. Togano, H. Kitou, H. Ihara, and S. Shin, cond-mat/0104489.
[18] D. C. Rorer, D. G. Onn, and H. Meyer, Phys. Rev. **138**, A1161 (1965).
[19] C. Caroli, P. G. de Gennes, and J. Matricon, Phys. Lett. **9**, 307 (1964).
[20] G. E. Volovik, JETP Lett. **58**, 469 (1993).
[21] K. A. Moler, D. L. Sisson, J. S. Urbach, M. R. Beasley, and A. Kapitulnik, Phys. Rev. B **55**, 3954 (1997).
[22] B. Revaz, J.-Y. Genoud, A. Junod, A. Erb, and E. Walker, Phys. Rev. Lett. **80**, 3364 (1998).
[23] D. A. Wright, J. P. Emerson, B. F. Woodfield, J. E. Golden, R. A. Fisher, and N. E. Phillips, Phys. Rev. Lett. **82**, 1550 (1999).
[24] J. E. Sonier, M. F. Hundley, and J. W. Beill, Phys. Rev. Lett. **82**, 4914 (1999).