Improved superconducting properties of MgB$_2$

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Abstract

We present electrical transport, magnetization, and specific heat measurements on bulk MgB$_2$ samples ($T_c = 38.5$ K) synthesized under 200 MPa pressure using a process based on hot isostatic pressing with cooling under pressure. The samples are fully dense and display excellent superconducting properties, including a narrow superconducting transition width ($\Delta T_c = 0.75$ K), a high upper critical field $H_{c2}(0) \sim 155$ kOe, and a critical current density $J_c$ that is the largest yet measured for bulk samples of MgB$_2$ ($J_c(0) \sim 1.4$ MA/cm$^2$). Specific heat measurements yielded a jump $\Delta C$ at $T_c$ of 92 mJ/mol K. These superconducting properties are comparable to those obtained with techniques that are not so well suited to industrial scale fabrication.

Key words: MgB$_2$, superconductivity
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1 Introduction

The discovery of superconductivity in the binary intermetallic compound MgB$_2$ with a superconducting critical temperature $T_c \approx 40$ K came as a great surprise and has attracted much interest.[1–4] This value of $T_c$ far exceeds the previous record high $T_c$ value of any binary intermetallic compound of 23 K for the A15 compound Nb$_3$Ge.[5] Only the oxides and compounds based on C$_60$ have comparable or higher values of $T_c$.[6] Moreover, this value of $T_c$ is near the limits of $T_c$ expected on theoretical grounds for superconductivity based
on the electron-phonon interaction mechanism.[7,8] It is of great interest to study the normal- and superconducting-state properties of MgB$_2$ to gain insight into the characteristics of the superconducting state and the underlying electron-pairing mechanism.

Up to date, high quality bulk samples of MgB$_2$ have been successfully produced by synthesis under high pressure. Superconductivity in MgB$_2$ was discovered by Nagamatsu et al. in samples prepared by hot isostatic pressing (HIPing) a mixture of Mg and B powders at 196 MPa.[1] While unequivocally displaying superconductivity, these initial MgB$_2$ samples were quickly surpassed in terms of superconducting properties by the compression of commercial MgB$_2$ powder in a cubic multi-anvil-type press with pressures up to 3 GPa.[9,10] These later results clearly demonstrate that high pressure synthesis is advantageous in producing fully dense bulk MgB$_2$ with electrical transport properties and high critical current densities superior to those of sintered samples. However, these reports also show the limitations on the amount of sample that can be prepared in each compression cycle.

In this paper, we report electrical transport, magnetization, and specific heat measurements on high quality bulk MgB$_2$ samples prepared from commercial powder by means of a process called dense material cooling under pressure (DMCUP), a technique based on HIPing that potentially can be scaled to larger sample sizes and more complex shapes.[11]

2 Experimental Details

Magnesium diboride (MgB$_2$) powders of −325 mesh size with 98% purity were obtained from Alfa Aesar, Inc., from which bulk MgB$_2$ samples were prepared by HIPing at 200 MPa as previously reported.[11] Magnetization measurements were made with a commercial Quantum Design SQUID magnetometer. DC magnetic susceptibility data were taken on a 14 mg sample in an applied field of 10 Oe from 5 to 60 K, using the conventional zero-field-cooled (ZFC) and field-cooled (FC) procedures. Magnetization $M$ vs applied field $H$ hysteresis loops were taken on a 0.43 mg sample at temperatures between 10 and 30 K and in applied fields between $-50$ and 50 kOe. Electrical resistivity measurements were made using the standard four-probe technique in a commercial Quantum Design Physical Properties Measurement System. The dc current was applied using a Keithley K220 current source and the sample voltage was measured with a Keithley K2182 nanovoltmeter.

Specific heat measurements were made between 4 and 90 K in a laboratory-built calorimeter using a standard semiadiabatic heat-pulse technique. The two samples measured consisted of (1) a 120 mg pellet pressed from the original
Alfa Aesar powder and (2) three pieces of the HIPed sample with a combined mass of 128 mg. The samples were attached to a sapphire platform using Apiezon N Grease. The sample temperature was measured with a Lakeshore Cernox 1030 thermometer and the heat pulse was applied with a thin-film chip heater; both the thermometer and the heater were attached to the underside of the sapphire platform.

3 Results and Discussion

The main portion of Figure 1 shows the evolution of the superconducting transition of MgB$_2$ with magnetic field up to 90 kOe as a plot of electrical resistivity $\rho$ vs temperature $T$. The resistivity as a function of temperature up to 300 K is shown in the inset to Figure 1. At 40 K, in the normal state right above $T_c$, the sample has a resistivity of 5.2 $\mu\Omega\cdot$cm, which is in the low range of the reported resistivity values for MgB$_2$ prepared from natural boron. The $\rho(T)$ data in Figure 1 yield a residual resistivity ratio $[\equiv \rho(300 \text{ K})/\rho(40 \text{ K})]$ of 3.46. The zero-field superconducting transition occurs at $T_c = 38.5$ K, defined as the temperature of the 50% value of the transition, and has a width $\Delta T_c = 0.75$ K, defined as the difference in the temperatures of the 10% and 90% values of the transition. The upper critical field $H_{c2}$ vs $T$ curve shown in Figure 3 was determined from the $\rho(T)$ curves in the same manner. The normal state ($T > T_c$) resistivity data display very small magnetoresistance at high fields, in contrast to data previously published on samples synthesized from a mixture of high purity Mg and B,[3,12] but in agreement with data previously published on samples sintered under high pressure from commercial 98–99% pure MgB$_2$ powder.[10,13] This implies that the presence of 1% to 2% of chemical impurities suppresses the normal state magnetoresistance almost entirely.

Magnetization $M$ vs magnetic field $H$ isotherms for the MgB$_2$ sample are shown in Figure 2. Displayed in the inset to Figure 2 is a plot of the dc magnetic susceptibility, $\chi_{dc}$, vs temperature, $T$, for the MgB$_2$ sample in a magnetic field of 10 Oe. The very slight tilting of the $M(H)$ data is due to a diamagnetic background in the normal state which was subtracted to facilitate the determination of the $H_{c2}$ data plotted in Figure 3. The high-field magnetization above the superconducting transition is described well by a linear function that passes through the origin. Once these linear functions were subtracted from the $M(H)$ data, the critical field $H_{c2}$ could be more conveniently determined as the field at which the magnetization vanished. These values of $H_{c2}$ are extremely close to the values derived from the resistivity measurements, as shown in Figure 3. The irreversibility field, $H_{irr}$, was easily found from the detailed $M(H)$ measurements as the magnetic field at which hysteresis sets in.
The critical field at zero temperature can be estimated from the Wherther-Helfand-Hohenberg (WHH) theory in the “dirty limit”[14] \((l/\xi \ll 1, \text{where } l \text{ is the mean free path and } \xi \text{ is the superconducting coherence length})\) by the formula \(H_{c2}(0) = \frac{1}{2}\sqrt{2T_c}|dH_{c2}/dT|_{T_c}\). Our data as presented in Figure 3 exhibit positive curvature at temperatures near \(T_c\), and becomes linear by 32 K. The slope from this lower temperature region is \(|dH_{c2}/dT| = 5.68 \text{ kOe/K} \); this yields \(H_{c2}(0) = 155 \text{ kOe}\). The low temperature coherence length can be estimated from the relation \(\xi_0 = \left(\frac{\phi_0}{2\pi H_{c2}(0)}\right)^{\frac{1}{2}}\); using the value for the flux quantum \(\phi_0\) of \(2.1 \times 10^{-7} \text{ Oe-cm}^2\), we find \(\xi_0 = 4.6 \text{ nm}\). An estimate of the mean free path \(l = 4.8 \text{ nm}\) can be obtained from the resistivity using the relation \(l = v_Fm_e/ne\rho(40 \text{ K})\), using the following values for the Fermi velocity \(v_F \approx 4.8 \times 10^7 \text{ cm/s}[15]\) the charge carrier density \(n \approx 6.7 \times 10^{22} \text{ e/cm}^3[4]\) and the resistivity \(\rho(40 \text{ K}) \approx 5.2 \mu\Omega\cdot\text{cm}\). The resulting ratio \(l/\xi \approx 1\) implies that the “dirty limit” is not really appropriate in the MgB\(_2\) specimen studied. However, it should be pointed out that many of the published results that are well into the “clean limit” \((l/\xi \gg 1)\) continue to use the “dirty limit” approximation to estimate \(H_{c2}(0)\).

The critical current density \(J_c\) of the MgB\(_2\) sample was determined from the magnetization data by applying the Bean critical state model,[16] according to which \(J_c\) is linearly related to the magnetization \(M\) by a proportionality constant which depends only on the dimensions of the sample being measured. Our triangular sample required the formula \(J_c = 15s\Delta M/A\); where \(s = \frac{1}{2}(a+b+c)\) is the semiperimeter of the triangle; \(\Delta M\) is the width of the magnetization loop; and \(A\) is the area of the triangle.[17] The results from applying this model are shown in the main portion of Figure 4. The value of the critical current density at low temperatures is extremely high, almost an order of magnitude greater than previously reported.[3,10,13] The inset to Figure 4 shows a plot of the critical current density at zero applied field versus temperature. The concavity of the curve seems to indicate a zero-temperature value for \(J_c\) of \(\sim 1.4 \text{ MA/cm}^2\). The rate at which \(J_c\) decreases with increasing field is also much slower compared to previously reported results.

Figure 5 compares the specific heat divided by temperature \(C_p/T\) vs \(T\) curves for both a pressed pellet of as-received Alfa Aesar MgB\(_2\) powder and HIPed MgB\(_2\). The HIPed sample exhibits a sharper superconducting transition as well as a smaller specific heat. The data for the HIPed sample yielded a superconducting transition temperature \(T_c\) of 38.1 K and a specific heat jump \(\Delta C\) of 92 mJ/mol K. These values, as well as the shape of the curve, are comparable to previously published specific heat data.[2,18] Since electrical transport and magnetization data were greatly improved by preparing MgB\(_2\) at high pressures, it appears that polycrystalline MgB\(_2\) simply does not display a sharp superconducting transition in its specific heat. At the present time we are unable to suppress the superconducting transition with a magnetic field in our calorimeter, and so a full comparison with previously published specific
heat data[2,18] will have to await a future publication. However, it should be noted that with the published Debye temperature $\Theta_D$ of $\sim 800$ K, a true fit of the equation $C = \gamma T + \beta T^3$ may not be valid above $\Theta_D/50 \approx 16$ K. This would require specific heat measurements in magnetic fields well above 9 T, which have not yet been carried out.

4 Summary

In summary, we have studied the superconducting properties of fully dense MgB$_2$ bulk specimens prepared using a procedure called DMCUP that is based on HIPing. Our samples displayed very small magnetoresistance in high fields, consistent with other measurements on samples prepared from commercial powder, as well as a narrow superconducting transition width $\Delta T_c$. We also observed large values of the upper critical field $H_{c2}$ and the critical current density $J_c$, and estimated these properties at $T = 0$ K. A comparison of the specific heat between powdered and HIPed MgB$_2$ samples showed only a small improvement in the specific heat jump $\Delta C$, suggesting that it may only be possible to observe a sharp specific heat jump for single crystal specimens of MgB$_2$. The HIPing technique used to prepare the MgB$_2$ sample has great potential as it is easily scaled up for larger samples.

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Fig. 1. Electrical resistivity $\rho$ vs temperature $T$ in several magnetic fields between 0 to 9 T of HIPed Alfa Aesar MgB$_2$. Inset: $\rho$ vs $T$ up to room temperature of HIPed Alfa Aesar MgB$_2$.

Fig. 2. Magnetization $M$ vs magnetic field $H$ of HIPed Alfa Aesar MgB$_2$. Inset: magnetic susceptibility $\chi_{dc}$ vs temperature $T$ of HIPed Alfa Aesar MgB$_2$.

Fig. 3. Critical field $H_{c2}$ and irreversibility field $H_{irr}$ vs temperature $T$ as determined by resistivity and magnetization measurements of HIPed Alfa Aesar MgB$_2$.

Fig. 4. Critical current density $J_c$ as a function of magnetic field $H$ of HIPed Alfa Aesar MgB$_2$. Inset: critical current density $J_c$ as a function of temperature $T$ of HIPed Alfa Aesar MgB$_2$.

Fig. 5. Specific heat divided by temperature $C_p/T$ vs $T$ of powder and HIPed samples of Alfa Aesar MgB$_2$. 

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Fig. 1

The figure shows the resistance ($\rho$) of HIPped Alfa Aesar MgB$_2$ as a function of temperature ($T$) under different magnetic fields ($0$ T, $1$ T, $3$ T, $5$ T, $7$ T, $9$ T). The inset graph provides a magnified view of the resistance behavior at low temperatures.
Fig. 2

HIPed Alfa Aesar MgB\textsubscript{2}

- 10 Oe
- 10 K
- 15 K
- 20 K
- 25 K
- 30 K
Fig. 3
HIPed MgB$_2$

$J_c$ (A/cm$^2$)

$J_c$ (H = 0)

$J_c$ (MA/cm$^2$)

$T$ (K)

$H$ (kOe)

Fig. 4
Fig. 5

Alfa Aesar MgB$_2$

- Pressed pellet
- HIPed