Correlation between the residual resistance ratio and magnetoresistance in MgB$_2$

X. H. Chen, Y. S. Wang, Y. Y. Xue, R. L. Meng, Y. Q. Wang and C. W. Chu$^1$
Department of Physics and Texas Center for Superconductivity, University of Houston, Houston, Texas 77204-5002, USA
$^1$also at Lawrence Berkeley National Laboratory, 1 Cyclotron Road, Berkeley, California 94720; and Hong Kong University of Science and Technology, Hong Kong
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Abstract

The resistivity and magnetoresistance in the normal state for bulk and thin-film MgB$_2$ with different nominal compositions have been studied systematically. These samples show different temperature dependences of normal state resistivity and residual resistance ratios although their superconducting transition temperatures are nearly the same, except for the thin-film sample. The correlation between the residual resistance ratio (RRR) and the power law dependence of the low temperature resistivity, $\rho$ vs. $T^c$, indicates that the electron-phonon interaction is important. It is found that the magnetoresistance (MR) in the normal state scales well with RRR, $a_0$(MR) $\propto$ (RRR)$^{2.2\pm0.1}$ at 50 K. This accounts for the large difference in magnetoresistance reported by various groups, due to different defect scatterings in the samples.
INTRODUCTION

The discovery of superconductivity in MgB$_2$ at temperatures as high as 40 K has attracted considerable interest because of its being a simple inter-metallic binary compound with negligible grain boundary effect and small anisotropy and thus its suitability for device applications. The appearance of superconductivity in MgB$_2$ with such a high transition temperature immediately raises the possibility of even higher superconducting temperatures in conventional metallic binary materials. The underlying mechanism of superconductivity in this system is still an open question. At least two competing models have been proposed to account for the superconducting properties in MgB$_2$ and the high $T_c$ of 40 K. While both models attribute the superconductivity to the boron-sublattice conduction bands, the pairing mechanisms proposed differ significantly. Kortus et al. proposed a well-established phonon-mediated BCS theory, in which the high $T_c$ value is believed to be due to the high phonon frequencies of the light boron atoms and the strong electron-phonon interactions. This mechanism is supported by a number of experiments, such as: isotope effect, a strong negative pressure coefficient of $T_c$, quasi-particle tunneling, specific heat, photoemission spectroscopy, and inelastic neutron scattering. Alternatively, Hirsch proposed a “universal” mechanism in which the superconductivity in MgB$_2$ is driven by the pairing of dressed holes. In fact, an indication of hole-type conduction in the normal phase was found in the positive thermoelectric power. The hole character of carriers was confirmed by Hall measurements.

Soon after the discovery of superconductivity in MgB$_2$, the resistivity and magnetoresistance in the normal state were studied. However, the results reported differ from group to group. The reported resistivity at room temperature ranges from 9.6 to 100 $\mu$Ωcm, and that at 40 K from 0.38 to 21 $\mu$Ωcm. Ames Laboratory reported that the resistivity in the normal state followed $T^3$ behavior and observed a large magnetoresistance, while Jung et al. and Takano et al. claimed that the resistivity in the normal state followed $T^2$ behavior and that the resistance in the normal state did not depend on the external magnetic field. Bud’ko et al. suggested that the clear magnetoresistance might be much harder to detect in the samples with defect scattering. Indeed, the residual resistance ratio, $\text{RRR} = \rho(300 \text{ K}) / \rho(40 \text{ K})$, reported varies with samples. The RRR reported by Ames Laboratory is about 25, much larger than those reported by other groups, typically 2–3, even for epitaxial thin films. It is worth noting that the superconducting transition temperatures of the samples seem to be nearly the same although their properties in the normal state are quite different. To understand the nature of the resistivity and magnetoresistance in the normal state, we report here a systematic study on transport properties and magnetoresistance of bulk and thin-film samples with different nominal compositions. It is found that these samples show almost the same transition temperature except for the thin-film sample, while their temperature- and magnetic-field-dependences of the normal state resistivity, as well as their residual resistance ratios, are very different. We found that the magnetoresistance is closely related to the residual resistance ratio and can be scaled by a simple formula that can be understood in terms of a reduction of the effective mean-free path of the carrier in the presence of a magnetic field.
EXPERIMENT

The polycrystalline MgB$_2$ samples studied were prepared by a solid-state reaction method. Small Mg chips (99.8% pure) and boron powder (99.7% pure) with stoichiometries of Mg:B=1:2, 1.25:2, and 1.5:2 were sealed inside Ta tubes in an Ar atmosphere. Each sealed Ta ampoule was in turn enclosed in a quartz tube. The ingredients were heated slowly up to 950 °C and kept at this temperature for 2 hr, followed by furnace-cooling to room temperature. The samples so-prepared were granular and porous and were used for measurements without further treatment. The thin-film boron was prepared by sputtering. The thin-film MgB$_2$ was synthesized by exposing thin-film boron to Mg vapor at 700 °C for adequate exposure time. Given that MgB$_2$ is the most Mg-rich binary Mg-B compound known, it was felt that excess Mg would aid in the formation of the proper, stoichiometric phase. It should be pointed out that most MgB$_2$ samples were synthesized with a stoichiometric starting composition. However, noticeable amounts of MgO and/or Mg are either frozen inside the samples or deposited on the walls of the sample containers. Thus, the true Mg composition is certainly not the starting composition. Oxygen contamination has also been widely discussed, particularly in terms of the $T_c$ degradation of MgB$_2$ films.[8] This could be why the thin film has a very small RRR. The structure was determined by powder X-ray diffraction, using a Rigaku DMAX-IIIB diffractometer. The resistivity was measured using the standard four-probe technique. The isothermal mangetoresistance was measured using a SQUID magnetometer (Quantum Design). The magnetic field was applied perpendicular to the measuring current direction. The transverse magnetoresistance in the normal state was measured.

RESULTS AND DISCUSSION

The powder X-ray diffraction (XRD) patterns of the samples show the hexagonal MgB$_2$ phase, but with a minor amount of MgO as an impurity. It is worth pointing out that no metal Mg is observed in the XRD pattern for any sample, including those with excess Mg as starting material. Figure[4] shows the temperature dependence of resistivity for all samples. For the bulk samples, the superconducting transition temperature ($T_c$) is 38.3–39.3 K; $T_c$ of the thin-film sample is 25 K. The residual resistance ratios (RRR) of these samples are different, and the RRR is 3.03, 2.65, and 8.3 for the samples with the nominal composition Mg:B=1:2, 1.25:2, and 1.5:2, respectively; it is only 1.16 for the thin-film sample. The resistivity values at room temperature are 14, 88, and 49 $\mu\Omega$cm, respectively; and 188 $\mu\Omega$cm for the thin film. It has been reported that the temperature dependence of resistivity follows the $a + bT^3$ form reported for the polycrystalline MgB$_2$ with a RRR of 25,[8] while Jung et al. claimed that the temperature dependence of resistivity follows $a + bT^2$ for the high pressure sample with a RRR of 2.4.[4] To investigate the resistivity behavior, the temperature dependence of resistivity in the normal state for all samples has been fitted by a formula $a + bT^c$, where $a$, $b$, and $c$ are fitting parameters. The solid lines in Fig. [4] are the fitting curves by $a + bT^c$. The experimental data could be fitted very well. These parameters are listed in Table 1. The superconducting transition temperature and width also show a systematic change, but their change is very small, especially for $T_c$. 

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From Table 1, RRR increases with increasing $x$. The fitting parameter $c$ also increases as $x$ increases, and is between 2.17 and 2.64, depending on the sample. These results indicate that the RRR and the fitting parameter $c$ are closely related to the nominal Mg content. The value of $c$ increases with RRR. This result is understandable from the empirical studies of conventional superconductors. Gurvitch has done exhaustive studies on how the power law of $\rho$ vs. $T$ depends on RRR or the residual resistivity. The power law behavior in low temperature resistivity changes from $T^n$ ($n=3$–$5$) for very clean samples to $T^2$ as disorder increases; the dirty superconductors reach a limit $n=2$. Such a transition only takes place in moderate- and strong-coupled superconductors. An example of this effect is found in superconducting VN, which can be prepared with a wide variation in disorder, while $T_c$ remains nearly constant and is quite insensitive to even large amounts of disorder, similar to MgB$_2$. For the well-ordered, stoichiometric VN film, the value of RRR is 8.4 ($\rho_0 = 5.0$ $\mu\Omega$cm); while the RRR value drops to 1.14 ($\rho_0=63$ $\mu\Omega$cm) for the same sample damaged by radiation. The low temperature-dependent resistivity $\rho(T)$ from 10 to 30 K was fit to a function of the form $\rho_0 + AT^n$. The fitting parameter $n$ is 4 and 2.25 for the clean and dirty (damaged) films, respectively. This is very similar to that observed in MgB$_2$ and explains why the different temperature-dependent resistivity is observed in MgB$_2$, as discussed in the introduction. In order to compare with superconducting VN, the low temperature resistivity $\rho(T)$ from 40 to 100 K is very well fit with the function of the form $a_1 + b_1 T^{c_1}$ for all samples. It should be pointed out that the fitting cannot be convergent for thin-film samples. Thus, the $c_1$ is missing in Table 1. The results of the present study on MgB$_2$ are consistent with the above, which might be another indication that electron-phonon interaction is important. In addition, the increased RRR and $c_1$ with excess Mg suggests that the disorder was induced by Mg loss in the sample processing, and excess Mg is needed to obtain more stoichiometric samples. In fact, high quality MgB$_2$ wire was produced with much excess Mg of a nominal ratio of Mg$_2$B. The disorder could arise from the Mg deficiency, which causes the scattering. In addition, the high pressure study on MgB$_2$ has suggested the existence of Mg non-stoichiometry.

Figure 2a shows the isothermal transverse MR at 50 K for all samples. It is found that the MR is always positive, and varies with field in a similar fashion. It is interesting to note that the value of magnetoresistance increases monotonously with increasing residual resistance ratio. This accounts for the huge MR observed by Ames Laboratory, while others observed almost zero MR; the Ames sample had a comparatively large RRR. It is customary to analyze the classical orbital MR using the Kohler plot. The motivation is that, in conventional metals, the coefficient of the $B^2$ term is proportional to the transport scattering time $\tau_{tr}(T)$. Since $\rho$ is proportional to $1/\tau_{tr}(T)$, a slope of $\Delta\rho/\rho_0$ vs. $(H/\rho)^2$ should fall on a straight line with a slope that is independent of $T$. The same data in Fig. 2a are plotted on a Kohler plot shown in Fig. 2b. It is found that the $\Delta\rho/\rho_0$ vs. $H$ curve is a straight line at constant temperature for all samples. The slope of $\alpha$ is between 1.6 and 2. It suggests that the magnetic field dependence of magnetoresistance follows $\Delta\rho(H)/\rho(0) \propto H^\alpha$ with $\alpha=1.6$–2, which is nearly the same as $\alpha$ predicted by Kohler’s rule. Figure 2c shows a Kohler plot of magnetoresistance at 100 K and 50 K for the sample with nominal composition Mg$_{1.3}$B$_2$. It is found that the data fall on the single curve, independent of temperature. These results suggest that there exists a single salient scattering time in the normal state transport of MgB$_2$. It should be pointed out that all samples with different nominal composition follow
the Kohler’s rule although the RRR is different. It implies that the normal state behavior of the samples with different nominal composition arises from the crystal grain rather than the grain boundary. Although the temperature dependence of the resistivity for a ceramic sample often depends on its porosity and inter-grain coupling, the large variation of RRR suggests intrinsic differences in samples.

In order to clarify the differences in MR of samples with different RRR, we plot the magnetoresistance at 50 K and under magnetic field of 5 Tesla vs. RRR, as shown in Fig. 3. It is found that the MR increases monotonously with increasing RRR. The data fit very well the relation \(0.04(\text{RRR})^{2.2\pm0.1}\) as shown in Fig. 3. It implies that the MR could be scaled by the residual resistance ratio. From our results, the magnetoresistance for the sample with RRR of 2–3 is only 0.2–0.5%, while about 5% for the sample with RRR of 8.3. For the sample with RRR of 25–26 a MR of about 50% at 50 K and under 5 Tesla could be obtained from the formula above, consistent with that reported by Ames Laboratory. Our results provide an explanation for the huge difference in magnetoresistance observed in MgB\(_2\) by various groups. In fact, this behavior is understandable. It has been pointed out that the magnetic field dependence of isothermal magnetoresistance follows the Kohler’s rule \(\Delta \rho/\rho_0 = \text{const.} [H/\rho(0)]^2\). In a metal, the \(\rho(0) \propto 1/l\) and \(l\) is the mean-free path, so that \(\Delta \rho/\rho_0 \propto (Hl)^2\). The RRR is proportional to the mean free path \(l\) at low temperature, so that \(\Delta \rho/\rho_0 \propto \text{RRR}^2\), which is in agreement with our observation. It further suggests that the magnetoresistance behavior arises from the crystal grain rather than the grain boundary. The different results for the magnetoresistance reported previously are thus attributed to the different mean-free paths due to defect scattering in grains. A significant sample-dependent defect scattering is expected. The differences in the RRR, the temperature dependence of resistivity in the normal state, and magnetoresistance for different samples have been previously attributed to either the pressure or the thermal history used during the synthesis. However, the fact that similar low RRR and negligible magnetoresistance have been observed in samples synthesized under both ambient and high pressure challenges these interpretations. The differences of resistivity and magnetoresistance observed in this paper arise only from the content of Mg in the samples, suggesting that the defect scattering comes from the Mg deficiency in the sample. In fact, Cooper et al. proposed in 1970 that boron in borides AB\(_2\) might be nonstoichiometric. In addition, Xue et al. observed a correlation between the Mg loss and XRD data as evidence for Mg deficiency.

**CONCLUSION**

The resistivity and magnetoresistance in the normal state have been investigated for samples with different RRR. The magnitude of magnetoresistance is found to vary with the residual resistance ratio, \(a_0(\text{MR})=0.04(\text{RRR})^{2.2\pm0.1}\). Although the transport properties of the samples are different, their superconducting transition temperatures are nearly the same. The magnetoresistance behavior follows the Kohler’s rule. The different MR’s and RRR’s reported previously arise from defects in grain rather than the bound boundary, due to Mg deficiency. It is found that the correlation between power law dependence of the low temperature resistivity (\(\rho\ vs. \ T^c\)) and the RRR is the same as that observed in the strongly coupled superconductor VN. Therefore, it is understandable that the \(\rho(T)\) behavior with different \(c\) is observed in different groups, arising from the disorder (Mg deficiency) in
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TABLES

TABLE I. Zero-resistance temperature ($T_c$), transition width (TW), RRR of the samples, and the fitting parameter $c$ of $a + bT^c$ to the temperature dependence of resistivity in the normal state.

| sample      | $T_c$ (K) | TW (K) | RRR  | $c$  | $c_1$ |
|-------------|-----------|--------|------|------|-------|
| MgB$_2$     | 38.3      | 0.8    | 3.03 | 2.17 | 2.87  |
| Mg$_{1.25}$B$_2$ | 38.8  | 0.2    | 2.65 | 2.27 | 3.05  |
| Mg$_{1.5}$B$_2$ | 39.3 | 0.08   | 8.30 | 2.43 | 3.41  |
| thin film   | 25        | 2.3    | 1.16 | 2.64 | -     |
FIGURES

FIG. 1. The temperature dependence of the normalized resistivity for bulk and thin-film samples with nominal composition Mg$_x$B$_2$ ($x$=1, 1.25, and 1.5). The solid lines are the fitting results of the formula $a + bT^c$ to experimental data.

FIG. 2. (a): The magnetic field dependence of isothermal magnetoresistance at 50 K for samples with nominal composition Mg$_x$B$_2$ ($x$=1, 1.25, and 1.5) and thin film; (b): Kohler’s plot for the same data as Fig. 2a; the straight line is a guide line; (c): Kohler’s plot for isothermal magnetoresistance at 50 and 100 K for the sample with nominal composition Mg$_{1.5}$B$_2$; the straight line is a guide line.

FIG. 3. The residual resistance ratio dependence of magnetoresistance at 50 K and under 5 Tesla; the solid line is a fitting curve of $0.04(RRR)^{2.2\pm0.1}$ to experimental data.
Figure 1

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Figure 2a

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Figure 2b
Figure 2c

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Figure 3

\[ \frac{\Delta \rho}{\rho_0} (\%) \]

50 K and 5 Tesla

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