Effects of unreacted Mg impurities on the transport properties of MgB$_2$

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We synthesized polycrystalline MgB$_2$ from a stoichiometric mixture of Mg and the $^{11}$B isotope under different conditions. All the samples showed bulk superconductivity with $T_c = 38 \sim 39$ K. The samples containing the least amount of unreacted Mg showed the highest $T_c$ and the sharpest transition width ($\Delta T_c$). A residual resistivity ratio (RRR) of $\sim 5.8$, and a magnetoresistance (MR), at 40 K, of 12% were obtained for these samples. Moreover, there was no upturn of resistivity in a low temperature region at 10 Tesla. The samples containing appreciable amounts of unreacted Mg showed quite different behaviors; the values of $\Delta T_c$, RRR, and MR were much larger. An upturn appeared in resistivity of the samples below about 50 K at 10 T and is thought to be due to the unreacted Mg.

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The recent discovery of the binary metallic MgB$_2$ superconductor has attracted great scientific and industrial interest. Even though basic issues, such as the isotope effect and the determination of the carrier type, were addressed immediately, there still exist conflicting results. For example, several groups have measured the transport properties of their polycrystalline MgB$_2$ and have reported different values for the residual resistivity ratio (RRR), magnetoresistance (MR), residual resistivity. The widely accepted opinion was that good bulk samples of MgB$_2$ (called ‘highRRR-MgB$_2$’) should have higher values of the RRR (20 \sim 25) with low residual resistivity ($\rho(40 \text{ K}) = 0.38 - 1 \mu\Omega\text{cm}$) and higher MR with a resistivity upturn at low temperature under high magnetic field. Insulating impurities and/or local strains were thought to be the causes of any behaviors different from the above highRRR-MgB$_2$. However, recent reports on all single crystals and many polycrystals have shown a RRR value of about 5. Moreover, the residual resistivity of single crystals ($\rho_{ab}(40 \text{ K}) = 1 - 2 \mu\Omega\text{cm}$) was higher than that of ‘highRRR-MgB$_2$‘. Thus, it has become an urgent matter to clarify the origin of the different reports on polycrystalline MgB$_2$.

Here, we report the transport properties of MgB$_2$ prepared under different conditions. For samples containing the least amount of unreacted Mg, we found $T_c \approx 39.2 \text{ K}$, $\Delta T_c = 0.3 - 0.5 \text{ K}$, RRR $\sim 5.8$, and MR$_{5T} \sim 3\%$. The last three values are very similar to those reported for single crystals. For the samples containing a relatively large amount of unreacted Mg, the values for $\Delta T_c$, RRR, and MR, were considerably larger. These higher values of RRR and MR are similar to those in ‘highRRR-MgB$_2$’. $T_c$ for these samples was about 38 K.

A Ta capsule containing a stoichiometric mixture of Mg chunks and the $^{11}$B isotope was heated up to 950-1000°C with $3\%$ under different pressure (3 GPa in a 12-mm cubic multi-anvil-type press). The maximum heating temperature (850 \sim 1000°C) and the preparation of the precursors were varied to obtain different samples. One batch, A-MgB$_2$, was heated at 950 \sim 1000°C after enough grinding of the precursors. For B-MgB$_2$ and C-MgB$_2$, the heating temperatures were about 900°C and 850°C respectively, and the precursors were ground less. Details of the high pressure synthesis have been reported previously. The pellet density was 2.48 \sim 2.6 g/cm$^3$ which is quite close to the crystallographic density, a common feature in high-pressure synthesis. As a result, grain connectivity was prevalent over the entire sample (\sim 1 mm).

A dc SQUID magnetometer (Quantum Design, MPMSXL), a field-emission scanning electron microscope (SEM), an optical microscope, and an X-ray diffractometer were used for this investigation. The re-

FIG. 1: Normalized magnetization of MgB$_2$ measured at 20 Oe. The solid line, the dashed, and the dotted lines are for A-MgB$_2$, B-MgB$_2$, and C-MgB$_2$, respectively. $T_c$ was 38 \sim 39 K and $\Delta T_c$ was 0.5, 3.5, and 4.5 K, respectively. The inset shows the magnetic hysteresis curve, $M(H)$, of a piece of A-MgB$_2$ (m \sim 78 mg) measured at 5 K and 30 K.
FIG. 2: SEM images of A-MgB$_2$ and C-MgB$_2$ at the same magnification with scale bar 50 µm in length: (a) well connected grains in A-MgB$_2$, (b) Unreacted Mg in C-MgB$_2$, as large as several tens of µm, are shown as dark islands. For example, see an island under caption of ‘C-MgB2’.

Resistance, $\rho(T, H)$, was measured by using a standard 4-probe technique on a bar shaped specimen ($\sim 0.5 \times 1 \times 4$ mm$^3$).

Figure 1 shows the normalized magnetization curves $M(T)$ measured at 20 Oe in the zero-field cooled mode for A-MgB$_2$, B-MgB$_2$, and C-MgB$_2$. All samples showed $M/H \gtrsim 150\%$ of $-1/4\pi$, as previously observed. The $T_c$ of A-MgB$_2$ was about 39 K, and its $\Delta T_c$ was 0.3 K, the RRR = 5.8 and the values of the MR at 40 K were 3% and 12% at 5 and 10 Tesla for A-MgB$_2$. For B-MgB$_2$, RRR = 9.9, and the values of the MR at 40 K were 49% and 111%. For C-MgB$_2$, RRR = 13.7 and the values of the MR at 40 K were 100% and 224%. The inset in Fig. 1 shows the magnetic hysteresis curves $M(H)$ for A-MgB$_2$ at 5 K and 30 K; a very clear flux jumping behavior was observed at 5 K. This kind of flux jump has also been reported for commercial MgB$_2$ (HIP-Alfa) after sintering under 3 GPa. Details of this result will be reported elsewhere.

To search for the origin of the above difference in $M(T)$, we investigated images of cleaved or polished surfaces by using a SEM and an optical microscope. The SEM image for A-MgB$_2$ in Fig. 2(a) shows well-connected grains, with no clear grain boundaries, over a very wide region. However, unreacted Mg was easily identified for C-MgB$_2$, as shown in Fig. 2(b). The dark islands, as large as several tens of µm, in Fig. 2(b) were identified to be unreacted Mg by a clear Mg peak at 1.25 keV in the energy dispersive spectrum (EDS) in the inset of Fig. 2(b). For example, see an island under caption of ‘C-MgB2’. Another evidence is that strong Mg peak in XRD pattern such as one near $2\theta \sim 37^\circ$ reported previously was also observed for C-MgB$_2$. Unreacted Mg grains were also found in B-MgB$_2$, but were nearly absent in A-MgB$_2$. The unreacted Mg grains in C-MgB$_2$ were bigger and had denser population than those in B-MgB$_2$. The unreacted Mg showed a characteristic white tint when viewed through the optical microscope. All these shows that the basic superconducting parameters $T_c$ and $\Delta T_c$ were degraded as the amount of unreacted Mg is increased. For C-MgB$_2$, insulating MgO impurity was also identified by a clear O peak at 0.52 keV in EDS and was shown as white dots in Fig. 2(b).

To further investigate the effect of unreacted Mg, we measured resistivity under a magnetic field. Figure 3 shows $\rho(T)$ at 0, 5, and 10 T. A-MgB$_2$ shows the highest $T_c$, $\sim 39$ K, and the smallest $\Delta T_c$, $\sim 0.3$ K. The values of the zero-field resistivity for A-MgB$_2$ at 40 K and 300 K
were 5.13 and 30.0 $\mu\Omega$cm, respectively. A RRR value of $\sim 5.8$ and a MR of 3\%(12\%) at 5(10) T were also observed. The RRR for all stoichiometric samples prepared under similar conditions had values from $\sim 4.5$ to $\sim 6$. The values of RRR and MR$_{57}$ were similar to those recently reported for single crystals[5] and polycrystals[6].

While $\rho(300)$ K was not much different, the $\rho(40)$ K of 2.11(1.29) $\mu$Omega cm for B-MgB$_2$ (C-MgB$_2$) was much smaller than that of A-MgB$_2$, giving a larger value of RRR = 9.9(13.7). Also, the MR$_{57}$ increased drastically up to 49\% and 100\%, as shown in Fig. 3(b) and Fig. 3(c). At a higher field of 10 T, MR$_{10}$T reached values as large as 111\%(224\%) for B-MgB$_2$(C-MgB$_2$). Another interesting observation is the peculiar resistivity upturn below 50 K for C-MgB$_2$ at 10 T. A similar upturn had been reported previously for high RRR-MgB$_2$[7].

Now let’s turn our attention to the resistivity behavior of Mg itself. Figure 3(d) shows the resistivity of a pressed bar of a commercial Mg block (Alfa Aesar #43355) measured at 0, 5, and 10 T. The observed temperature dependence of $\rho(T, H = 0)$ with very high RRR values is consistent with that reported in the literature[4] for pure Mg except for the slightly higher value of 0.12 $\mu$Omega cm at 40 K. The resistivity of Mg under an applied magnetic field shows several interesting features, especially at lower temperatures, such as high MR values and a large resistivity upturn below 50 K. The MR at 5(10) T is more than 400\%(1300\%) at 40 K, and the resistivity upturn became more pronounced at higher fields. Because $\rho(T)$ of Mg is much smaller than $\rho(T)$ of stoichiometric A-MgB$_2$ in the region of $T > T_c$ and $H < 10$ T, $\rho(T, H)$ of MgB$_2$ containing unreacted Mg will have some of the character of Mg. The unreacted Mg in MgB$_2$ will decrease the resistivity at 40 K more than it will at 300 K, as observed in Figs. 3(b) and 3(c), so the resulting increase in the RRR should be accompanied by an increase in the MR. Moreover, the Mg in C-MgB$_2$ also explains the resistivity upturn below 50 K at 10 T.

Incomplete reaction of polycrystalline MgB$_2$ due to either unoptimized growth conditions or a Mg-rich precursor may result in unreacted Mg. Unlike the insulting oxide impurities in high-$T_c$ cuprates, unreacted conducting Mg may not be so detrimental in bulk transport applications of MgB$_2$, especially for the case of quenching of the superconductivity. However, if a correct understanding of the intrinsic properties of MgB$_2$ such as resistivity, which can be screened by the unreacted conducting Mg impurities, is to be obtained, then phase-pure MgB$_2$ is essential.

In conclusion, we synthesized MgB$_2$ and investigated systematically the effect of unreacted Mg in the MgB$_2$ on its transport properties. For the stoichiometric MgB$_2$, RRR was $\sim 5.8$, and MR$_{57}$ was $\sim 3\%$. We found that the larger transition width and the higher values of the RRR and the MR were due to the unreacted Mg in the MgB$_2$. The appearance of peculiar resistivity upturn at a lower temperatures at higher field of 10 T was also explained as being due to the unreacted Mg in the MgB$_2$ materials. This conclusion is also supported by the results for single crystals of MgB$_2$.

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7 P. Seneor, C. -T. Chen, N.-C. Yeh, R.P. Vasquez, L.D. Bell, C. U. Jung, Min-Seok Park, Hoon-Jung Kim, W. N. Kang, and Sung-Ik Lee, Phys. Rev. B 65, 12505 (2002).
8 R. P. Vasquez, C. U. Jung, Min-Seok Park, Hoon-Jung Kim, J. Y. Kim, and Sung-Ik Lee, Phys. Rev. B 64, 52510 (2001).
9 W. N. Kang, Hyeong-Jin Kim, Eun-Mi Choi, C. U. Jung, and Sung-Ik Lee, Science 292, 1521 (2001).
10 C. U. Jung, Min-Seok Park, W. N. Kang, Mun-Seog Kim, S. Y. Lee, and Sung-Ik Lee, Physica C 353, 162 (2001).
11 X. H. Chen, Y. S. Wang, Y. Y. Xue, R. L. Meng, Y. Q. Wang, and C. W. Chu, Phys. Rev. B 65, 24502 (2002).
12 Y. Zhu, L. Wu, V. Volkov, Q. Li, G. Gu, A. R. Moodenaugh, M. Malac, M. Suenaga, and J. Tranquada, Physica C 356, 239 (2001).
13 N. A. Frederick, S. Li, M. B. Maple, V. F. Nesterenko, and S. S. Indrakanti, Physica C 363, 1 (2001).
14 S. S. Indrakanti, V. F. Nesterenko, M. B. Maple, N. A. Frederick, W. M. Yuhasz, and Shi Li, Phil. Mag. Lett. 81, 849 (2001).
15 G. Fuchs, K. -H. Müller, A. Handstein, K. Nenkov, V. N.

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1 Jun Nagamatsu, N. Nakagawa, T. Muranaka, Y. Zenitani, and J. Akimitsu, Nature 410, 63 (2001).
2 P. C. Canfield, D. K. Finnemore, S. L. Bud’ko, J. E. Ostenson, G. Lapertot, C. E. Cunningham, and C. Petrovic, Phys. Rev. Lett. 86, 2423 (2001).
3 S. L. Bud’ko, G. Lapertot, C. Petrovic, C. E. Cunningham, N. Anderson, and P. C. Canfield, Phys. Rev. Lett. 86, 1877 (2001).
4 W. N. Kang, C. U. Jung, Kijoong H. P. Kim, Min-Seok Park, S. Y. Lee, Hyeong-Jin Kim, Eun-Mi Choi, Kyung Hee Kim, Mun-Seog Kim, and Sung-Ik Lee, Appl. Phys. Lett. 79, 982 (2001).
5 S. L. Bud’ko, C. Petrovic, G. Lapertot, C. E. Cunningham, P. C. Canfield, M-H. Jung, and A. H. Lacerda, Phys. Rev. B 63, 220503 (2001).
6 D. K. Finnemore, J. E. Ostenson, S. L. Bud’ko, G. Lapertot, and P. C. Canfield, Phys. Rev. Lett. 86, 2420 (2001).
Narozhnyi, D. Eckert, M. Wolf, and L. Schultz, Solid State Commun. 118, 497 (2001).

16 R. F. Klie, J. C. Idrobo, N. D. Browning, K. A. Regan, N. S. Rogado, and R. J. Cava, Appl. Phys. Lett. 79, 1837 (2001).

17 A. Serquis, Y. T. Zhu, E. J. Peterson, J. Y. Coulter, D. E. Peterson, and F. M. Mueller, Appl. Phys. Lett. 79, 4399 (2001).

18 Kijoon H. P. Kim, Jae-Hyuk Choi, C. U. Jung, P. Chowdhury, Min-Seok Park, Heon-Jung Kim, J. Y. Kim, Zhongliang Du, Eun-Mi Choi, Mun-Seog Kim, W. N. Kang, Sung-Ik Lee, Gun Yong Sung, and Jeong Yong Lee, Phys. Rev. B 65, 100510 (2002), C. U. Jung et al., cond-mat/0203123 (2002).

19 S. Lee, H. Mori, T. Masui, Yu. Eltsev, A. Yamamoto, and S. Tajima, J. Phys. Soc. Jpn. 70, 2255 (2001).

20 M. Xu, H. Kitazawa, Y. Takano, J. Ye, K. Nishida, H. Abe, A. Matsushita, N. Tsuji, and G. Kido, Appl. Phys. Lett. 79, 2779 (2001).

21 A.V. Sologubenko, J. Jun, S. M. Kazakov, J. Karpinski, and H.R. Ott, cond-mat/0111272 (2001).

22 S.-W. Cheong, APCTP Miniworkshop on new superconductors, POSTECH, Korea, July 7 - 9, 2001.

23 C. U. Jung, Min-Seok Park, W. N. Kang, Mun-Seog Kim, Kijoon H. P. Kim, S. Y. Lee, and Sung-Ik Lee, Appl. Phys. Lett. 78, 4157 (2001).

24 C. U. Jung, J. Y. Kim, Min-Seok Park, Heon-Jung Kim, Mun-Seog Kim, and Sung-Ik Lee, 65, 172501 (2002).

25 C. U. Jung, J. Y. Kim, Min-Seok Park, Kyung Hee Kim, and Sung-Ik Lee, (unpublished) (2002).

26 Y. Takano, H. Takeya, H. Fuji, H. Kumakura, T. Hatano, K. Togano, H. Kito, and H. Ihara, Appl. Phys. Lett. 78, 2914(2001).

27 The $T_c$ of B-MgB$_2$ and C-MgB$_2$ seem to be a little bit lower than that of A-MgB$_2$, which seems to invoke some intragranular origin. As suggested in a previous report(Ref. 11), the unreacted Mg may cause local off-stoichiometry, resulting in a micro-strain.

28 Mun-Seog Kim, C. U. Jung, Min-Seok Park, S. Y. Lee, Kijoon H. P. Kim, W. N. Kang, and Sung-Ik Lee, Phys. Rev. B 64, 12511 (2001).

29 Mun-Seog Kim et al., (unpublished).

30 Even though the in-plane resistivity of a single crystal has not been determined accurately($\rho(40 \text{ K}) = 1 - 2 \mu\Omega\text{cm}$ in Ref. 19 and Ref. 21.), the comparison of the RRR with that of our polycrystalline sample($\rho(40 \text{ K}) \sim 5 \mu\Omega\text{cm}$) is reasonable if the in-plane resistivity is more conductive than the c-axis resistivity of MgB$_2$, which has been generally assumed to be the case due to its layered structure. If the driving current flows main along the ab-plane of each grains, the effective area will be reduced and the effective length will be increased. All these can account for the factor of difference of about 3. However, more rigorous study of the c-axis resistivity, as well as the in-plane resistivity, seems to be necessary for a clear comparison.

31 CRC Handbook of Chemistry and Physics 74th ed., 1993-1994, pp 12-32.

32 Unreacted Mg was also observed in a previous work on high$RRR$-MgB$_2$. See the text, ‘a surface Mg layer left during synthesis’ by R. Prozorov, R. W. Giannetta, S. L. Bud’ko, and P. C. Canfield, Phys. Rev. B 64, 180501 (2001).