Significant enhancement of irreversibility field in clean-limit bulk MgB_2

V. Braccini
Applied Superconductivity Center, University of Wisconsin, 1500 Engineering Drive, Madison, Wisconsin 53706 and I.N.F.M.-LAMIA, Dipartimento di Fisica, Via Dodecaneso 33, 16146 Genova, Italy

L. D. Cooley, S. Patnaik, and D. C. Larbalestier[a)]
Applied Superconductivity Center, University of Wisconsin, 1500 Engineering Drive, Madison, Wisconsin 53706

P. Manfrinetti and A. Palenzona
I.N.F.M.-LAMIA, Dipartimento di Chimica e Chimica Industriale, Via Dodecaneso 31, 16146 Genova, Italy

A. S. Siri
I.N.F.M.-LAMIA, Dipartimento di Fisica, Via Dodecaneso 33, 16146 Genova, Italy

(Received 16 August 2002; accepted 17 October 2002)

Low resistivity MgB_2 bulk samples annealed in Mg vapor show an increase in irreversibility field $\mu_0 H^*(T)$ by a factor of ~ 2 in both transport and magnetic measurements. The best sample displayed a magnetic irreversibility field $\mu_0 H_M^* > 14$ T at 4.2 K and ~ 6 T at 20 K. These changes were accompanied by an increase of the 40 K resistivity from 1 to 18 $\mu\Omega$ cm and a lowering of the resistivity ratio from 15 to 3, while the critical temperature T_c decreased by only 1–2 K. These results show that systematic processing changes can make MgB_2 attractive for magnet applications.
 [DOI: 10.1063/1.1528289]

A major obstacle to applying MgB_2 superconductors in magnets is their rather low value of irreversibility field $\mu_0 H^*(T)$. Typical $\mu_0 H^*$ values for bulk samples, ~ 4 T at 20 K and ~ 7 T at 4.2 K, lie well below those for Nb 47 wt. % Ti (10.5 T at 4.2 K) and $(Nb,Ta)_3Sn$ (~ 25 T at 4.2 K), the present materials used to make high field superconducting magnets. Irreversibility fields of ~ 4 T at 20 K are marginal for magnet use, because high values of the critical current density J_c occur only below $\sim 0.6 H^*(T)$. On the other hand, some thin films of MgB_2 have $\mu_0 H^*(4.2\ \mathrm{K})$ values approaching 20 T in perpendicular field and 40 T in parallel field.[1] Such films have very high resistivity at T_c, 400 $\mu\Omega$ cm, as compared to clean-limit bulk samples, 1 $\mu\Omega$ cm or less.[2,3] This suggests that films can be driven to dirty-limit superconductivity, for which the zero temperature upper critical field $\mu_0 H_{c2}(0)$ is

$$\mu_0 H_{c2}(0) = 3110 \rho \gamma T_c \ \text{tesla}, \tag{1}$$

and where $\mu_0 H^*(T)$ is approximately 85% of $\mu_0 H_{c2}(T)$.[1] The very high normal state resistivity just above T_c, $\rho(40\ \mathrm{K})$ for MgB_2, of many films strongly enhances $\mu_0 H^*$, even if the Sommerfeld coefficient γ and the critical temperature T_c are reduced somewhat. However, a simple application of this formula is problematic, in that lack of texture, porosity, and second phases can all interrupt the current path. Resistivity comparisons are then uncertain by a factor of ~ 2, making it unclear how different fabrication procedures change the actual intragrain scattering length, which is what really determines $\mu_0 H_{c2}$. Thus, a central question for MgB_2, whether significant electron scattering can be developed in bulk specimens to meet or exceed $\mu_0 H_{c2}$ values found in thin films, is still quite unclear.

Previous experiments have found that irradiation,[4,5] high energy ball milling,[6] and mechanical crushing during wire drawing or tape rolling,[7–9] all raise $\mu_0 H^*$, although crystallographic texture is sometimes a complicating factor. Samples prepared from prereacted MgB_2 have $\rho(40\ \mathrm{K})$ typically >50 $\mu\Omega$ cm, while samples made from direct reaction of Mg and B can reach values as low as 0.4-1 $\mu\Omega$ cm.[3,4] In this letter, we show that it is possible to double the irreversibility field by annealing low resistivity, bulk MgB_2 in Mg vapor, while T_c is only slightly reduced. $\rho(40\ \mathrm{K})$ also increases from 1.0 to 18 $\mu\Omega$ cm, while the resistivity ratio decreases from ~ 15 to ~ 3. These results point to a simple means of making MgB_2 much more suitable for magnet applications.

A low resistivity control sample (sample A) was prepared using a similar technique[10] as earlier works,[2,11] from isotopically 99.5% enriched crystalline ^{11}B (-325 mesh, Eagle-Picher) and pure Mg. A stoichiometric mixture was put in a Ta crucible, welded under argon, sealed in a quartz tube under vacuum, then reacted at 950 °C for 24 h, and quenched to room temperature. X-ray and neutron diffraction detected only peaks from MgB_2, without any indication of Mg, MgO, or MgB_4. Condensed Mg was evident on the top of the Ta crucible after the quench and a Rietveld refinement performed on neutron diffraction spectra showed an overall composition of $Mg_{0.83}B_{2.0}$.[12] These observations provoked us to make two additional samples (B and C) by annealing pieces of sample A in Mg vapor, although others do not support the idea of such a large nonstoichiometry.[13] Samples B and C were separately sealed with Mg flakes in an evacuated Nb tube, the Nb crucible being sealed in evacuated quartz. To avoid contact between liquid Mg and MgB_2, the Mg was isolated behind partial crimps. Heat treatment took place in a horizontal furnace at 960 °C for 10 h. Sample B was slow cooled (10 h from 960 °C to room temperature)

a)Electronic mail: larbales@engr.wisc.edu

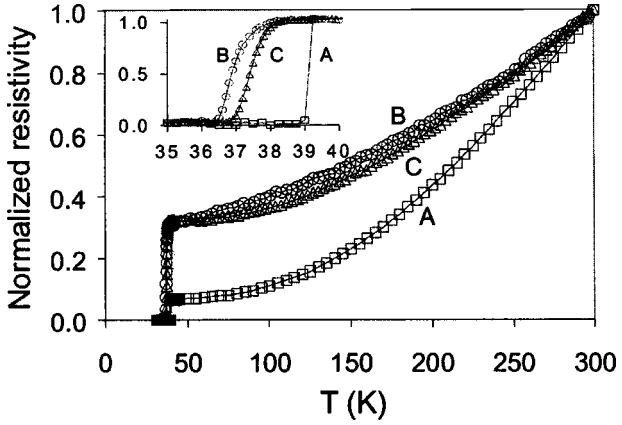

FIG. 1. Resistivity normalized to $\rho(300\ \mathrm{K})$ vs temperature for sample A (squares), sample B (circles), sample C (triangles). The inset shows the transitions near T_c normalized to $\rho(40\ \mathrm{K})$.

while C was quenched. Only the slow cooled sample had detectable free Mg from x-ray patterns, but neither MgO nor MgB_4 were detected in B or C; the lattice parameters of samples A, B, and C were 3.0850(4) Å, 3.0768(4) Å, and 3.0800(4) Å for *a* and 3.5212(8) Å, 3.5249(8) Å and 3.5252(8) Å for *c*. Neither x-ray diffraction nor subsequent transmission electron microscopy showed any direct evidence of texture in the three samples.

To define the geometry for transport and magnetization experiments, bars $5.0\times1.5\times0.3\ \mathrm{mm}^3$ were made by grinding parallel faces with a tripod polisher. AC electrical resistance measurements were made at a current density of $\sim1\ \mathrm{A/cm}^2$ in a 9 T Quantum Design physical property measurement system (PPMS), while an Oxford 14 T vibrating sample magnetometer (VSM) and a Quantum Design superconducting quantum interference device magnetometer were used for magnetization and inductive T_c measurements.

Sample A exhibits superconducting and normal state properties similar to those reported for other clean limit bulk samples,[3] as indicated by its resistivity ratio $RR=\rho(300)/\rho(40)\approx14.7$ and $\rho(40\ \mathrm{K})=1.0\ \mu\Omega\,\mathrm{cm}$ (Fig. 1). The T_c (Fig. 1 inset) is very narrow ($\Delta T_c=0.2$ K), with a midpoint at 39.0 K. Samples B and C exhibit a small reduction in midpoint T_c to 36.9 and 37.4 K and a decrease in *RR* to 3, as is also shown in Fig. 1. Their $\rho(40\ \mathrm{K})$ values are much higher: 18 $\mu\Omega\,\mathrm{cm}$ (B) and 14 $\mu\Omega\,\mathrm{cm}$ (C).

In-field resistive transitions are shown in Fig. 2. Reaction with Mg vapor markedly shifts the onset of resistance to higher fields, narrowing the transition width, and significantly reduces the strong magnetoresistance of sample A. We define the polycrystalline irreversibility field $\mu_0H_R^*$ and upper critical field μ_0H_{c2} by the 10% and 90% points on the resistive transition curve.[1,14,15] In the inset of Fig. 2, $\mu_0H_{c2}(T)$ is plotted for the three samples. The field at which $\mu_0H_R^*=9$ T occurs at 10 K for sample A, but at $\sim$24 K for samples B and C. This implies more than a doubling of the slope of $\mu_0H_R^*(T)$ for B and C, since the T_c values of all three samples are comparable. We note that the magnetoresistance is small for sample B and absent in C.

Critical current density J_c was determined from the magnetization hysteresis loops using the appropriate critical state model,[16] as shown in Fig. 3. The J_c values of sample A are rather low, being below $10^5\ \mathrm{A/cm}^2$ in fields above 2 T at 4.2 K, which is consistent with weak grain boundary flux pinning (due to the large, ~2 μm grain size) and weak intragrain pinning when the coherence length is long. Samples B and C exhibit comparable J_c values at low fields, and possess much less field dependence than for A. Since the Kramer

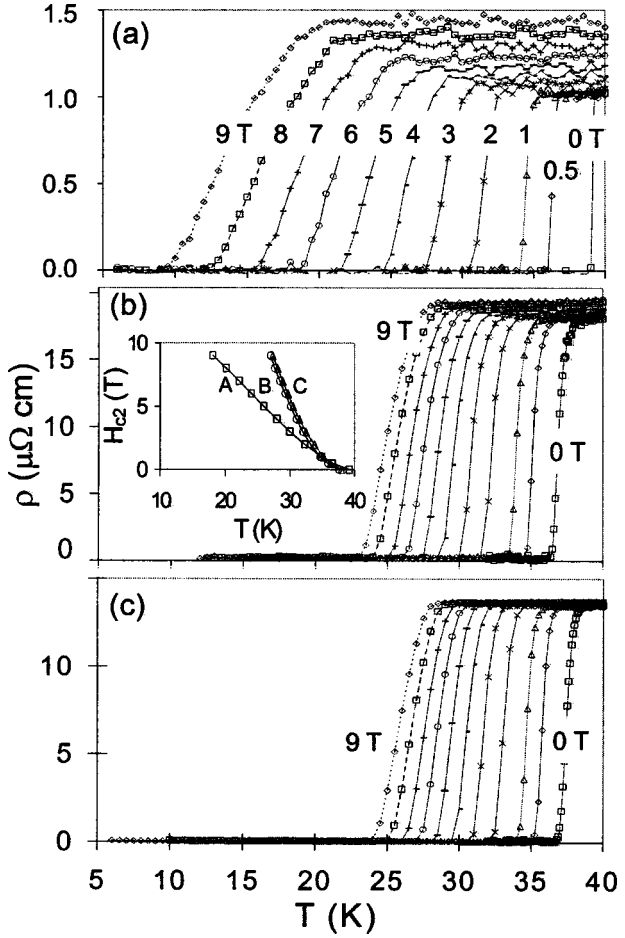

FIG. 2. Resistive transitions of samples A (a), B (b), and C (c) in applied magnetic fields up to 9 T, made at a measuring current density $\sim1\ \mathrm{A/cm}^2$. The 10% of $\rho(40\ \mathrm{K})$ resistivity points are plotted as the irreversibility fields in Fig. 4. The inset shows the parallel upper critical field as a function of the temperature taken as the 90% of the resistive transition. We believe that this transition is dominated by the percolative connectivity of those grains with highest H_{c2}, that is those oriented with their *c* axes perpendicular to the field.

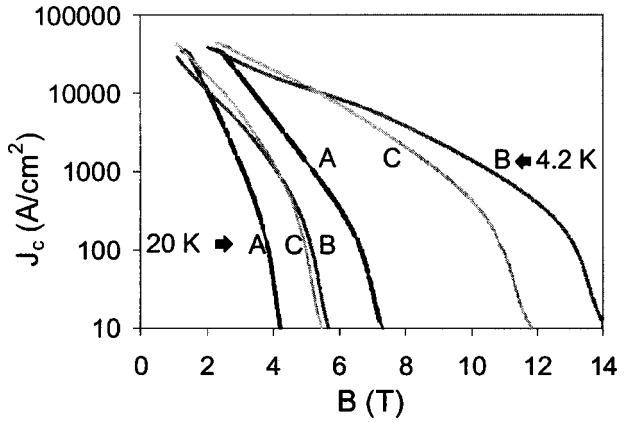

FIG. 3. Critical current density calculated from $M-H$ loops for samples A, B, C at 4.2 and 20 K. The magnetic irreversibility fields are determined at 10 $\mathrm{A/cm}^2$.

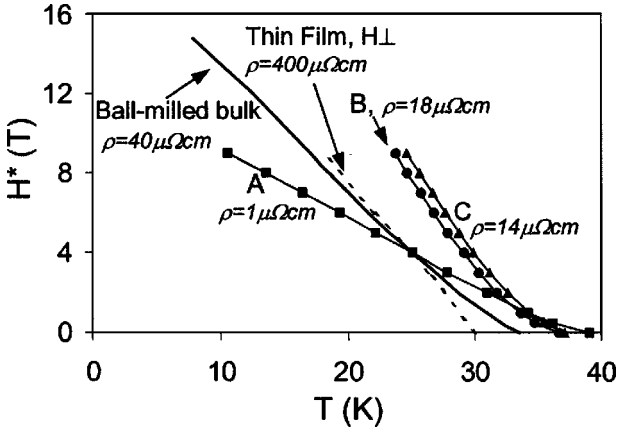

FIG. 4. Temperature dependence of the irreversibility line as determined by small-current transport measurements for MgB_2 samples from various sources. H^* is defined when the resistivity is 10% of the value at 40 K. Data from sample A (squares), B (circles), and C (triangles), are compared with data from Ref. 6 on a ball-milled nanocrystalline sample (solid line) and from Ref. 1 on a *c*-axis textured thin film (film 1) with H perpendicular to the film plane (dotted line).

function is not a good fit for any data set, we apply an empirical definition of the magnetic irreversibility field $\mu_0 H_M^*(T)$, namely the field at which J_c falls to 10 A/cm^2, about a factor of 5 above the resolution limit of the VSM. This definition is unambiguous because J_c falls steeply as H increases. $\mu_0 H_M^*$ rises from 4.2 T (sample A) to ~6 T (B and C) at 20 K and from 7.4 T (A) to 14.5 T (B) and 11.8 T (C) at 4.2 K. The 14.5 T magnetic irreversibility field of sample B is among the highest values obtained magnetically for bulk MgB_2 at 4.2 K. Magnetization J_c values of Gümbel *et al.*[6] at 20 K fell below 10 A/cm^2 at about 6.1 T, slightly higher than for samples B and C. To check for possible effects of enhanced $\mu_0 H^*$ due to texture, sample B was measured in two orthogonal orientations, but no difference was seen.

Figure 4 compares $\mu_0 H_R^*(T)$ to other literature values. We plot onset (i.e., $\rho = 0$) values for the ball-milled, nanocrystalline sample of Ref. 6 and the 10% of ρ(40 K) values for film 1 of Ref. 1 with H perpendicular to the film plane. Taken as a whole, Fig. 4 depicts a clear trend of resistivity, critical temperature, and the slope dH_R^*/dT. As ρ(40 K) increases from 1 to 360 $\mu\Omega$ cm, T_c is reduced from 39 to 31 K, while dH_R^*/dT increases from ~0.3 to ~0.8 T/K. We note that the $\mu_0 H^*(T)$ slopes for samples B and C are about the same as for the ball-milled sample, but samples B and C have superior properties because their T_c is above 37 K, producing the high extrapolated value for $\mu_0 H_R^*$ of 13–14 T at 20 K. Furthermore, the somewhat lower resistivity of samples B and C, as compared to the ball-milled and the thin film samples, indicates that further improvement in H^* can still be obtained.

An important conclusion of these analyses is that, whether the irreversibility field is defined by magnetic or by transport criteria, samples B and C show a factor of ~2 increase over $\mu_0 H^*(T)$ of sample A. We note that our magnetic and transport measurements of $\mu_0 H^*(T)$ for the clean limit sample A agree very well with those measured by Finnemore *et al.*[2] for low resistivity MgB_2.

Comparison of Figs. 3 and 4 underscores the difficulty of comparing irreversibility fields from different sources and measurement methods using polycrystals of an anisotropic superconductor. As seen elsewhere too,[2] the $\mu_0 H_M^*(T)$ curve lies a factor of ~2 below the corresponding transport curve, while there is good agreement for textured thin films.[1] A rough estimate is that $\mu_0 H_M^*$ is defined by current paths connected by grains with *c* axis parallel to H, while $\mu_0 H_R^*$ approximates the perpendicular case. However, percolative effects clearly dominate the current paths through the samples between these two limits.

In summary, we have shown that alloying clean-limit MgB_2 bulk samples in Mg vapor results in a significant increase of $\mu_0 H^*$ and $\mu_0 H_{c2}$. Both transport and magnetic measurements showed enhanced upper critical fields and irreversibility lines. More stringent magnetic measurements showed $\mu_0 H^* > 14$ T at 4.2 K and ~6 T at 20 K, while transport measurements indicated that $\mu_0 H^*$ could reach 13 T at 20 K. T_c slightly decreased and the resistivity increased from 1 to ~18 $\mu\Omega$ cm at 40 K for the alloyed sample. The irreversibility field enhancements are still well short of the potential limit observed in thin films.

We acknowledge discussions and assistance from E. Hellstrom, B. Senkowicz, J. Fournelle, J. Jiang, A. Polyanskii, A. Squitieri, E. Bellingeri, and G. Grasso. This work was supported by the National Science Foundation through the MRSEC on Nanostructured Materials and the US Department of Energy. One of the authors (V.B.) also thanks the University of Genova for financial assistance.

[1] S. Patnaik *et al.*, Supercond. Sci. Technol. **14**, 315 (2001).
[2] D. K. Finnemore, J. E. Ostenson, S. L. Bud'ko, G. Lapertot, and P. C. Canfield, Phys. Rev. Lett. **86**, 2420 (2001).
[3] 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).
[4] Y. Bugoslavsky, L. F. Cohen, G. K. Perkins, M. Polichetti, T. J. Tate, R. Gwilliam, and A. D. Caplin, Nature (London) **411**, 561 (2001).
[5] M. Eisterer, M. Zehetmayer, S. Tönies, H. W. Weber, M. Kambara, N. Hari Babu, D. A. Cardwell, and L. R. Greenwood, Supercond. Sci. Technol. **15**, L9 (2002).
[6] A. Gümbel, J. Eckert, G. Fuchs, K. Nenkov, K.-H. Müller, and L. Schultz, Appl. Phys. Lett. **80**, 2725 (2002).
[7] H. L. Suo, C. Beneduce, M. Dhallé, N. Musolino, J.-Y. Genoud, and R. Flükiger, Appl. Phys. Lett. **79**, 3116 (2001).
[8] W. Goldacker, S. I. Schlachter, S. Zimmer, and H. Reiner, Adv. Cryog. Eng. **48B**, 864 (2002).
[9] G. Grasso *et al.*, *Proceedings of BOROMAG Workshop*, Genoa, 17–19 June 2002 [Supercond. Sci. Technol. (in press)].
[10] A. Palenzona, P. Manfrinetti, and V. Braccini, INFM Patent No. TO2001A001098 (Nov. 2001).
[11] R. A. Ribeiro, S. L. Bud'ko, C. Petrovic, and P. C. Canfield, cond-mat/0204510.
[12] E. Bellingeri *et al.*, *Proceedings of BOROMAG Workshop*, Genoa, 17–19 June 2002 [Supercond. Sci. Technol. (in press)].
[13] D. G. Hinks, J. D. Jorgensen, H. Zheng, and S. Short, Physica C **382**, 166 (2002).
[14] Y. Ando, G. S. Boebinger, A. Passner, L. F. Schneemeyer, T. Kimura, M. Okuya, S. Watauchi, J. Shimoyama, K. Kishio, K. Tamasaku, N. Ichikawa, and S. Uchida, Phys. Rev. B **60**, 12475 (1999).
[15] K. Gupta, M. Decroux, T. C. Willis, Ø. Fischer, Physica C **235–240**, 2541 (1994).
[16] J. E. Evetts, *Concise Encyclopedia of Magnetic and Superconducting Materials* (Pergamon, New York, 1992) p. 99.