Systematic effects of carbon doping on the superconducting properties of Mg(B_{1-x}C_x)_2

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Abstract

The upper critical field, \( H_{c2} \), of Mg(B_{1-x}C_x)_2 has been measured in order to probe the maximum magnetic field range for superconductivity that can be attained by C doping. Carbon doped boron filaments are prepared by CVD techniques, and then these fibers are then exposed to Mg vapor to form the superconducting compound. The transition temperatures are depressed about 1 \( K/\% \) C and \( H_{c2}(T = 0) \) rises at about 5 \( T/\% \) C. This means that 3.5 \( \% \) C will depress \( T_c \) from 39.2 \( K \) to 36.2 \( K \) and raise \( H_{c2}(T = 0) \) from 16.0 \( T \) to 32.5 \( T \). Higher fields are probably attainable in the region of 5\% C to 7\% C. These rises in \( H_{c2} \) are accompanied by a rise in resistivity at 40 \( K \) from about 0.5 \( \mu\Omega cm \) to about 10 \( \mu\Omega cm \). Given that the samples are polycrystalline wire segments, the experimentally determined \( H_{c2}(T) \) curves represent the upper \( H_{c2}(T) \) manifold associated with \( H \perp c \).

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The discovery of superconductivity with $T_c \sim 40 \, K$ [1] focused a lot of attention on the previously ignored compound, MgB$_2$. Over the past few years, a great deal has been learned about high purity samples of this material, ranging from the anisotropic nature of the upper critical field, $H_{c2}$, to the two gap nature of the superconducting state [2]. On the other hand, despite much effort, systematic studies of the properties of doped MgB$_2$ have been made difficult by the fact that, under more common reaction routes that often involve diffusing Mg vapor into the B matrix at or near atmospheric pressure, it is difficult to homogenously substitute atoms for either the Mg or B sites [3]. Despite this uncertainty about the distribution of impurity atoms, it has been possible to raise $H_{c2}$ by a factor of 2 or more with the upper critical field at $T = 0$, $H_{c2}(0)$, rising from 16 $T$ for pure samples to $\sim 30 \, T$ or even $\sim 48 \, T$ in “dirty” thin films [4]. These reports clearly indicate that there is very likely a way of judiciously doping MgB$_2$ to increase $H_{c2}$ dramatically.

Recently it has been demonstrated that carbon can be uniformly substituted for boron if the carbon and boron are mixed at an atomic length scale by using B$_4$C as the starting material [5]. The resulting Mg(B$_{1-x}$C$_x$)$_2$ material [5, 6] had $x = 0.10 \pm 0.02$ and a sharp superconducting transition at 22 $K$. The remaining C goes into an MgB$_2$C$_2$ phase. Even with this strongly suppressed transition temperature, the $x \approx 0.10$ Mg(B$_{1-x}$C$_x$)$_2$ sample manifests clear evidence of two gap superconductivity [5, 7] and had $H_{c2}(0) \sim 25 \, T$, a value that exceeds the 16 $T$ $H_{c2}(0)$ of pure MgB$_2$. These data strongly supported the idea that carbon may well be a key dopant for tuning $H_{c2}$ in bulk and perhaps also in thin films.

It is clearly desirable to systematically study the effects of low carbon concentration on the superconducting properties of MgB$_2$, but the C-B binary phase diagram indicates that B$_4$C is the most B-rich compound. Even though there is a substantial width of formation for B$_4$C, the smallest amount of C that can be present in equilibrium in a boron/carbon binary compound is about 10% C [3]. In order to study the systematic effects for $x \leq 0.1$ in Mg(B$_{1-x}$C$_x$)$_2$, some non-equilibrium method of intimately mixing B and C must be used. Fortunately wire segments of MgB$_2$ can be synthesized from boron filaments made by a chemical vapor deposition (CVD) process similar to the methods used to make commercial boron filaments in kilometer lengths [10]. Carbon can be co-deposited with the boron in a controlled manner by introducing CH$_4$ in the BCl$_3$ and H$_2$ gas streams used in the CVD fiber processing.

In this work, we present a systematic study of the changes in $H_{c2}$ that occur in
Mg(B$_{1-x}$C$_x$)$_2$. For the addition of C up to $x \sim 0.035$ by this CVD method the transition temperature, $T_c$, is suppressed only slightly, from 39.2 K to 36.2 K, whereas the $H_{c2}(0)$ is increased from 16 T to 32 T. With these data, as well as our earlier data on $x \sim 0.10$ we can tentatively explain the $H_{c2}(0)$ values seen in some thin film samples, even an $H_{c2}(0)$ of $\sim 48$ T. These data indicate that not only does Mg(B$_{1-x}$C$_x$)$_2$ have a $T_c$ that vastly exceeds other intermetallic superconductors such as Nb$_3$Sn, but it also can have $H_{c2}(0)$ values that exceed Nb$_3$Sn’s upper critical field performance.

To prepare a carbon doped B fiber, a W wire about 15 $\mu$m in diameter is passed through a Hg seal at the rate of a few cm/s into a long glass tube. A flowing gas stream of BCl$_3$, H$_2$, and CH$_4$ move through the full length of the chamber. The fiber is heated electrically to temperatures in the 1100 – 1300$^\circ$C range, and the boron and carbon are deposited together to form a fiber of about 75 $\mu$m diameter and a few hundred meters length. Nominal ratios of C to B in the gas stream were selected to be zero, 0.5%, 1%, and 2% and several hundred meters of fiber were made. Short lengths of fiber are placed in a Ta tube with excess Mg with about a Mg/B ratio of 1. The sealed Ta tube is again sealed in quartz and placed in a box furnace and heated to about 1200$^\circ$C. Preparation using a steady ramp from 650$^\circ$C to 1200$^\circ$C gave the best flux pinning and these are the samples reported here. One of the unexpected aspects of sample preparation was that C doping, even at the lowest level studied, substantially slows the formation of the Mg(B$_{1-x}$C$_x$)$_2$ phase. Whereas pure B converts completely to MgB$_2$ in the presence of Mg vapor at 950$^\circ$C for 2 h, the boron doped with 0.5% C fiber requires about 1200$^\circ$C for 48 h to transform to Mg(B$_{1-x}$C$_x$)$_2$. Short wire segments of Mg(B$_{1-x}$C$_x$)$_2$ are removed from the Ta container and lead wires are attached with Ag epoxy.

X-ray patterns for each of the reacted Mg(B$_{1-x}$C$_x$)$_2$ samples show the MgB$_2$ phase, Mg lines, and the fiducial Si lines that were used to calibrate the 2$\Theta$ angle measurements. A search was made for the obvious impurity lines, but no evidence of MgO or B$_4$C are present. Fig. 1a shows an expanded view of the (002) peak and the (110) peak of the Mg(B$_{1-x}$C$_x$)$_2$ phase. Within the accuracy of these measurements, there is no shift in the (002) peak indicating that there is no measurable change in the c-axis lattice parameter. The (110) peak shifts systematically from 59.85 degrees for the pure sample to 60.10 degrees for the nominal 2% sample. Using these measured changes in the a-lattice parameter we can determine the amount of carbon in our samples via comparison to $\Delta a(x)$ from the Lee
et al. Auger electron spectroscopy (AES) analysis\textsuperscript{[13]} as well as the Avdeev et al. neutron diffraction data.\textsuperscript{[6]} This comparison is shown graphically in Fig. 1b and indicates that our Mg(B\textsubscript{1-x}C\textsubscript{x})\textsubscript{2} samples have $x = 0.0095$, $x = 0.017$, and $x = 0.035$. Carbon doping raises the the resistivity at 40 K, $\rho(40 K)$ from the pure MgB\textsubscript{2} value of $0.5 \pm 0.2 \mu\Omega \text{ cm}$ to the $x = 0.035$ value of $10 \pm 4 \mu\Omega \text{ cm}$. This uncertainty may arise from the rather short distance between voltage contacts on the sample, less than 1 mm, and the different time temperature profiles in making the Mg(B\textsubscript{1-x}C\textsubscript{x})\textsubscript{2} samples. In order to address this problem, a series of three samples of the $x = 0.035$ material prepared with a ramp from 650°C to 1200°C with somewhat longer distance between voltage contacts were measured and the $\rho(40 K)$ values in zero field were found to be 9.9, 10.1, and 10.6 $\mu\Omega \text{ cm}$.

The $T_c$ values, shown in Fig. 2 for each x-value, were measured both from magnetization and resistivity vs. temperature sweeps as shown by the two insets. With a measuring field of 50 Oe, magnetization always shows about 60 – 80 G Meissner screening at 5 K. The data are plotted on the inset as values normalized by the 5 K magnetization. The magnetization $T_c$ is defined by the onset of flux exclusion. The resistive $T_c$ is defined by an onset criterion (extrapolation of maximum slope up to normal state resistivity) so as to be consistent with the criterion used below for higher field data. For these measurements a current density of $\sim 6 A/cm^2$ was used. Values of $T_c$ derived from magnetization (solid circles) and resistivity (solid squares) are plotted on Fig. 2. The initial slope is about 1 K/% C in the $x = 0$ to $x = 0.035$ range.

The $H_{c2}$ values have been determined from both $\rho$ vs $T$ data up to 14 T taken on a Quantum Designs PPMS and from $\rho$ vs. $H$ sweeps taken at the National High Magnetic Field Laboratory. Results for the $x = 0.035$ sample are shown in Fig. 3a and 3b respectively. The resistivity vs field sweeps show a classic zero resistance range up to a critical depinning current followed by a linear $\rho$ vs. $H$ characteristic of flux flow resistivity.\textsuperscript{[14]} It should be noted that given the polycrystalline nature of our samples, our measurements of $H_{c2}(T)$ are determinations of the uppermost $H_{c2}(T)$ curve which is $H_{c2}^{\perp}(T)$ for the pure compound.\textsuperscript{[2, 15, 16]}

The central result of this work is shown in the $H_{c2}$ vs. $T$ plots of Fig. 4. The data for two different $x = 0.035$ samples shown by the solid and open squares are quite linear and rise well above a Werthamer, Helfand, and Hohenberg prediction\textsuperscript{[18]} of $H_{c2}(0) = 24.5 T$ determined by fitting the slope in the 20 to 30 K range. To show the behavior near $T_c$,
an inset on Fig. 4 shows the behavior of the $x = 0.035$ sample with both $R$ vs. $H$ data (solid triangles) taken at the National High Magnetic Field Laboratory and $R$ vs. $T$ data (solid squares) taken on the PPMS up to 14 $T$. Magnetization data ($M$ vs. $H$) is reversible near $T_c$ and show a very clean change in slope when the sample begins to expel flux. These results were taken down to 30 $K$ and are shown by the open squares. These three methods to determine $H_{c2}$ are very consistent especially when it is noted that each was made with different samples. Results for the $x = 0.017$ sample is similar to the $x = 0.035$ sample except that the $T_c$ is higher at 37.9 $K$ and $H_{c2}(0) = 25$ $T$. For $x = 0.0095$, the values are $T_c = 38.6$ $K$ and $H_{c2}(0) = 20$ $T$. The $H_{c2}$ vs. $T$ curves, all of these samples show positive curvature near $T_c$ and negative curvature near $T = 0$ with a rather linear behavior over much of the temperature range.

For standard type II superconductors decreases in the electronic mean free path directly manifest themselves as increases in $H_{c2}(T)$. In the case of MgB$_2$ though, even a change in the residual resistivity of an order of magnitude may not be enough to place this sample into the dirty limit ($l \ll \xi_0$). These statements, though, are based on single band, single scattering time arguments which are very likely to be incorrect or incomplete for MgB$_2$, given its two bands and gaps and at least three scattering times (two intraband scattering times and one interband scattering time). Gurevich [19] has made predictions about the form and size of $H_{c2}(T)$ for MgB$_2$ in the dirty limit, but this model requires assumptions about all three scattering times. The data we present in Fig. 4 along with our measured changes in resistivity provide points of reference for this theory, i.e. for an order of magnitude increase in $\rho_0$ we double $H_{c2}(0)$, but still have upward curvature near $T_c$ (Fig. 4 inset) and also have a clear roll-over at low temperatures.

To summarize our results and place them in context with other data on Mg(B$_{1-x}$C$_x$)$_2$ we have plotted both $T_c$ and $H_{c2}(0)$ as a function of carbon content for our own data as well as selected experiments on single crystals on Fig. 5. The carbon content for the data by Avdeev et al. [6] was determined by neutron diffraction whereas Lee et al. [13] used AES and Kazakov et al. [18], as well as the present work used the shift in the $a$-lattice parameter. The first point that is worth noting is that the $T_c(x)$ manifold, which contains data from 4 different groups on samples synthesized by a variety of ways (low and high pressure synthesis) and in a variety of forms (small single crystals, bulk wire segments and sintered pellets), is quite reproducible and robust. This is very encouraging and indicates
that $T_c$ may be used as a rough caliper of how much carbon is in a given sample. Focusing on the $H_{c2}(0)$ of this work at low C concentration (filled circles), the rapid rise of $H_{c2}(0)$ at $\sim 5 \, T/\% \, C$ would seem to indicate that values in the 45 $T$ range may well be possible. On the other hand the measurements of $H_{c2}(0) = 25 \, T$ for a carbon content of about $x \sim 0.10$, indicate that the initial rapid rise of $H_{c2}(0)$ seen for lower C contents will eventually bend over and reach a maximum at intermediate carbon concentrations. The region from $x = 0.04$ to $x = 0.07$ is clearly of interest. Whereas these data show a systematic increase in $H_{c2}(0)$ for $x \leq 0.035$ carbon doping levels, they also indicate that higher $H_{c2}(0)$ values clearly should be anticipated for slightly higher $x$-values. Indeed, one of the largest $H_{c2}(0)$ values reported to date ($H_{c2}(0) \sim 47 \, T$ for a thin film with a $T_c \sim 31 \, K$ [4]) is not inconsistent with a linear extrapolation of the $H_{c2}(0)$ line for $x \leq 0.035$ from this work to larger values of $x$. This is consistent with the $T_c$ value of the film implying a carbon content in the vicinity of $x \approx 0.07$. This strongly suggests that carbon may have been the dominant impurity changing $H_{c2}(0)$ in this film. All of these data taken together strongly suggest that with judicious carbon doping, Mg(B$_{1-x}$C$_x$)$_2$ can be tuned to have remarkably large upper critical field values, making this already fascinating material of even greater interest.

Acknowledgments

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[1] J. Nagamatsu, N. Nakagawa, T. Muranaka, Y. Zenitani, and J. Akimitsu, Nature, 410, 63 (2001).
[2] Paul C. Canfield and George W. Crabtree, Physics Today, 56 (3), 34 (2003).
[3] R. J. Cava, H. W. Zandbergen, and K. Inumaru, Physica C, 385, 8 (2003).
[4] A. Gurevich, S. Patnaik, V. Braccini, K. H. Kim, C. Mielke, X. Song, L. D. Cooley, S. D. Bu, D. M. Kim, J. H. Choi, L. J. Belenky, J. Giencke, M. K. Lee, W. Tian, X. Q. Pan, A. Siri, E. E. Hellstrom, C. B. Eom, D. C. Larbalestier, cond-mat/0302474.
[5] R. A. Ribeiro, S. L. Bud’ko, C. Petrovic, and P. C. Canfield, Physica C, 384, 227 (2003).
[6] M. Avdeev, J. D. Jorgensen, R. A. Ribeiro, S. L. Bud’ko, and P. C. Canfield, Physica C 387, 301 (2003).
[7] P. Samuely, Z. Holanova, P. Szabo, J. Kacmarcik, R. A. Ribeiro, S. L. Bud’ko, and P. C. Canfield, Phys. Rev. B 68, 020505 (2003).
[8] Z. Holanova, J. Kacmarcik, Z. Szabo, P. Samuely, I. Sheikin, R. A. Ribeiro, S. L. Bud’ko, and P. C. Canfield, (unpublished).
[9] Binary Alloy Phase Diagrams, Second Edition, Edited by T. Massalski, (A.S.M International, 1990).
[10] R. J. Suplinskas, J. V. Marzik, Boron and Silicon Carbide Filaments, in Handbook of Reinforcements for Plastics, J. V. Milewski and H. S. Katz (Eds.)Van Nostrand Reinhold, New York, 1987.
[11] Study of Transition Temperatures in Superconductors, Final Report, prepared by L. J. Vieland, and R. W. Cohen, RCA Laboratories, Princeton, NJ 08540, 1970.
[12] P. C. Canfield, D. K. Finnemore, S. I. Bud’ko, J. E. Ostenson, G. Lapertot, C. E. Cunningham, and C. Petrovic, Phys. Rev. Lett. 86, 2423 (2001).
[13] S. Lee, T. Masui, A. Yamamoto, H. Uchiyama, and S. Tajima, Physica C, 397, 7 (2003).
[14] Y. B. Kim and M. J. Stephen, Flux flow and Irreversible effects, p. 1107 in Superconductivity, R. D. Parks Ed. Marcel Dekker, Inc. New York, 1969.
[15] S. L. Bud’ko, V. G. Kogan, and P. C. Canfield, Phys. Rev. B, 64, 180506 (2001).
[16] M. Angst, R. Puzniak, A. Wisniewski, J. Jun, S. M. Kazakov, J. Karpinski, J. Roos, H. Keller, Phys. Rev. Lett. 88, 167004 (2002).
[17] N. R. Werthamer, E. Helfand, and P. C. Hohenberg, Phys. Rev. 147, 295 (1966).

[18] S. M. Kazakov, J. Karpinski, J. Jun, P. Geiser, N. D. Zhigadlo, R. Puzniak, and A. V. Mironov, cond-mat/0304656

[19] A. Gurevich, Phys. Rev. B 67 184515 (2003).
FIG. 1: (a) selected regions of powder X-ray diffraction data from Mg(B₁₋ₓCₓ)₂ wire segments synthesized from boron filaments with 0%, 0.5%, 1%, and 2% nominal carbon substitution. Note that whereas there is no detectable shift of (002) peak, (110) shifts systematically with carbon substitution. (b) Shift in \( a \)-lattice parameter as a function of carbon content from neutron diffraction data [6] shown as dashed line and AES data [13] shown as solid line with our shift in \( a \)-lattice parameter shown as large triangles on y-axis. Projection of our \( \Delta a \) data onto the \( \Delta a(x) \) lines (shown as dotted lines) indicate that the our three carbon substituted Mg(B₁₋ₓCₓ)₂ samples have \( x \approx 0.0095, 0.017, \) and 0.035. Inset shows data for an enlarged carbon range, \( x < 0.15 \).
FIG. 2: Superconducting transition temperature as a function of carbon content. Data inferred from temperature dependent resistivity (shown in lower inset) shown as squares and data inferred from temperature dependent, low field magnetization (shown in upper inset) shown as circles. Data from Ribeiro et al. [5] for $x \approx 0.10$ are also shown. For insets squares indicate $x = 0$, circles - $x = 0.0095$, triangles - $x = 0.017$, stars - $x = 0.035$. 
FIG. 3: Temperature (a) and magnetic field (b) dependent electrical resistivity of Mg(B$_{1-x}$C$_x$)$_2$ with $x = 0.035$. The data presented in (a) are for $H \leq 14T$ and taken in a Quantum Design PPMS system. The data in (b) are for $H \leq 33T$ and were taken at the NHMFL, Tallahassee.
FIG. 4: Superconducting upper critical field, $H_{c2}$, as a function of temperature for Mg(B$_{1-x}$C$_x$)$_2$, $x \leq 0.035$ samples. Inset: $H_{c2}(T)$ closer to $T_c$ determined from temperature dependent resistivity (filled square), field dependent resistivity (triangle) and field dependent magnetization (open square).
FIG. 5: Superconducting upper critical field, $H_{c2}$, and superconducting transition temperature, $T_c$, as a function of $x$ for Mg(B$_{1-x}$C$_x$)$_2$ samples. $T_c(x)$ data are (open circles) this study, (open square) $x \approx 0.10$ from Ribeiro et al.[5], (stars) and (asterisks) for single crystal samples from Lee et al. [13] and Kazakov et al. [18] respectively. $H_{c2}(0)$ data are (filled circles) this work and (filled square) $x \approx 0.10$ from Holanova et al.[8]. It should be noted that (i) all of the $T_c(x)$ data agree quite well and (ii) that there clearly will be a maximum $H_{c2}(0)$ for $0.035 < x < 0.10$ that can be expected to be between $\sim 35$ and $\sim 55T$. 
