Systematic Effects of Carbon Doping on the Superconducting Properties of $Mg(B_{1-x}C_x)_2$

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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 MgB_2 filaments were prepared, and for carbon levels below 4% the transition temperatures are depressed by about 1 K/% C and $H_{c2}(T = 0)$ rises by about 5 T/% C. This means that 3.8% C substitution will depress T_c from 39.2 to 36.2 K and raise $H_{c2}(T = 0)$ from 16.0 to 32.5 T. These rises in H_{c2} are accompanied by a rise in resistivity at 40 K from about 0.5 to about 10 $\mu\Omega$ cm.

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 homogeneously substitute atoms for either Mg or B [3]. Despite these difficulties and uncertainty about the nature and 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 ~ 30 T or even ~ 48 T in "dirty" thin films [4]. These reports clearly indicate that there should be a way of judiciously doping MgB_2 so as to increase H_{c2} dramatically and systematically.

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_4C as the starting material [5]. The resulting $Mg(B_{1-x}C_x)_2$ material [5,6] has $x = 0.10 \pm 0.02$ and a sharp superconducting transition at 22 K. 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 has $H_{c2}(0) \sim 25$ T [8], 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 the tuning of H_{c2}.

It is clearly desirable to systematically study the effects of low level carbon substitution on the superconducting properties of MgB_2, but the C-B binary phase diagram

indicates that B_4C is the most B-rich compound. Even though there is a substantial width of formation for B_4C, the smallest amount of C that can be present in equilibrium in a boron/carbon binary compound is about 10% C [9]. In order to study the systematic effects for $x \lesssim 0.1$ in $Mg(B_{1-x}C_x)_2$, some nonequilibrium 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 [10]. Carbon can be codeposited 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 T_c, ρ_0, and $H_{c2}(T)$ that occur in $Mg(B_{1-x}C_x)_2$. For the substitution of C up to $x \sim 0.038$ by this CVD method, the transition temperature T_c is suppressed only slightly, from 39.2 to 36.2 K, whereas the $H_{c2}(0)$ is increased from 16 to 32 T. With these data, as well as our earlier data on $x \sim 0.10$ [5–8], we can tentatively explain the $H_{c2}(0)$ values seen in some thin film samples, even $H_{c2}(0)$ values in excess of 40 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_3Sn [11], but it also can have $H_{c2}(0)$ values that exceed the upper critical field performance of Nb_3Sn.

To prepare a carbon doped B fiber, a W wire about 15 μm in diameter is passed through a Hg seal at the rate of a few cm/s into a long glass tube [10]. A flowing gas stream of BCl_3, H_2, and CH_4 moves through the full length of the chamber. The fiber is heated electrically to temperatures in the 1100–1300 °C range, and the boron and carbon are deposited together to form a fiber of about 75 μm 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%. $Mg(B_{1-x}C_x)$ is made by

placing short lengths of fiber into a Ta tube with excess Mg [12] (Mg/B ratio of 1) and heating from 650 °C to 1200 °C over 100 h. Short wire segments of $Mg(B_{1-x}C_x)_2$ are removed from the Ta container and lead wires are attached with Epotek H20E silver 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 2Θ angle measurements. A search was made for the obvious impurity lines, but no evidence of MgO or B_4C are present. Figure 1(a) 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 60.16 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 Avdeev et al. neutron diffraction data [6]. This comparison is shown graphically in Fig. 1(b) and indicates that our $Mg(B_{1-x}C_x)_2$ samples have $x = 0.0047$, $x = 0.021$, and $x = 0.038$.

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 shows a 60–80 G Meissner screening at 5 K. For clarity, the data are plotted 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 ~ 6 A/cm² was used. Values of T_c derived from magnetization (solid circles) and resistivity (solid squares) are plotted in Fig. 2. The initial slope is about 1 K/% C in the $x = 0$ to $x = 0.038$ range. It is worth noting that carbon doping raises the resistivity at 40 K, $\rho(40\,K)$, from the pure MgB_2 value of 0.5 ± 0.2 $\mu\Omega$ cm to the $x = 0.038$ value of 10.2 ± 0.4 $\mu\Omega$ cm.

The H_{c2} values have been determined from both ρ vs T data up to 14 T taken on a Quantum Design Physical Property Measurement System (PPMS) and from ρ vs H sweeps taken at the National High Magnetic Field Laboratory. Results for the $x = 0.038$ sample are shown in Fig. 3. The resistivity vs field sweeps show zero resistance up to a critical depinning current followed by a rise in ρ vs H consistent with flux flow resistivity [14]. Whereas this Letter focuses on samples with relatively smaller grain sizes and higher J_c values, measurements on samples with larger grain sizes and lower J_c were also made. For these samples a larger resistive transition width was measured but $H_{c2}(T)$ curves as inferred by the onset criterion were essentially the same. It should be noted that, given the polycrystalline nature of our samples, our
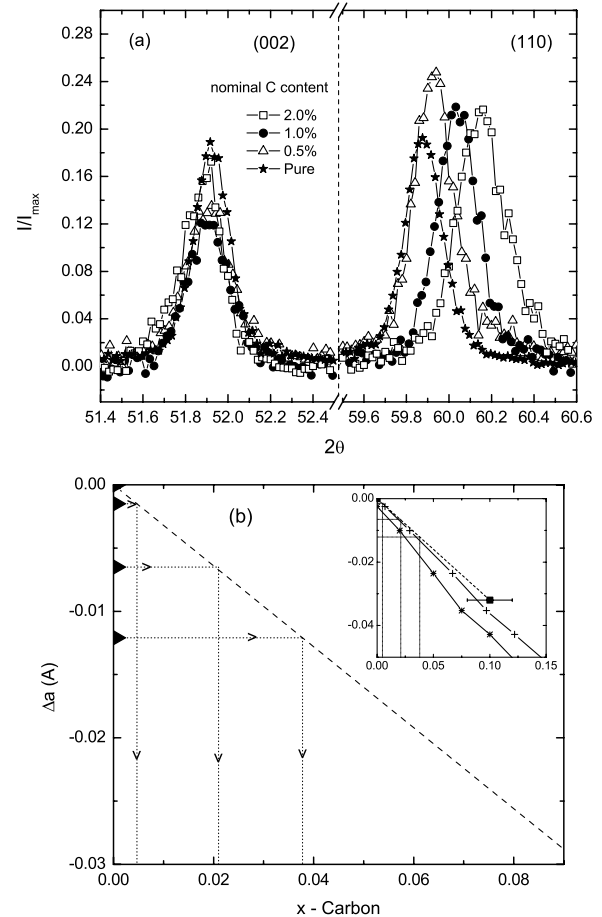

FIG. 1. (a) Selected regions of powder x-ray diffraction data from $Mg(B_{1-x}C_x)_2$ wire segments synthesized from boron filaments with 0%, 0.5%, 1%, and 2% nominal carbon substitution. Note that whereas there is no detectable shift of (002) peak, the (110) peak shifts systematically with carbon substitution. (b) Shift in the a-lattice parameter as a function of carbon content from neutron diffraction data [6] shown as a dashed line with our shift in the a-lattice parameter shown as large triangles on the y axis. Projection of our Δa data onto the $\Delta a(x)$ line (shown as dotted lines) indicates that the our three carbon substituted $Mg(B_{1-x}C_x)_2$ samples have $x \approx 0.0047$, 0.021, and 0.038. The inset shows data for an enlarged carbon range, $x < 0.15$, and includes the $x \sim 0.10$ sample [5,6] as well as data from Lee et al. [13] showing their nominal carbon concentrations (*) as well as Auger electron spectroscopy data (+).

measurements of $H_{c2}(T)$ are determinations of the uppermost $H_{c2}(T)$ curve which is $H_{c2}^{\perp c}(T)$ for the pure compound [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 $x = 0.038$ samples shown by the solid and open squares are quite linear and rise well above a Werthamer, Helfand, and Hohenberg prediction [17] 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, the inset of Fig. 4 shows the behavior of the $x = 0.038$ sample with both R vs H data
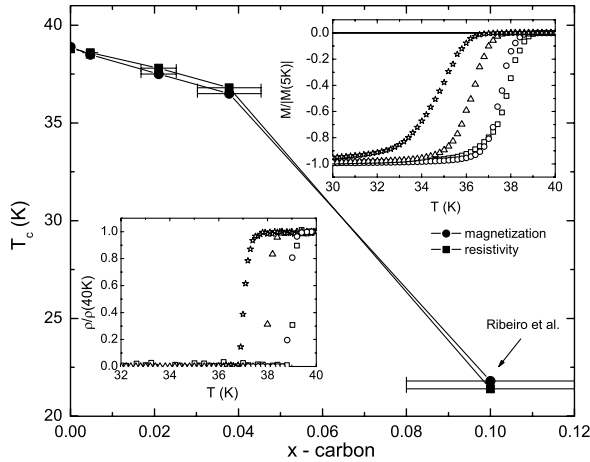
FIG. 2. Superconducting transition temperature as a function of carbon content. Data inferred from temperature dependent resistivity (shown in lower inset) is shown as squares and data inferred from temperature dependent, low field magnetization (shown in upper inset) is shown as circles. Data from Ribeiro *et al.* [5] for $x \approx 0.10$ are also shown. Insets: squares indicate $x = 0$; circles, $x = 0.0042$; triangles, $x = 0.021$; stars, $x = 0.038$. The carbon content error bars are projections of the Avdeev *et al.* error bars for $x \sim 0.10$ back toward $x = 0$ (see inset of Fig. 1).

(solid triangles) taken at the National High Magnetic Field Laboratory and R vs T data (solid squares) taken in the PPMS up to 14 T. Magnetization data (M vs H) are 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 $x = 0.021$ sample are similar to the $x = 0.038$ sample except that the T_c is higher at 37.9 K and $H_{c2}(0) = 25$ T. For $x = 0.0047$, the values are $T_c = 38.6$ K and $H_{c2}(0) = 20$ T. The H_{c2} vs T curves for 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 [18] 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
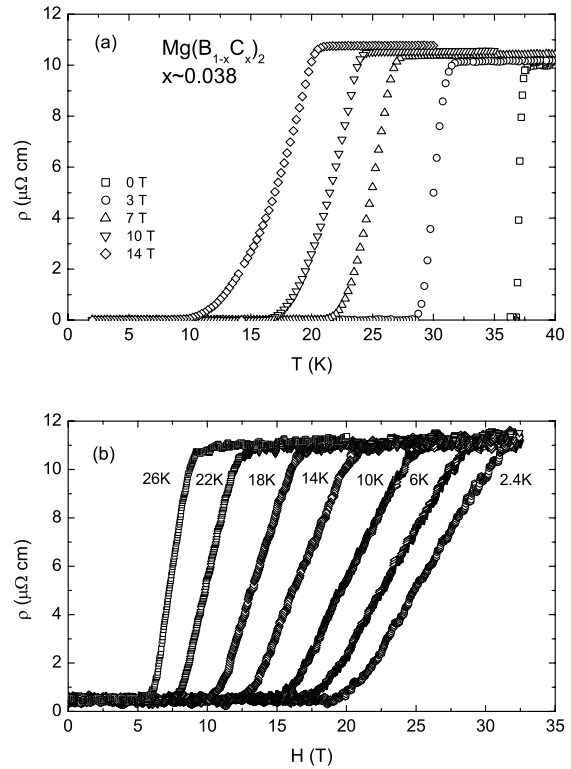

FIG. 3. Temperature (a) and magnetic field (b) dependent electrical resistivity of Mg(B$_{1-x}$C$_x$)$_2$ with $x = 0.038$. The data presented in (a) are for $H \leq 14$ T and taken in a Quantum Design PPMS system. The data in (b) are for $H \leq 33$ T and were taken at the NHMFL, Tallahassee.

measured changes in resistivity provide points of reference for this theory; i.e., for an order of magnitude increase in ρ_0 we double $H_{c2}(0)$, but still have upward curvature near T_c (Fig. 4 inset) and also have a clear rollover at low temperatures.
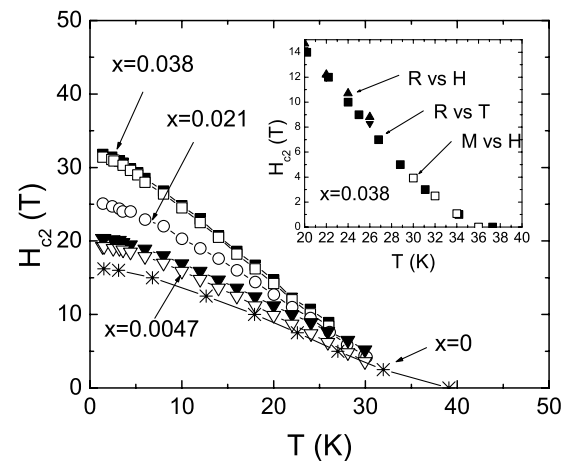

FIG. 4. Superconducting upper critical field H_{c2} as a function of temperature for Mg(B$_{1-x}$C$_x$)$_2$, $x \leq 0.038$ samples. Inset: $H_{c2}(T)$ closer to T_c determined from temperature dependent resistivity (solid squares), field dependent resistivity (triangles), and field dependent magnetization (open squares).
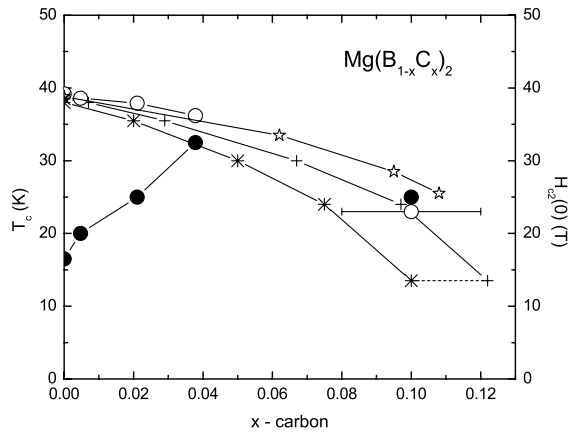
FIG. 5. Superconducting upper critical field H_{c2} and superconducting transition temperature T_c as a function of x for $Mg(B_{1-x}C_x)_2$ samples. $T_c(x)$ data is shown as open circles for this study and for $x \approx 0.10$ from Ribeiro *et al.* [5], stars for single crystal samples from Kazakov *et al.* [19], and the asterisk/cross pairs show the nominal and inferred carbon content given by Lee *et al.* [13]. $H_{c2}(0)$ data are shown as solid circles for this work and for $x \approx 0.10$ from Holanova *et al.* [8].

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 in Fig. 5. The carbon content for the sample used by Avdeev *et al.* [6] was determined by neutron diffraction, and Kazakov *et al.* [19], as well as the present work, used the shift in the a-lattice parameter to determine carbon content. Lee *et al.* [13] presented nominal carbon content and results of Auger electron spectroscopy for their samples. The first point that is worth noting is that the $T_c(x)$ manifold, which contains data from four 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), overlap. Determining the exact level of carbon substitution is difficult, but within the error bars given by Avdeev *et al.* [6], or spread of data from other groups, the suppression of T_c with carbon substitution is clear and fairly consistent. 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 $H_{c2}(0)$ data from this work at low C concentration (solid circles), the rapid rise of $H_{c2}(0)$ at ~ 5 T/% C would seem to indicate that values in excess of 40 T may well be possible. On the other hand, the measurements of $H_{c2}(0) = 25$ T, for a carbon content of about $x \sim 0.10$ [8], 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 $x \lesssim 0.038$ 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 $x \lesssim 0.038$ 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.

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