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Enhancement of the upper critical field of MgB_2 by carbon-doping

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Abstract

We have measured the temperature dependence of the upper critical field, $H_{c2}(T)$, of carbon-doped MgB_2. $H_{c2}(T)$ does not follow the well-known Werthamer–Helfand–Hohenberg (WHH) result for a one-gap dirty superconductor but can be described well by the result of a recent theoretical calculation for a two-gap dirty superconductor. $H_{c2}(0)$ of the carbon-doped material is determined to be between 29 and 38 T, substantially higher than that of pure MgB_2 (15–23 T).

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1. Introduction

The superconductivity of MgB_2 [1] is unusual not only because its transition temperature of 39 K is the highest outside the copper oxide family, but also because there are two superconducting gaps [2–9]. MgB_2 is also a type II superconductor. The temperature dependence of the upper critical field, $H_{c2}(T)$, of a one-gap type II superconductor, in both the clean and dirty limits, has been theoretically understood since the 1960's [10–12]. For pure MgB_2, evidence suggests that the σ band is in the clean limit and π band is in the dirty limit [13,14]. The upper critical field has a small upturn near T_c. This behavior can be understood in terms of the two gap Ginzburg–Landau theory [15]. When MgB_2 is doped with nonmagnetic impurities, however, there is a much more noticeable upturn in $H_{c2}(T)$ [16] as has been observed in dirty MgB_2 films with MgO as the impurity [17].

We show in this paper that for MgB_2 doped with carbon the upturn of $H_{c2}(T)$ at low temperatures is even more dramatic and is in stark contrast with what one would expect from the Werthamer–Helfand–Honenberg (WHH) result for a one-gap dirty superconductor. We find that with suitably chosen parameters, our results fit well with recent theoretical calculations relevant to a dirty two-gap superconductor.

2. Experiment

Carbon-doped ($MgB_{2-x}C_x$) polycrystalline samples are synthesized [18] using variants on established methods [19,20]. To produce the carbon-doped material, magnesium turnings (99.8%, Alfa Aesar) and boron carbide (B_4C powder 91-7 mm, 99.7%, Sigma-Aldrich) are mixed in a 1:2 stoichiometric ratio and placed in tantalum foil, which is crimped shut. The tantalum foil is heated to 600 °C and then 700 °C for 1–3 h each in a tube furnace under Ar atmosphere.

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The carbon-doped sample has been determined by X-ray diffraction to have two phases. The majority phase, having the MgB_2 structure with 10% of the B-sites replaced by carbon atoms, is the superconducting phase. Due to the carbon substitution, the in-plane (*a*-axis) lattice constant is contracted by about 1% and the *c*-axis lattice parameter is virtually unchanged. By chemical analysis experiments, it is also determined that the minority phase, MgB_2C_2, which is non-superconducting, is about 20% by weight.

The resistance vs. temperature measurements are carried out by the four-probe technique using a linear AC resistance bridge operating at 16 Hz. Measurements are performed in magnetic fields up to 15 T. We have also performed susceptibility measurement up to 5 T on a second sample in a SQUID magnetometer (Quantum Design MPMS-5).

3. Results and discussion

Fig. 1 shows the results of resistance vs. temperature measurements for sample A ($\sim 1\ mm^2 \times 100\ \mu m$) of $MgB_{1.8}C_{0.2}$ in magnetic fields from 0 to 15 T. At $H=0$, $T_c=32.2$ K by the resistive onset criterion and $T_c=31$ K by the resistive midpoint criterion (see inset). Susceptibility measurements for sample B of $MgB_{1.8}C_{0.2}$ are shown in Fig. 2, which yield $T_c=29$ K at $H=0.01$ T, 3.2 and 2.2 K lower than T_c determined resistively for sample A, using the onset and midpoint criterion, respectively. This discrepancy is not uncommon for granular superconductors, including high-T_c copper oxides, and has been attributed to resistive measurements reflecting the onset of filamentary superconductivity whereas susceptibility measurements reflecting the onset of bulk superconductivity.

We plot $H_{c2}(T)$ determined from both resistance and susceptibility measurements in Fig. 3. For the purpose of easy comparison, susceptibility data points have been shifted by 3.2 K. The trend is that there are roughly two linear regimes, one near T_c, which has a lower absolute slope, and the other at low temperatures with a higher absolute slope. The transition between these two regimes is around 14 K. Fig. 3 also shows the WHH prediction, fit to the experimental data (resistive onset or resistive midpoint) near T_c. Clearly, WHH underestimates H_{c2} at low temperatures. Linear extrapolations of the low temperature data (between 5 and 10 K) yield $H_{c2}(0)$ values between 30 and 40 T. As we show below, the true $H_{c2}(0)$ (between 29 and 38 T), obtained by fitting experimental data to the relevant theoretical model, are very close to the linear extrapolations of the low temperature data between 5 and 10 K. The naive $H_{c2}(T)$ prediction from WHH, $H_{c2}(T=0)=0.69T_c dH_{c2}(T=T_c)/dT$, underestimates $H_{c2}(T)$ by a factor of six or more (Fig. 3).

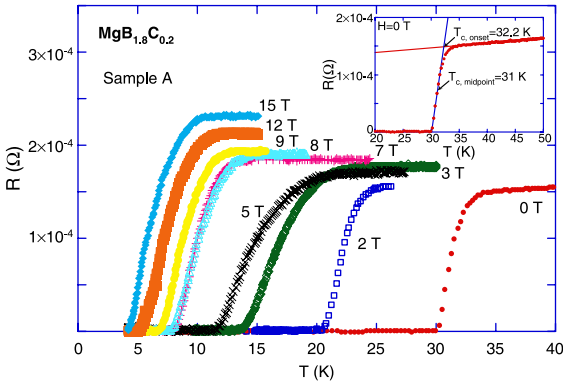

Fig. 1. Resistance vs. temperature measurements for carbon-doped MgB_2, sample A, at 0, 2, 3, 5, 7, 8, 9, 12, 15 T. The inset shows how T_c is determined by the resistive onset and midpoint criteria.

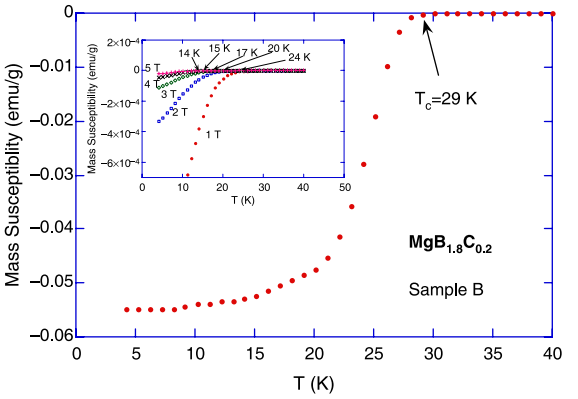

Fig. 2. Mass susceptibility vs. temperature for carbon-doped MgB_2, sample B, in a magnetic field of 100 Oe. Inset shows the onset transition temperatures at $H=1$, 2, 3, 4, 5 T.

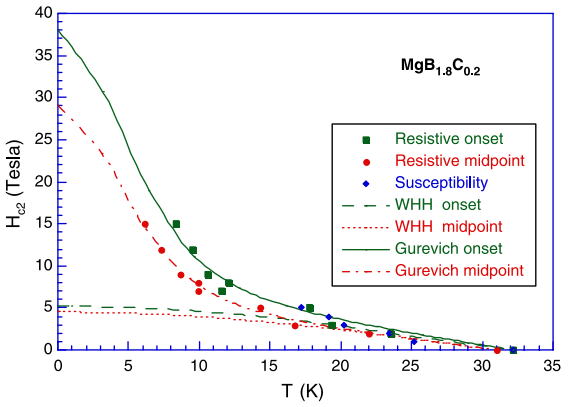

Fig. 3. $H_{c2}(T)$ of $MgB_{1.8}C_{0.2}$. The squares are generated by using the resistive onset criterion and the disks are generated by using the resistive midpoint criterion. The diamonds are from susceptibility measurements, shifted by 3.2 K. The long-dash curve is the WHH fit using the onset data near T_c and short-dash curve is the WHH fit using the midpoint data near T_c. The solid curve is the best fit based on the model of a two-gap dirty superconductor of Ref. [16] for the onset data and the long-short-dash curve is the best fit for the midpoint data.

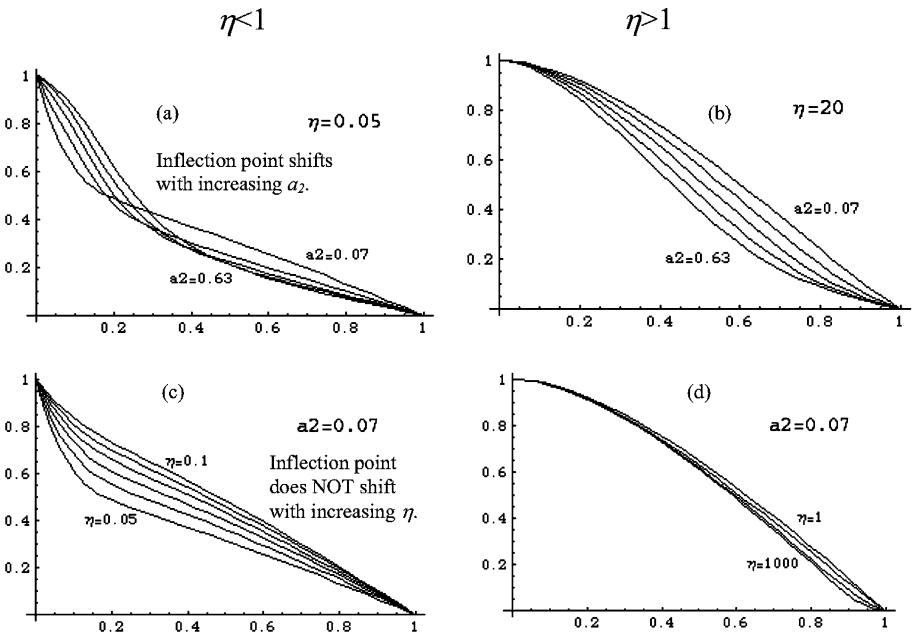

Fig. 4. Using Eq. (1) (see text), we explore how the shape of $H_{c2}(T)$ for a dirty two-gap superconductor depends on a_2 and η. We set $\eta=0.05<1$ in (a) and $\eta=20>1$ in (b) and plot $H_{c2}/H_{c2}(0)$ vs. $t=T/T_c$ for $a_2=0.07$, 0.21, 0.35, 0.49 and 0.63. We then set $a_2=0.07$ and plot for $\eta=0.05$, 0.06, 0.07, 0.08, 0.09 and $0.1<1$ in (c), and for $\eta=1$, 10, 100 and $1000\geq 1$ in (d).

Theoretical calculations performed by Gurevich for the upper critical field of a dirty two-gap superconductor [16] are relevant to our data for $H_{c2}(T)$ of carbon-doped MgB_2, with appropriate extensions of model parameters. We introduce some of the relevant parameters from Ref. [16] here. The λ matrix is defined by $\lambda_{mm'}=\lambda^{(ep)}_{mm'}-\mu_{mm'}$ with m, $m'=1$, 2, where $\lambda^{(ep)}_{mm'}$ is the matrix of electron–phonon coupling constants, $\mu_{mm'}$ is the Coulomb pseudo-potential matrix and $1=\sigma$ band and $2=\pi$ band. Some related quantities are defined as follows $\lambda_{\pm}=\lambda_{11}\pm\lambda_{22}$, $\lambda_0=(\lambda_-^2+4\lambda_{12}\lambda_{21})^{1/2}$, $w=\lambda_{11}\lambda_{22}-\lambda_{12}\lambda_{21}$, and $a_0=2w/\lambda_0$, $a_1=1+\lambda_-/\lambda_0$, and $a_2=1-\lambda_-/\lambda_0$. For pure MgB_2, the λ matrix was calculated by Golubov et al. [21] to be $\lambda_{\sigma\sigma}=0.81$, $\lambda_{\pi\pi}=0.285$, $\lambda_{\sigma\pi}=0.119$, and $\lambda_{\pi\sigma}=0.09$.

Since, the off-diagonal elements of the λ matrix are a measure of how strongly the two bands couple, so is a_2. D_1 and D_2 are the diffusivities for the two bands, with ratio $\eta=D_2/D_1$. For pure MgB_2, using the values for the λ matrix listed above, $a_2=0.07$.

Eq. (34) in Ref. [16] is a transcendental equation [22] for $t=T/T_c$ and $h=H_{c2}D_1/2\phi_0T$, where ϕ_0 is the flux quantum:

$$a_0[\ln t+U(h)][\ln t+U(\eta h)]+a_2[\ln t+U(\eta h)]+a_1[\ln t+U(h)]=0 \quad (1)$$

Here, $U(x)=\psi(1/2+x)-\psi(x)$ and $\psi(x)$ is the di-gamma function.

There are four parameters in Eq. (1), a_0, a_1, a_2 and η. For simplicity, we use the value of a_0 that is calculated for pure MgB_2. Since, $a_1+a_2=2$, there are two independent fitting parameters, a_2 and η. In order to make a good fit to our data, we explore how the shape of $H_{c2}(T)$ depends on these two parameters. In Fig. 4(a) and (b), we set $\eta=0.05$ and $\eta=20$, respectively, and vary a_2 from 0.07 to 0.7; the inflection point shifts towards higher t for $\eta=0.05$ and lower t for $\eta=20$. In Fig. 4(c) and (d), we fix a_2 at 0.07 and vary η to explore the dependence of $H_{c2}(T)$ on η. As can be clearly seen, for $\eta<1$, varying η does not significantly change the point of inflection along the t-axis but it does change how strong the upturn at low T is. For $\eta>1$, the shape of the

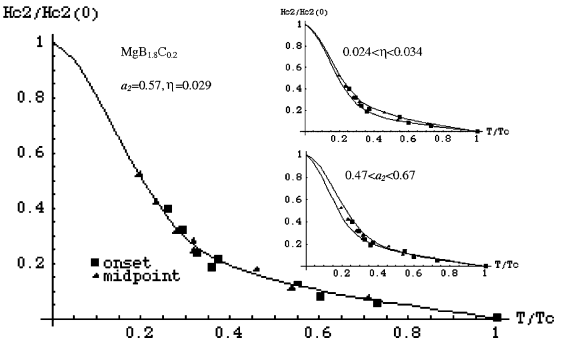

Fig. 5. $H_{c2}/H_{c2}(0)$ vs. reduced temperature T/T_c. The data generated by the resistive midpoint criterion are plotted with triangles and those generated by the resistive onset criterion with squares. Also shown is the best theoretical fit. Due to the small spread in the data points, there are uncertainties in both parameters and they are shown in the insets.

curve is insensitive to the value of η. Experimentally, the inflection point for the carbon-doped material is close to $T=14$ K, or $t=0.4$. In Fig. 5, we show the best fit and the range of a_2 and η that enclose all the data points. The widths of the ranges are considered uncertainties in a_2 and η. The best fit is $a_2=0.57\pm0.10$ and $\eta=0.029\pm0.005$. The best fits are also plotted in Fig. 3 and as solid and long-short-dash lines indicate, $H_{c2}(0)$ is between 29 and 38 T for carbon-doped MgB_2.

The value $a_2=0.57$ here determined for carbon doped MgB_2 is almost an order of magnitude larger than the theoretical value for the pure material, $a_2=0.07$. This could reflect carbon-doping changing the interband coupling. Of course one must keep in mind the accuracy limitations on λ (determined by ab initio calculations) on which the a_2 value for pure MgB_2 is based.

The value of η determined in Ref. [17] for MgO doped MgB_2 is 0.1, three to four times larger than the value $\eta=0.029$ determined here. Also $\eta<1$ implies the scattering in the π-band is stronger than in the σ-band. This may seem contradictory to the expectation that carbon doping in the boron plane would most likely increase the scattering in the σ-band and probably leave π-band undisturbed. However, this phenomenon, that the scattering in the π-band is stronger than that in the σ-band after the boron plane is doped with impurities, has also been observed by Gurevich et al. [17]. One possible explanation offered by Ref. [17] is that the Mg plane becomes buckled after the boron plane is doped, which then causes more scattering in the π-band. This analysis does not take into account the interband scattering [16]. Since, T_c drops by 7 K after carbon-doping, including the interband scattering should give a more reliable estimate of the interband coupling constant.

In conclusion, $H_{c2}(T)$ of carbon-doped MgB_2 cannot be described by the WHH result for a one-gap superconductor, but it is well described by a model predication for a dirty two-gap superconductor. This indicates that the two-gap nature is preserved after carbon-doping, consistent with point contact [23], tunneling [24] and heat capacity [25] measurements on carbon-doped MgB_2. $H_{c2}(0)$ for carbon-doped MgB_2 is determined to be between 29 and 38 T, depending on the criterion of how T_c is determined. This range is significantly higher than that of the pure material ($\sim$15–23 T) [26,27]. This is consistent with recent reports on the upper critical field of dirty MgB_2 thin films [17,28], filaments [29], and single crystals [30,31] and makes dirty MgB_2 a very attractive candidate for magnetic applications.

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