Enhancement of the irreversibility field by carbon substitution in single crystal MgB$_2$

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Abstract

We report the detailed study of the irreversibility field $H_{irr}$ of single crystals of Mg(B$_{1-x}$C$_x$)$_2$ ($x=0$, 2, 3.5, 5 and 7%) in strong magnetic fields of up to 40 T. High sensitive torque measurements revealed that the $H_{irr}$ is greatly enhanced by a factor of two ($\mu_0 H_{irr}(0) \approx 33$ T in $x=5\%$) by carbon substitution compared to the pristine MgB$_2$ owing to a reduction in the inplane coherence length. We also observed the temperature-dependent $H_{irr}$ anisotropy in all the carbon contents. This fact strongly suggests that the two-gap superconductivity of MgB$_2$ is less influenced by a small amount of carbon substitution. We discuss these results focusing on the impact of carrier doping and impurity scattering on two-gap superconductor.

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It is widely accepted that MgB$_2$ is a two-gap superconductor based upon numerous experimental results. In MgB$_2$, two different order parameters reside on two types of distinct Fermi surfaces (FS) originating from two-dimensional (2D) $\sigma$ and three-dimensional (3D) $\pi$ bands, respectively. The $\sigma$ band, strongly coupled with the inplane $E_{2g}$ phonon mode, exhibits a larger superconducting gap than the $\pi$ band. The disparity between both bands suppresses impurity interband scattering that causes pair-breaking in a multigap superconductor, and thus two superconducting gaps with different energies are retained, even if the sample quality is not so high.

Carbon substitution for boron in MgB$_2$ is of great interest from the viewpoint of both carrier doping and impurity scattering in a multigap superconductor. Since carbon has one more electron than boron, it is expected that electrons are doped into the system by carbon substitution. This indicates that the hole $\sigma$ band dominating the superconductivity in MgB$_2$ is filled up, and thus the superconducting properties would be substantially modified. On the other hand, carbon substitution brings about inplane scattering. As mentioned above, if the interband impurity scattering rate is substantially increased, the two-gap model is no longer valid. Experiments with controlled impurity contents would be a critical test for the two-band model. Another interest in introduction of scattering centers is the enhancement of the upper critical field as usually seen in conventional superconductors. The improved superconducting properties are important from the viewpoint of practical application.

In the present study, we performed high sensitive torque ($\tau$) measurements with high quality single crystals of carbon-substituted MgB$_2$ in fields of up to 40 T and at low temperatures down to 0.5 K. In order to investigate the detailed physical properties of anisotropic materials such as MgB$_2$, single crystals are indispensable. In this paper, we report the detailed study of the irreversibility field $H_{\text{irr}}$, one of the most fundamental superconducting properties, of Mg(B$_{1-x}$C$_x$)$_2$ ($x=0$-7.5%). We find that $H_{\text{irr}}$ is enhanced by a factor of two in carbon-substituted sample, exceeding 30 T even at 4.2 K. We also observed a monotonous decrease in the $H_{\text{irr}}$-anisotropy $\gamma$ ($=H_{\text{irr}}^{ab}/H_{\text{irr}}^{c}$) with carbon content as well as the temperature-dependent $\gamma$ in all the carbon contents. We discuss these results focusing on the impact of carrier doping and impurity scattering on the two-gap superconductor MgB$_2$.

High quality single crystals of carbon-substituted MgB$_2$ were prepared by a high pressure...
Carbon contents were determined by Auger electron spectroscopy. Samples were of plate-like shape with shiny surfaces (the ab plane) with typical dimensions of $\sim 200 \times 200 \mu m^2$. In this torque study, we have measured a set of $Mg(B_{1-x}C_x)_{2}$ ($x=0, 2, 3.5, 5, \text{ and } 7.5\%$) (hereafter denoted as C0%, C2%, C3.5%, and so on). With increasing carbon content, the superconducting transition temperature $T_c$ monotonically decreased: $T_c=39 \text{ K}$ in C0% sample and $T_c=20 \text{ K}$ in C7.5% sample. Besides, the in-plane residual resistivity substantially increased more than by an order of magnitude in C7.5% sample compared to C0% sample. This is because boron atoms in the conducting layer are randomly replaced with carbon atoms.

High field torque measurement was performed with use of a commercial piezoresistive microcantilever \cite{18} (inset of Fig. 1). A sample is glued at the end of a cantilever beam with a small amount of epoxy. Dimensions of the microcantilever are $120 \times 50 \times 5 \mu m^3$, thus enabling us to measure very small samples such as MgB$_2$. A compensation lever is incorporated in the same platform for the purpose of eliminating temperature drift and magnetoresistance effect of piezoresistor. The eigenfrequency of 250-300 kHz is high enough to use in combination with a long pulse magnet with duration of 60 ms (maximum field of 42 T). The microcantilever was mounted on a rotating stage, and field orientation was changed with resolution of 1°. The polar angle $\theta$ is defined as the one tilted from the c axis.

Figure 1 shows the typical behavior of torque divided by field ($\tau/H$) of C0% sample at $\theta=75^\circ$ at different temperatures. Hysteretic behavior characteristic for type-II superconductor was observed below $T_c$. We define the irreversibility field $H_{irr}$ as the field where the hysteresis vanishes. The $H_{irr}$ determined in this way coincides with the field $H_{\rho \to 0}$ where the resistivity becomes zero. In this paper, we define $H_{c2}$ as the transition onset field and distinguish from $H_{irr}$. At elevated temperatures, the hysteresis becomes less pronounced, and thus the ambiguity in determining $H_{irr}$ is inevitably large near $T_c$. It is worth noting that the peak effect is clearly observed slightly below $H_{irr}$ as reported \cite{18}. The peak amplitude becomes small with temperature, and it is almost invisible above 25 K. The detailed analysis will be published elsewhere.

In determining the $H_{irr}$ in the highly symmetric directions such as $H\parallel c$ axis or $H\parallel ab$ plane, field orientation was set to be slightly off the direction (typically 1-2°). This is because when magnetic field is aligned to the principle axis, torque signals vanish in principle. The systematic error originating from this field misalignment is estimated to be less than 0.1%,
since the anisotropy $\gamma$ of carbon-substituted MgB$_2$ is modest (as discussed later, $\gamma \approx 2-6$) compared to high-$T_c$ cuprates giving $\gamma \sim 10-50$.

Shown in Fig. 2 are the main results of this paper, the temperature dependence of $H_{\text{irr}}$ in field orientations of $H \parallel ab$ and $H \parallel c$ at each carbon content. In C0% sample, the extrapolated $\mu_0 H_{\text{irr}} \parallel ab(0)$ and $\mu_0 H_{\text{irr}} \parallel c(0)$ are 16.4 and 2.9 T, respectively, both of which are in agreement with the previously reported values of single crystal [20, 21]. Surprisingly, C2% and C5% samples exhibit much higher $H_{\text{irr}}$ in both $H \parallel ab$ and $H \parallel c$ directions, though $T_c$'s are substantially decreased by carbon substitution: $\mu_0 H_{\text{irr}} \parallel ab(0)= 26.8$ T and $\mu_0 H_{\text{irr}} \parallel c(0)= 5.5$ T in C2% sample ($T_c=35$ K) and $\mu_0 H_{\text{irr}} \parallel ab(0)=33.4$ T and $\mu_0 H_{\text{irr}} \parallel c(0)=8.1$ T in C5% sample ($T_c=27$ K). With further increasing carbon content to 7.5% ($T_c=20$ K), $\mu_0 H_{\text{irr}} \parallel ab(0)$ decreased to $\sim 20$ T while $\mu_0 H_{\text{irr}} \parallel c(0)$ still increased to $\sim 9$ T [22]. This indicates that the zero-temperature anisotropy $\gamma(0)=H_{\text{irr}} \parallel ab(0)/H_{\text{irr}} \parallel c(0)$ is reduced to about 2 compared to $\gamma(0)=5.5$ in C0% sample. Figure 3 summarizes the experimental results shown in Fig. 2. Both $H_{\text{irr}} \parallel ab(4.2K)$ and $H_{\text{irr}} \parallel c(4.2K)$ exhibit a maximum at around 3.5%-carbon doping (Fig. 3(a)). So far, much effort has been devoted to increase the $H_{\text{irr}}$ for practical application. The present data give a high $H_{\text{irr}}$ value greater than 30 T even at 4.2 K in bulk single crystals, which exceeds the $\mu_0 H_{c2}(0)\sim 29$ T of Nb$_3$Sn [23]. $T_c$ and $\gamma$ monotonously decrease with carbon content in a similar manner (Fig. 3(c)). In the following, we explain these systematic changes from the viewpoint of carrier doping and impurity scattering caused by carbon substitution.

First, we discuss the enhancement of $H_{\text{irr}}$ by a factor of two by carbon substitution. To understand this, the change of coherence lengths becomes essential. Shown in Fig. 3(b) are the inplane and interplane coherence length $\xi_{ab}(4.2K)$ and $\xi_c(4.2K)$ derived from $H_{\text{irr}}$ according to the relations $\mu_0 H_{c2} \parallel c=\Phi_0/2\pi \xi_{ab}^2$ and $\mu_0 H_{c2} \parallel ab=\Phi_0/2\pi \xi_{ab} \xi_c$ by assuming $H_{\text{irr}}=H_{c2}$. Since $H_{\text{irr}}<H_{c2}$ in a real material, particularly for $H \parallel c$ [24, 25], the estimated $\xi_{ab}$ above is regarded as the uppermost value of the inplane coherence length. With increasing carbon content, the resistive transition width becomes narrower, and the broadening effect is small even in $H \parallel c$ [26]. Therefore, the error due to the difference between $H_{\text{irr}}$ and $H_{c2}$ is smaller in the higher carbon content region. The radical increase in $H_{\text{irr}}$ may be partly due to the reduction in the difference $H_{c2}-H_{\text{irr}}$

It is found in Fig. 3(b) that $\xi_{ab}$ monotonically decreases ($\xi_{ab}(4.2K)=10.5$ nm in C0% sample and $\xi_{ab}(4.2K)=6$ nm in C7.5% sample), while $\xi_c$ is almost constant at lower carbon
content, and is slightly increasing at higher carbon content. This drastic change in $\xi_{ab}$ indicates that carbon substitution has a strong influence on inplane properties as expected. A simple calculation gives that the inplane mean free path $\ell_{ab}$ for C0% sample reaches several ten nm, while it is reduced down to several nm for C7.5% sample owing to the increased impurity scattering rate [26]. This fact strongly suggests that a crossover from a clean superconductor to a dirty one occurs with carbon content. Therefore, it is considered that $H_{\text{irr}}$ is enhanced due to the reduced coherence length according to the well-known relation

$$\xi_{ab}^{-1} = \xi_{0ab}^{-1} + \ell_{ab}^{-1}$$

where $\xi_{0ab}$ is the inplane coherence length without impurity scattering. Since $H_{\text{irr}}$ also depends on $T_c$ (approximately $H_{\text{irr}} \propto T_c$), further carbon substitution, which decreases $T_c$, leads to manifestation of a maximum as shown in Fig. 3(a).

It is not straightforward to explain the reduction in $\gamma(0)$, because both of impurity scattering and electron doping may affect $\gamma(0)$. The increase of the interband impurity scattering rate $\Gamma_{\text{inter}}$ wipes out two-gap superconductivity due to mixing of 2D $\sigma$ and 3D $\pi$ bands, so that we expect the reduced $\gamma(0)$. However, the change of FS topography accompanied by doping is also directly reflected in $\gamma(0)$ (e.g. $\gamma(0)$ is given by a square root of effective mass anisotropy in a one-gap superconductor). To answer the question what is the main mechanism for the reduction in $\gamma(0)$, the temperature dependence of $\gamma$ in carbon-substituted samples is a critical test to evaluate the amplitude of interband impurity scattering rate $\Gamma_{\text{inter}}$. In a pure MgB$_2$, the contribution of the 3D $\pi$-band superconductivity is strongly suppressed in high magnetic fields, which result in a rapid increase in $\gamma$ with lowering temperature, followed by a saturation at low temperatures [27]. In a naive picture, if $\Gamma_{\text{inter}} \ll \Gamma_{\text{intra}}$, where $\Gamma_{\text{intra}}$ is the intraband impurity scattering rate, the system is still described by a two-gap model where $\gamma$ would be temperature dependent as in C0% sample, while if $\Gamma_{\text{inter}} \approx \Gamma_{\text{intra}}$, then the system would behave like a one-gap superconductor with temperature-independent $\gamma$.

Figure 4 shows the temperature dependence of the anisotropy $\gamma$ in each carbon content. Since ambiguity of $H_{\text{irr}}$ is not negligible in the high temperature region, the $\gamma$’s obtained from the resistivity measurements are plotted together. We confirmed that both of the torque and resistivity data give consistent $\gamma$ values in the intermediate temperature region. In C0% sample, our data showed significant temperature-dependent $\gamma$ values ranging from 2 to 5.5, which is consistent with the previous reports [6, 28]. With increasing carbon content, the value monotonously decreases, but still $\gamma$ is temperature-dependent in all the carbon content.
contents \((\gamma(\text{C2\%})=2.5, \text{ and } \gamma(7.5\%)=1.2)\). This results strongly suggest that the two-gap superconductivity picture is still valid in carbon-substituted samples, and that the smaller \(\pi\)-band gap is robust against carbon substitution in contrast to an appreciable decrease in the larger \(\sigma\)-band gap. Thus, we conclude that the situation \(\Gamma_{\text{inter}} \ll \Gamma_{\text{intra}}\) holds for small carbon contents. Therefore, the mechanism of the reduction in \(\gamma(0)\) is predominantly attributable to the effect of carrier doping. The evidences for electron doping are found in Hall coefficient \([26]\) and photoemission spectroscopy \([29]\) measurements indeed.

As demonstrated in the specific heat \([27]\) and discussed theoretically in Ref. \([30, 31]\), \(\gamma\) in the low temperature region is dominated by the anisotropy of the \(\sigma\) band. So, the reduced anisotropy \(\gamma(0)\) indicates more three-dimensional \(\sigma\) FS. According to the band calculation \([10]\), the \(\sigma\) band consists of a pair of quasi two-dimensional hole cylinders. When electrons are doped into a hole cylindrical FS, it gradually shrinks, then becomes an ellipsoidal FS, and is finally filled up completely. Therefore, we consider that the reduction in \(\gamma(0)\) primarily reflects the doping process into the \(\sigma\) band. This view is supported by the fact that C12\% sample shows completely isotropic behavior \([14]\).

Finally, we briefly mention the anomalous behavior of \(H_{\text{irr}}-T\) curves, especially in \(H||ab\) (Fig. 2). \(H_{\text{irr}}(\text{C0\%})\) and \(H_{\text{irr}}(\text{C2\%})\) show conventional negative curvatures, but \(H_{\text{irr}}(\text{C5\%})\) grows almost linearly, and \(H_{\text{irr}}(\text{C7.5\%})\) even exhibits a positive curvature down to the lowest temperature. Since the transition broadening is small for \(H||ab\) and becomes small both for \(H||ab\) and \(H||c\) in the high carbon contents, similar behavior is also expected in \(H_{c2}\). Here we remind that a positive curvature of \(H_{\text{irr}}\) was observed at temperature very close to \(T_c\) even in a pure MgB\(_2\) \([32]\). As is theoretically proposed \([33]\), it reflects the fact that \(H_{c2}\) is dominated by the \(\pi\)-band gap near \(T_c\), while, at \(T<T_c\), the \(\sigma\) band determines \(H_{c2}\). It is likely that the carbon substitution introduces scattering also in the \(\pi\) band and makes the \(\pi\)-band gap more robust against magnetic field. The change of \(H_{\text{irr}}-T\) curves observed in Fig. 2 can be understood as the evidence that carbon substitution widens the temperature range where \(H_{\text{irr}}\) is affected by the \(\pi\) band.

In conclusion, we have shown the enhancement of the irreversibility field \(H_{\text{irr}}\) at \(T=0\) by a factor of two by carbon substitution in single crystal of MgB\(_2\), although the transition temperature \(T_c\) monotonically decreases with substitution. The enhancement is explained by the crossover from the clean to the dirty limit regime where the in-plane mean free path \(\ell_{ab}\) is less than the coherence length \(\xi_{0ab}\) due to increased impurity scattering caused by carbon
substitution. The reduced anisotropy in $H_{\text{irr}}$ is ascribable to the reduced two-dimensionality of the $\sigma$ band as a result of electron doping. We also observed temperature-dependent anisotropy in all the carbon contents (C=0-7.5%), which strongly suggests that the two-gap superconductivity model is still valid in these carbon-substituted MgB$_2$.

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FIG. 1: Typical behavior of torque divided by field ($\tau/H$) in C0% sample at $\theta=75^\circ$ at different temperatures, where $\theta$ denotes the angle measured from the $c$ axis. Inset: scanning electron microscope image of a microcantilever. A MgB$_2$ single crystal is attached at the end of the cantilever beam.
FIG. 2: Temperature dependence of $H_{\text{irr}}^{\parallel ab}$ and $H_{\text{irr}}^{\parallel c}$ in (a) C0%, (b) C2%, (c) C5%, and (d) C7.5% samples.
FIG. 3: (a) The irreversibility field $H_{\text{irr}}^{\parallel ab}$, $H_{\text{irr}}^{\parallel c}$ at 4.2 K, (b) the coherence length $\xi_{ab}$, $\xi_c$ at 4.2 K, and (c) the transition temperature $T_c$ and the $H_{\text{irr}}$ anisotropy $\gamma$ at 4.2 K as a function of carbon content.
FIG. 4: Temperature dependence of $\gamma$ in C0%, C2%, C5%, and C7.5% samples. The data shown by open and solid symbols are obtained by resistivity and torque measurement, respectively. The solid lines are guides for the eye.