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Evidence for transformation from $\delta T_c$ to $\delta l$ pinning in MgB2 by graphene oxide doping with improved low and high field $J_c$ and pinning potential

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**Abstract**

Flux pinning mechanism of graphene oxide (GO) doped MgB$_2$ has been systematically studied. In the framework of the collective pinning theory, a B-T phase diagram has been constructed. By adjusting the GO doping level, the pinning mechanism in MgB$_2$ transformed from transition temperature fluctuation induced pinning, $\delta T_c$ pinning, to mean free path fluctuation induced pinning, $\delta l$ pinning, is observed. Furthermore, in terms of the thermally activated flux flow model, the pinning potential in high field ($B > 5$ T) is enhanced by GO doping. The unique feature of GO is the significant improvement of both low field Jc and high field Jc.

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Evidence for transformation from $\delta T_c$ to $\delta l$ pinning in MgB$_2$ by graphene oxide doping with improved low and high field $J_c$ and pinning potential

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Flux pinning mechanism of graphene oxide (GO) doped MgB$_2$ has been systematically studied. In the framework of the collective pinning theory, a $B$-$T$ phase diagram has been constructed. By adjusting the GO doping level, the pinning mechanism in MgB$_2$ transformed from transition temperature fluctuation induced pinning, $\delta T_c$ pinning, to mean free path fluctuation induced pinning, $\delta l$ pinning, is observed. Furthermore, in terms of the thermally activated flux flow model, the pinning potential in high field ($B > 5$ T) is enhanced by GO doping. The unique feature of GO is the significant improvement of both low field $J_c$ and high field $J_c$.© 2013 American Institute of Physics. [http://dx.doi.org/10.1063/1.4799360]

In type-II superconductors, due to its short coherence length, the most effective elementary interaction between vortex and pinning center is core interaction, which originates from the coupling of locally distorted superconducting properties with the periodic variation of the superconducting order parameter. Inhomogeneities in different parameters cause different "elementary pinning mechanisms." There exists two predominant mechanisms of core pinning, i.e., $\delta T_c$ pinning and $\delta l$ pinning. Whereas $\delta T_c$ pinning is caused by the spatial variation of the Ginzburg-Landau coefficient $\kappa$ associated with disorder in the transition temperature $T_c$, variations in the charge-carrier mean free path $l$ near lattice defects is the main cause of $\delta l$ pinning. For MgB$_2$ superconductor, it has been shown that $\delta T_c$ pinning is dominant in un-doped MgB$_2$ samples, and $\delta l$ pinning is dominant in carbon doped MgB$_2$ bulks, while $\delta T_c$ and $\delta l$ pinning coexist in silicone oil doped bulk samples. $\delta T_c$ and $\delta l$ pinning has not been observed.

Thermal energy may allow flux lines jump from one pinning site to another, which causes the finite resistivity below the transition temperature. It manifests a field-dependent broadening of the resistive transition. This phenomenon is very prominent in high temperature superconductors (HTSs) because of their large anisotropy induced by the two-dimensional (2D) structure and high transition temperatures. With a layer structure and relatively high $T_c$, thermally activated flux flow (TAFF) also results in the field-dependent broadening of the resistive transition in MgB$_2$. But it exhibits different behaviour compared to the high temperature superconductors. First, the pinning potential, $U_0$, is very large in low field, on the order of $10^4$ K; second, it exhibits very strong field dependence in high field. So far, research on MgB$_2$ has been focused on pristine samples, however, with only limited studies reported on doping effects on $U_0$. Due to lack of intrinsic pinning, the $J_c$ value of pristine MgB$_2$ drops very fast in field. Chemical doping by nano-SiC, Si, C, and other carbon or silicon containing dopants has shown positive effects on high field $J_c$ enhancement; however, the self field and low field $J_c$, as well as $T_c$, deteriorate. Recently, our team has found that graphene can improve $J_c$ at self field and low field with very little reduction in $T_c$, but its high field $J_c$ is not competitive with that of nano-SiC doped one. Also, we very recently found the graphene oxide (GO) doping can improve both the low and the high field $J_c$, which is different from the above dopants.

In this work, we represent systematical study on the flux pinning mechanism of GO doped MgB$_2$ with much improved low field and high field $J_c$. By analysis of the flux pinning mechanism, the vortex pinning diagram is derived. According to the collective pinning theory, by adjusting the doping level, the transformation from transition temperature fluctuation induced pinning, $\delta T_c$ pinning, to mean free path fluctuation induced pinning, $\delta l$ pinning, was observed. In addition, the pinning potential is enhanced in high field ($B > 5$ T) by GO doping.

Figures 1(a) and 1(b) show the magnetic field dependence of the critical current density $J_c$ for the un-doped and 1 wt. % GO doped MgB$_2$ samples at various temperatures. Fig. 1(a) shows the high field $J_c$ of the 1 wt. % GO doped sample is enhanced compared with the un-doped sample from 5 K up to 25 K. For example, at 5 K and 10 T, the $J_c$ for the un-doped sample is about 100 A/cm$^2$, approaching the irreversibility field, but with 1 wt. % GO doping, the $J_c$ is as high as 5200 A/cm$^2$, about 52 times greater. As shown in Fig. 1(b), the GO doping increases the impurity scattering, which can cause an increase in the upper critical field ($H_{c2}$) and higher irreversibility field ($H_{c1}$). In addition, the defects, smaller grain size, and/or strain caused by doping could also improve the $J_c$ in field. The enhanced $H_{c1}$ and $H_{c2}$ are shown in the inset of Fig. 1(a). Fig. 1(b) presents the low field $J_c$ for the un-doped and 1 wt. % GO doped samples. It can be seen that the low field $J_c$ for 1 wt. % GO addition is also improved compared with the un-doped sample. It is believed that the enhancement of $J_c$ at low field is due to the improvement in the grain connectivity, and we used Rowell’s model to calculate the effective conducting area or active fraction ($A_F$). Normally using the methodology of Rowell to estimate connectivity

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suggests that few alloyed samples of MgB$_2$ have connectivity fractions that exceed 0.1.\textsuperscript{25} In the inset in Fig. 1(b), it can be seen that the effective conducting area is improved by doping with GO, the 1 wt. % GO doped sample shows the best grain connectivity with $A_F$ value of 0.4 comparing with 0.135 of un-doped sample. But after that the effective conducting area shows a decrease, which could be because a high concentration of GO decreases the volume of the superconducting phase.

When the pinning is induced by uncorrelated disorder, the collective pinning theory has been proven very successful in describing the vortex behavior and analyzing the corresponding vortex pinning mechanisms in high temperature superconductors and MgB$_2$.\textsuperscript{1–3} According to this theory, the magnetic field dependence of $J_c$ obeys different laws in different magnetic fields. First, when the magnetic field is smaller than $B_{sb}$ (the crossover field from the single vortex to the small vortex bundle pinning regime), the $J_c$ is field independent, exhibiting a plateau in the $J_c/C_0$ vs. field diagram. Then, when $B > B_{sb}$ (in the small bundle pinning regime), $J_c(B)$ obeys an exponential law as

\[ J_c(B) = J_c(0) \exp\left(-\frac{B}{B_0}\right)^{3/2}, \quad (1) \]

where $B_0$ is a constant. In Fig. 2(a), we can observe the $J_c$ plateau in the GO doped MgB$_2$ sample, which corresponds to the single vortex pinning regime. Using Eq. (1) for the small bundle pinning to fit the $J_c$ curves, it can be seen that at intermediate field, the solid fitting lines fit the experimental data very well, while a deviation between the fitting line and the experimental data exists at low and high fields. In order to clearly determine the crossover field $B_{sb}$ from the single vortex pinning regime to the small bundle pinning regime, the data were replotted on a double logarithmic plot as $-\ln\left(J_c(B)/J_c(0)\right)$ vs. field, as shown in Fig. 2(b). At intermediate field, a straight line was clearly observed, corresponding to the small bundle pinning regime. The deviation at low field of the fitting line from the experimental data is $B_{sb}$. Meanwhile, the deviation at high field first is considered as the transition from the small bundle pinning to the large bundle pinning regime, although the high-field experimental data cannot be fitted by the power law of $J_c(B)$.

From Fig. 2(a), the irreversibility field, $H_{ irr}$, can also be determined by the criterion $J_c = 100$ A cm$^{-2}$, which is shown in Fig. 2(c). These data can be fitted by the following equation:
where $t = T/T_c$. The data indicate that giant flux creep also plays an important role in the 2 wt. % GO doped MgB$_2$ sample.\textsuperscript{26}

After deriving the $B_{sb}$, the crossover field to the thermal fluctuation regime ($B_{fl}$), $H_{irr}$, and $H_{c2}$, we can then try to construct the vortex phase diagram, as shown in Fig. 2(d), where $H_{c2}$ is deduced using the criteria of 0.9 of $\rho (H,T)$ at the transition to superconductivity by measuring the resistivity at varying temperatures and fields. Below $B_{sb}$, there is a single vortex pinning regime, while the small bundle pinning regime is in between the $B_{fl}$ and $B_{sb}$. There exists a small regime between $B_{fl}$ and $H_{c2}$ governed by the thermal fluctuation effect. Above the $H_{irr}$ and below the $H_{c2}$ is the vortex liquid pinning regime, and above the $H_{c2}$, there is the normal state regime. Compared with the un-doped sample, the GO doped sample shows a wider vortex phase region due to the enhanced flux pinning and $H_{c2}$, which also can be seen in silicone-oil-doped samples.\textsuperscript{5}

Griessen et al.\textsuperscript{27} derived that in the single vortex regime of a system with randomly distributed weak pinning centers, for $\delta l$ pinning and $\delta T_c$ pinning, the $J_c$ obeys the following laws, respectively:

$$J_c(t)/J_c(0) = (1 - t^2)^{5/2} (1 + t^2)^{-1/2}$$

and

$$J_c(t)/J_c(0) = (1 - t^{27/6}) (1 + t^2)^{-5/6},$$

where $t = T/T_c$.

With this model, the $\delta l$ pinning was found to be the dominant pinning mechanism in YBa$_2$Cu$_3$O$_{7-x}$ (YBCO) films, and $\delta T_c$ pinning dominates in single domain (Y, Pr)$_{123}$.\textsuperscript{27,28} For MgB$_2$, $\delta T_c$ pinning and $\delta l$ pinning are, respectively, found in un-doped and carbon doped samples, and $\delta T_c$ and $\delta l$ pinning coexist in silicone oil doped bulk samples.\textsuperscript{3-5} So far, however, there has been no report on systematical transformation of the pinning mechanism by using one dopant. Here, we observed that depending on the doping level of GO, the pinning mechanism is systematically transformed from $\delta T_c$ to $\delta l$ pinning. We used the two equations given above to fit the experimental data. Clearly, it can be seen that in Fig. 3(a), the data for the un-doped sample are well fitted by the $\delta T_c$ pinning model, which is consistent with Ref. 3; in Fig. 3(b), the data for the 1 wt. % GO doped sample are in between the $\delta T_c$ and $\delta l$ fitting lines, which means that both $\delta T_c$ and $\delta l$ pinning play an important role; and Fig. 3(c) shows that the 2 wt. % GO doped sample is dominated by $\delta l$ pinning. In Fig. 3(d), we use the normalized temperature dependence to give a clearer picture of the different temperature dependence of $J_c$ for the un-doped, and the 1 wt. % and 2 wt. % GO doped samples. The transformation from the $\delta T_c$ pinning to $\delta l$ pinning is in a good agreement with the varying trend in the residual resistivity ratio (see Fig. S1(b) of the supplemental material).\textsuperscript{32} That is, with increasing doping level, the RRR becomes smaller, and the electron scattering becomes stronger, therefore, decreasing the charge carrier mean free path and increasing the $\delta l$ pinning. This result can be ascribed to the low dimensionality of GO, which carries both C and O into the MgB$_2$ formation process. The simultaneous formation of MgB$_2$ with C incorporation, in combination with the formation of highly dispersed MgO within the MgB$_2$ matrix, results in multiple types of pinning centers, which are GO doping level dependent. Therefore, through adjusting the doping level, the electron scattering intensity can be tuned effectively.

Now, let us discuss the GO doping effect on the pinning potential based on the TAFF model. The field-dependent broadening of the resistive transition for the layered superconductors is interpreted by the dissipation of energy caused...
by thermally activated flux flow, which can be described by the Arrhenius law, \( \rho(T) = \rho_0 \exp(-U_0/k_BT) \), where \( U_0 \) is the flux-flow activation energy and derived from the slope of the linear part of an Arrhenius plot, \( \rho_0 \) is a parameter, and \( k_B \) is Boltzmann’s constant.\(^1\)\(^6\) This phenomenon was previously observed in the layered cuprate superconductors, un-doped bulk and thin film MgB\(_2\), and iron based superconductors,\(^5\)\(^-\)\(^10\) but reports of doping effects on the pinning potential are very limited for MgB\(_2\). Fig. S2 in the supplemental material shows that the \( T_c \) is broadened upon applying magnetic field.\(^2\)\(^2\) The transition width, defined by 90\% to 10\% of the corresponding resistivity transition, is about 0.99 K at zero field, while it is 3.85 K in 13 T.\(^2\)\(^2\) We replotted the data as \( \ln \rho \) vs. \( 1/T \), as shown in Fig. 4(a). The linear part of the transition is clearly observed, corresponding to the thermally activated flux flow regime. The pinning potential \( U_0 \) is obtained by calculating the slope. The \( U_0 \) values of other samples are also obtained by the same method. In Fig. 4(b), our results show that the \( U_0 \) values of the un-doped and doped MgB\(_2\) samples exhibit a plateau in low field (\( B < 1 \) T), but drop very fast in high field. In low fields, the pinning potential gradually decreases with increasing doping level. In high field, for the 0.5 wt. \% GO doped sample, the field dependence of the pinning potential is similar to that of the un-doped sample; whereas for the 1 wt. \% and 2 wt. \% GO doping samples, the \( U_0 \) shows different field dependence and is much larger than for the un-doped sample in high field (\( B > 5 \) T). Compared with the power law field dependence of the activation energy, \( U_0 (B) \propto B^{-n} \) with the exponent \( n < 1 \), which is usually observed for other layered systems, such as HTS and iron based superconductors.\(^6\)\(^-\)\(^9\) MgB\(_2\) shows similar behavior in low field, but in high field it exhibits a much stronger field dependence (\( B > 1 \) T), which is consistent with MgB\(_2\) films. The strong field dependence in high field can be fitted by the exponential law: \( U_0 \approx 10^{-k}B^0 \), where \( k \) is the fitting parameter and \( B \) is the magnetic field. From the inset of Fig. 4(b), while there is deviation in low field between the fitting line and the experimental data for the un-doped, and the 0.5 wt. \% and 1 wt. \% GO doped samples, for the 2 wt. \% sample, the fitting line is in good agreement with the experimental data both at low and at high fields.

In conclusion, we have systematically studied the flux pinning mechanism of GO doped MgB\(_2\). By GO doping, \( J_c \) is enhanced significantly both at low and high fields, which is due to the improvements in grain connectivity, \( H_{J_c} \), and \( H_{J_c} \). In the framework of the collective pinning theory, a \( B-T \) phase diagram has been derived for GO doped MgB\(_2\). By adjusting the GO level, the pinning mechanism transforms from \( \partial T \) to \( \delta I \) pinning. Furthermore, in terms of the TAFF model, the pinning potential in high field (\( B > 5 \) T) is enhanced by GO doping.

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22See supplementary material at http://dx.doi.org/10.1063/1.4799360 for experimental method, X-ray diffraction and resistivity results, and field-dependent broadening of transition temperature.