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Graphene micro-substrate induced high electron-phonon coupling in MgB2

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**Publication Details**

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Abstract
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Graphene micro-substrate induced high electron-phonon coupling in MgB$_2$

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Abstract—Electron-phonon coupling (EPC) strength was studied in graphene-MgB$_2$ composites to explore the possibilities for a higher superconducting transition temperature ($T_c$). For the first time in the experimental work on MgB$_2$, the Raman active $E_{2g}$ mode was split into two parts: a softened mode corresponding to tensile strain and a hardened mode attributed to the carbon substitution effect. The tensile strain effect is suggested to improve $T_c$ of graphene-MgB$_2$ composites because it increases the EPC strength of MgB$_2$.

Index Terms—Raman spectroscopy, electron-phonon coupling, superconductivity, MgB$_2$

I. INTRODUCTION

SELF-OPTIMIZATION of intermetallic MgB$_2$ compound in terms of both electronic structure and phonon dispersion has left only a slight margin for further enhancement in the superconducting transition temperature, $T_c$, above ~39.4 K [1]. Higher $T_c$ of Mg$_{10}$B$_2$ and band structure calculations have indicated that MgB$_2$ is a Bardeen-Cooper-Schrieffer (BCS)-Eliasberg superconductor with two superconducting gaps and strong electron-phonon coupling (EPC): the superconducting bands consist of the strong coupling $\sigma$-band and the weakly coupling $\pi$-band [2]. The dominant nature of the $\sigma$-band is attributed to its coupling with B-B stretch modes, since the boron layer is responsible for the $E_{2g}$ symmetry mode, the only Raman active phonon mode [3]. Chemical substitution and external pressure compress the MgB$_2$ lattice with a Grüneisen parameter, $\gamma$, of 2.0–4.0 to stiffen the $E_{2g}$ mode and reduce its contribution to the EPC [4]. Tensile strain has been proved to be effective in increasing the $T_c$ to as high as 41.8 K in MgB$_2$ thin films on SiC substrates with a softened $E_{2g}$ mode [5]. Substrates with a slightly larger biaxial lattice constant than bulk MgB$_2$, such as AlN, GaN, Al$_x$Ga$_{1-x}$N, and Mg$_{1-x}$Ca$_x$B$_2$, have also proven to be effective candidates to induce tensile strain in MgB$_2$ thin films [6]. Graphene, which has been proved to introduce a strong flux pinning force into MgB$_2$ [7], is another potential substrate for this purpose. Alternating MgB$_2$ and graphene layers has also been suggested to expand the lattice parameters by a factor of 1.1% in bulk MgB$_2$ [8]. In this work, the $T_c$ behavior was studied, based on the two-gap feature and the phonon dispersion in graphene-added MgB$_2$, with the graphene doping level up to 20 wt% via the diffusion method. It was found that the tensile strain effect was the dominant effect in the 5 wt% low graphene added MgB$_2$, compensating for the carbon substitution effect, based on the X-ray diffraction (XRD) results. The most exciting result came with the observed softening of the $E_{2g}$ mode in graphene-MgB$_2$ composites, which might lead to possible higher $T_c$ values in graphene-MgB$_2$ composites if the processing conditions are optimized. Although tensile strain effects are clearly demonstrated in the composites, judging from the phonon behavior, graphene added samples showed no sign of $T_c$ improvement, due to the strong dominance of carbon substitution and impurity scattering.

II. EXPERIMENTAL SECTION

Graphene-MgB$_2$ composites were fabricated via a diffusion process using ball-milled crystalline boron powder (0.2 to 2.4 $\mu$m, 99.999%), with graphene (micrometer extent, supplied by Prof. J. Stride) added up to 20 wt% in a toluene medium. Then, the vacuum dried powders were mixed and pressed into pellets 13 mm in diameter by 1 mm in thickness. The pellets were sealed in an iron tube filled with Mg powder (-325 mesh 99%) and sintered at 850°C for 10 hrs in a quartz tube furnace with a heating rate of 5°C/min in high purity argon (Ar 99.9%) flow. Based on their graphene contents of 0, 0.5, 1, 2, 3, 5, 10, and 20 wt%, the samples were denoted as G000, G005, G010, G020, G030, G050, G100, and G200 in the following context, respectively.

All samples were characterized by X-ray diffraction (XRD, D/max-2200), and the crystal structure was refined with the aid of JADE 5.0 software. The microstructures were observed with field emission scanning electron microscopy (SEM, JSM-6700F) and the transmission electron microscopy (TEM: JEOL-2010). The $T_c$ values were deduced from the temperature dependence curves of AC susceptibility, which were measured using a Physical Properties Measurement System (PPMS: Quantum Design). The Raman scattering was measured by a confocal laser Raman spectrometer (Renishaw inVia plus) with a 100× microscope. The 514.5 nm Ar$^+$ laser was used for excitation, with the laser power maintained at about 20 mW, measured on the laser spot on the samples, in order to avoid laser heating effects on the studied materials. Several spots were selected on the same sample to collect the Raman signals in order to make sure that the results were consistent.
III. RESULTS AND DISCUSSION

According to the XRD patterns, no second phase was found in G000-G030, as shown in the left inset of Fig. 1. A trace of MgB$_2$C$_2$ was observed in G050, and the amounts became significant in G100 and G200 due to the high graphene contents. A small amount of MgO can also be found in G100 and G200. The refinement results also show little difference in the length of the c-axis parameter, as shown in Fig. 1. The a-axis shrinkage can be deduced from both the refinement results and obvious shifts of the (1 1 0) planes with graphene addition, as shown in the right inset of Fig. 1. Carbon substitution on the boron sites in the MgB$_2$ lattice leads to lattice contraction, due to the fact that the length of the C-B bond, 0.172 nm, is shorter than that of the B-B bond, 0.178 nm. Compared with nanocarbon doped MgB$_2$ [9-11], the lattice parameters estimated from the XRD patterns show weak dependence on the graphene content compared with MgB$_2$ doped with normal carbon, as shown in Fig. 1. The small variation in the a lattice parameter in the graphene-MgB$_2$ can be attributed to either the expanding effect of tensile strain or the weak carbon substitution effect, similar with the magnetic processing effect of carbon nano tube doped MgB$_2$ [12-14].

![Graphene-MgB$_2$ XRD patterns](image1.png)

Fig. 1. The effects of graphene addition in MgB$_2$ on the refined lattice parameters, which are comparable with those of carbon [9-11]. The lattice parameters of pure MgB$_2$ are $a = 0.3084$ nm and $c = 0.3525$ nm, respectively. The left inset shows the X-ray diffraction patterns of graphene-MgB$_2$ composites indexed with MgB$_2$, MgB$_2$C$_2$, and MgO, and the right inset shows the diffraction peak shift of the (1 1 0) and (0 0 2) planes of MgB$_2$.

The magnetic transition temperature, $T_c$, shows slightly higher values compared with the $T_c$ in nano-carbon doped samples at the same doping levels [9-11]. It should be noted that the $T_c$ depression on graphene is concave up, which means that $T_c$ depression is restrained by the graphene micro-substrates compared with previous reported work on other forms of carbon, as shown in Fig. 2. The $T_c$ dependences on the lengths of a-axis for different carbon sources are compared in the inset of Fig. 2. It clearly shows that the $T_c$ depends greatly on the lattice parameter for all carbon sources. Figs. 3(a)-3(c) show the SEM images of graphene, G000, and G050. The micrometer extent of graphene is much bigger than the grain sizes of G000 and G050, 200-400nm, which means that the graphene sheets are big enough acting as micro-substrates for MgB$_2$ crystals. Figs. 3(d)-3(g) show the TEM and high resolution transmission electron microscopy (HREM) images of G000 and G050. Both the TEM and HREM images of G000 show homogeneous structure with low density of defects. However, G050 has relatively higher density of defects. It should be noted that the order of fringes varies from grain to grain, indicates that the defect is due to highly anisotropic of the interface. Similar fringes have been reported in the MgB$_2$ where these fringes were induced by tensile stress with dislocations [5]. As the graphene-MgB$_2$ composites were sintered at 850 °C for 10 hrs, the samples are expected to be well crystalline and contain few defects. The large amount of defects and amorphous phases on the nanoscale are attributed to the residual thermal strain between the graphene and the MgB$_2$ during cooling process because the thermal expansion coefficient of graphene is very small while that for MgB$_2$ is large and highly anisotropic. The in-plane lattice parameter, $a$, is 0.246 nm for graphene, which has a C-C bond length of 0.142 nm, which is much shorter than the a-axis parameter of MgB$_2$, 0.3084 nm. The a-axis length would be shrinking due to lattice mismatch if MgB$_2$ crystals were grown on graphene along the c-axis. However, the mismatch is relaxed due to the weak interlayer coupling, and an expanded MgB$_2$ lattice is generated in proper supercell structures [8]. It should be noted that such a complex supercell structure is very hard to synthesize by the current solid state reaction method. What we can imagine is that MgB$_2$ crystals grow on the graphene surfaces, which act as micro-substrates in the polycrystalline composite.

![TEM and HREM images](image2.png)

Fig. 2. Comparison of the effects of graphene and carbon addition in MgB$_2$ on the critical transition temperature [9-11]. The normalized moment dependence on temperature is shown in the inset.

To confirm the effects of tensile strain on the EPC, Raman scattering was employed to examine the phonon properties. Fig. 4(a) shows the typical Raman spectrum of pure MgB$_2$, which consists of three broad peaks. The most prominent phonon peak located at lower frequency ($\omega_2$: centered at ~600 cm$^{-1}$) is assigned to the $E_{2g}$ mode [3],[15]. The other two Raman bands, ($\omega_1$: centered at 400 cm$^{-1}$ and $\omega_4$: centered at 730 cm$^{-1}$) are attributed to the phonon density of states (PDOS) due to disorder [3],[16, 17]. The EPC strength in MgB$_2$ depends
greatly on the frequency and full width at half maximum (FWHM or $\Gamma$) of the $E_{2g}$ mode [18], while the other two modes, especially the $\omega_3$ mode, are responsible for the $T_c$ depression in chemically doped MgB$_2$ [4]

![Fig. 3. SEM images of graphene (a), G000 (b), and G050 (c); and TEM and HRTEM images of (d), (e) G000 and (f), (g) G050.](image)

![Fig. 4. Influence of graphene content on the Raman spectra of graphene-MgB$_2$ composites, with measurement at room temperature. The spectra are fitted with $\omega_1$, $\omega_2$, and $\omega_3$, arising from the sampling of the phonon density of states due to disorder, and $\omega_4$ and $\omega_5$, representing the split $E_{2g}$ mode.](image)

Graphene addition to MgB$_2$ induces splitting of the $E_{2g}$ mode, resulting in one softened mode ($\omega_2$) and another hardened mode ($\omega_3$). The strong tensile strain stimulates the shift of $\omega_2$ to lower frequency with increasing graphene addition. The softening of the $E_{2g}$ mode was previously observed only in MgB$_2$–SiC thin films due to tensile-strain-induced bond-stretching, which resulted in a $T_c$ as high as 41.8 K [5]. $\omega_2$ modes are dominant in the low graphene content samples, and no substantial drop in $T_c$ was observed. This is in agreement with the energy gap behavior, as with carbon substitution induced band filling and interband scattering. According to the McMillan-Allen-Dynes analysis [19, 20], $T_c = \omega_c e^{-f(\lambda, \mu)}$, where $\omega$ is the phonon frequency, $f(\lambda, \mu) = (1 + \lambda) / (1 - \mu)$, where $\mu$ is equal to the Coulomb repulsion, $\mu^*$ and $\lambda$ is EPC strength. The EPC due to the $\sigma$-band and the bond-stretching mode becomes

$$\omega \propto \frac{m^* [P]}{M \omega^2},$$

where the $\sigma$-band effective mass $m^*$ is proportional to the density of states (DOS) of holes in the $\sigma$-band at the Fermi level, $D$ is the $\sigma$-band deformation potential, and $M$ is the B mass. A change in $T_c$ can arise from any combination of changes in $\omega$, $D$, $m^*$, or $\mu$. In strained MgB$_2$, a small deviation in $\Delta a$ and $\Delta c$ of the lattice constants results in the variation of $\lambda$, $\omega_{E_{2g}}$, $\mu^*$, and $T_c$. The change in $T_c$ can be expressed as

$$\frac{\Delta T_c}{T_c} = \frac{\Delta \omega_{E_{2g}}}{\omega_{E_{2g}}} - \alpha \frac{\Delta \mu^*}{\mu^*} + \beta \frac{\Delta \lambda}{\lambda}$$

with

$$\alpha = \frac{1.04(1 + \lambda_0)(1 + 0.62 \lambda_0)}{\left[ \lambda_0(1 - 0.62 \mu_0) - \mu_0^* \right]^2}, \quad \beta = \frac{1.04 \lambda_0(1 + 0.38 \mu_0^*)}{\left[ \lambda_0(1 - 0.62 \mu_0) - \mu_0^* \right]^2},$$

and

$$\frac{\Delta \lambda}{\lambda} = \frac{\Delta N_\sigma(E_F)}{N_\sigma(E_F)} + \frac{2 \Delta [D]}{[D]} - 2 \frac{\Delta \omega_{E_{2g}}}{\omega_{E_{2g}}} \cdot$$

All variables with subscript 0 are for strain-free MgB$_2$. It is clear that the enlarged lattice parameter and low frequency $E_{2g}$ mode induced by tensile strain will surely enhance the EPC of MgB$_2$. However, the lattice shrinkage and the high frequency $\omega_3$ peak induced by unavoidable C substitution effects counteract the possibility of increased $T_c$ in graphene-MgB$_2$ composites. $\omega_3$ is marginal in G100 and vanishes in G200. $\omega_3$ is gradually shifted to higher frequency in low graphene content samples because the tensile strain has confined the lattice shrinkage. The tensile strain cannot counteract the intensive carbon substitution effects when graphene content is higher than 10 wt%, and $\omega_3$ cannot counteract the intensive carbon substitution effects and C substitution, as well as the competition between $E_{2g}$ and other modes. The contributions of $\omega_2$ and $\omega_3$ to the strength of EPC($\lambda$), where $\lambda$ is the electron-phonon coupling constant, can be estimated by the Allen equations,

$$\Gamma_2 = 2 \pi \lambda_0 N(E_F) \omega_{E_{2g}}^2$$

and

$$\Gamma_3 = 2 \pi \lambda_0 N(E_F) \omega_{E_{2g}}^2,$$

respectively [18, 21], where $\Gamma_2$ and $\Gamma_3$ represents the FWHM of $\omega_2$ and $\omega_3$, respectively, in the Raman spectra and $N(E_F)$ is the density of states (per spin per unit energy per unit cell) on the Fermi-surface. The $N_\sigma(E_F)$ and $N_\sigma(E_F)$ dependences on $T_c$ were

![Diagram](image)
deduced from the results in the literature [22], as shown in the inset of Fig. 5, and \( N(E_F) = [N_d(E_F) + N_s(E_F)]/2 \) because only one spin was considered in the estimation [16, 23]. The estimated values of \( \lambda_2 \) and \( \lambda_3 \) are plotted in Fig. 5. Consistent with the decay of \( \lambda_2 \), \( \lambda_2 \) decreases from 2.41 in G000 to 0.92 in G100, which is attributed to the narrowed \( \Gamma_2 \). \( \lambda_3 \) increases from 0.65 in G005 to 1.36 in G100 before it drops to 0.81 in G200. Although the tensile strain should be more significant in the high graphene content samples due to the increased contact area between the graphene and the MgB₂, the effect of tensile strain on the superconductivity is counteracted by the carbon substitution, which introduces chemical pressure due to lattice shrinkage. Furthermore, the impurity scattering effects of residual graphene, MgB₂C₂, and MgO become significant in low \( T_c \) samples.

Fig. 5. Electron-phonon coupling constants \( \lambda_2 \) and \( \lambda_3 \) for \( \omega_2 \) and \( \omega_3 \) calculated as a function of \( T_c \) according to the Allen equation. The inset shows the calculated densities of states at the Fermi energy for the \( \sigma \)- and the \( \pi \)-band, \( N_d(E_F) \) and \( N_s(E_F) \), as a function of \( T_c \) [22].

IV. CONCLUSIONS

In summary, tensile strain, which increases the EPC strength of MgB₂, was unambiguously detected in graphene-MgB₂ composites made by the diffusion process. The bond-stretching \( E_g \) phonon mode splits into a softened mode due to the tensile strain and another hardened mode due to the carbon substitution on boron sites. Up to 5 wt% of graphene addition is recommended to improve the superconductivity of MgB₂. Higher \( T_c \) values are expected in graphene-MgB₂ composites processed using optimized techniques or doped with stabilized high purity graphene to avoid C substitution.

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