Increased superconductivity for CNT doped MgB2 sintered in 5T pulsed magnetic field

Wenxian Li  
*University of Wollongong, wenxian@uow.edu.au*

Ying Li  
*Shanghai University*

Rong Hua Chen  
*Shanghai University*

Rong Zeng  
*University of Wollongong, rzeng@uow.edu.au*

Lin Lu  
*University of Wollongong, ll972@uowmail.edu.au*

See next page for additional authors

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Authors
Wenxian Li, Ying Li, Rong Hua Chen, Rong Zeng, Lin Lu, Yun Zhang, Michael Tomsic, Matthew Rindfleisch, and S. X. Dou
Abstract—The superconductivity of carbon nanotube (CNT) doped MgB$_2$, sintered in pulsed magnetic field (PMF) was investigated with Raman scattering measurements and Raman spectral fit analysis. Although the carbon (C) substitution for the boron (B) is increased for the sample sintered in PMF, its superconductivity is advanced compared with the sample sintered without PMF. The improved critical transition temperature, $T_c$, is attributed to the strengthening of the electron-phonon coupling (EPC) in MgB$_2$, as reflected by the broadened $E_{2g}$ mode in the Raman spectra, because the carbon atoms are homogeneously distributed in the boron planes.

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

I. INTRODUCTION

The MgB$_2$ superconductor has attracted intense scientific interest on superconductivity research and development due to the surprisingly high critical transition temperature for a binary system ($T_c = 39$ K) [1]. There has not much exciting result been reported except that $T_c$ is higher by $\sim 1$ K for the Mg$_{10}$B$_2$ comparing with Mg$_{11}$B$_2$ [2] and the onset $T_c$ is 41.8 K for the strained MgB$_2$ thin film [3]. To improve the application temperature of MgB$_2$, we report a method which takes the advantages of magnetic field processing to advance the superconductivity of MgB$_2$ [4]. Electromagnetic inductive dopants in liquid Mg can be induced easily by the applied magnetic field during the in-situ reaction process. The presence of liquid phase provides an opportunity for applying magnetic field processing technique to achieve crystalline refinement, homogeneous distribution of additives and inclusions, and alignment of both matrix materials and additives. Although the mechanism is still ambiguous, there is evidence that the $T_c$ values are improved slightly for chemically doped MgB$_2$ sintered in 5 T pulsed magnetic field (PMF) [5]–[8]. To understand the $T_c$ enhancement in MgB$_2$, we have conducted Raman spectroscopy on CNT doped MgB$_2$ sintered in PMF. The $T_c$ improvement is explained by the stronger electron-phonon coupling (EPC) reflected in Raman spectra.

II. EXPERIMENTAL SECTION

Magnesium powders (99%) and amorphous boron (99%) were well mixed with 5wt% multi-wall carbon nanotube (CNT) (OD: 20 nm and length: 0.5–2 $\mu$m) in glove box under argon atmosphere. The mixtures were ground sufficiently long and then pressed into pellets of 10 mm in diameter and about 5 mm in thickness under the pressure of $\sim 600$ MPa. Some of the pellets were sintered in a tube furnace at 800 $^\circ$C for 30 min under 5 T PMF ($H_{1x}$), and then furnace-cooled to room temperature. A flow of high purity argon gas was maintained throughout the sintering process. The same process was repeated on the other pellets without PMF for reference purposes.

All samples were characterized by X-ray diffraction (XRD, Dmax-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). 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 100x 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

Fig. 1 shows the indexed XRD patterns of the pellets processed at 800 $^\circ$C for 30 min in 0 and 5 T PMF, respectively. The patterns of both samples represent a single phase of MgB$_2$ except a small amount of MgO. The diffraction peak centers of crystal planes (1 0 0) and (0 0 2) do not show obvious shifts with the different process. The lattice parameters calculated from the XRD patterns show that the $a$-axis lattice parameter of the sample sintered in 5 T PMF ($a = 3.0758$ Å, $c = 3.5240$ Å, $V = 28.87$ Å$^3$) is a little smaller than that of the sample sintered without PMF ($a = 3.0780$ Å, $c = 3.5236$ Å, $V = 28.91$ Å$^3$). Although the decrease of the lattice parameter is not so obvious, it is evidence for the more intensive substitution of carbon (C) atoms from the CNT for boron (B) atoms in the MgB$_2$ lattice [9]. It can be estimated from the $a$-axis length that the molecular formula is MgB$_{1.075}$C$_{0.025}$ for the sample sintered in 5 T PMF, while the C content is 0.020 for the sample sintered without
PMF. The increased C substitution for B comes from the more contact chances of the CNT and Mg-B mixture.

As good conductors with anomalous decrease of the electrical resistivity with increasing temperature [10], CNTs will induce pulsed eddy currents ($\mathbf{j}_e$) in PMF. The pulsed eddy currents, in turn, induce Lorentz force ($\mathbf{f}_L$). The Lorentz force is defined as $\mathbf{f}_L = \mathbf{j}_e \times \mathbf{B}$. Referencing the Maxwell equation $\nabla \times \mathbf{B} = \mu_0 \mathbf{J}$, the Lorentz force can be written as $f = -(1/2 \mu_0) \nabla \mathbf{B}^2 + (1/\mu_0) \mathbf{B} \cdot \nabla \mathbf{B}$. CNTs will be driven to move in the mushy environment of melting magnesium by the Lorentz force, which enhances carbon substitution for boron because of the increased contact area between the CNT and the MgB$_2$ during the reaction. At the same time, the liquid magnesium is also driven by the Lorentz force. In order to investigate the CNT response on the PMF, microstructures of the pellets processed with and without PMF were detected by SEM. Fig. 2 shows the typical SEM images of the cross sections of those samples. Although both samples have well-grown and well-connected grains, the CNTs in the two samples show very different situations. The sample processed without PMF shows inhomogeneous microstructure. Some of the CNTs have converged at certain points out of the MgB$_2$ matrix. The CNTs’ surfaces are clear and their outside diameters are almost as the same as that of the raw materials. In contrast, Fig. 2(b) shows homogeneous microstructure for the sample processed in 5 T PMF. The CNTs are embraced in the continuous MgB$_2$ matrix. The MgB$_2$ grows adhering on the CNTs framework while the microdroplets caused by volume contraction during in situ reaction are distributed in the framework’s interspaces. The improved microstructure is an evidence that both the CNTs and the Mg droplets have been driven to move during the in situ reaction. Due to the anisotropy of the susceptibility, composites align in high magnetic fields ($H > 1T$) when the anisotropy energy, $\nabla E = \mu_0 \nabla \chi V H^2_\alpha /2$ is larger than the energy of thermal disordering effects, $\sim kT$, where $V$ is the volume of an individual particle, $H_\alpha$ is the applied magnetic field, and $\Delta \chi = \chi_\parallel - \chi_\perp$ is the anisotropy of susceptibility [11]. Studies on the normal state magnetism of MgB$_2$ show that the net susceptibility will be very small, of the order of $10^{-6}$ atomic units [12]. Furthermore, the size of each of the crystallites is very small (about $\leq 200$ nm). These factors may account for the absence of crystalline orientation in MgB$_2$ processed in PMF. According to previous researches, any chemical substitutions for magnesium or boron will suppress the $T_c$ performance of MgB$_2$ superconductor [13]. Yeoh et al. have also studied the superconductivity dependence on the $\alpha$-axis value for the CNT substitution effects and the drop in $T_c$ value from ~37.8 K to ~34.8 K with $\Delta \chi$ of $\sim$ $0.13 \AA$ [14]. In contrast with these results, the AC susceptibility reveals that the sample sintered in 5 T PMF shows higher onset $T_c$, ~36.3 K, as indicated in Fig. 3. A phenomenological explanation for the $T_c$ abnormality is the effect of magnetic shielding due to the improved connectivity of the MgB$_2$ matrix based on the observation of micro-structure as shown in Fig. 2.

To explain the $T_c$ enhancement, Raman scattering was employed to examine the EPC intensity. Fig. 4 contains the fitted ambient Raman spectra of CNT doped MgB$_2$ sintered at 800°C for 30 min with and without PMF. The MgB$_2$ spectra were fitted in the range of 250–1000 cm$^{-1}$ by a function used successfully in strongly correlated systems for estimating broad Raman spectra [15]

$$S(\omega) = [1 + n(\omega)] \left[ \frac{A_\omega \Gamma}{\omega^2 + \Gamma^2} + \sum_{i=1}^{N} \frac{A_{\omega_i} \Gamma_{i}}{(\omega^2 - \omega_i^2)^2 + \omega^2 \Gamma_{i}^2} \right]$$

where the quantity $[1 + n(\omega)] = [1 - \exp(-\hbar \omega/k_B T)]^{-1}$ is the Bose-Einstein thermal population factor. The first term in (1) represents the low frequency electronic contribution to Raman scattering due to the wide and unstructured electronic background in strongly correlated systems, where $A_\omega$ and $\Gamma$ are the peak and linewidth. The sum in the second term accounts for the high frequency contribution to Raman scattering from all three fitting phonon peaks, where $\omega_i$, $A_{\omega_i}$, and $\Gamma_{i}$ are the peak frequency, amplitude, and linewidth, respectively. The consistency between the experimental data and the fitting curve was quite good in all the investigated samples, as shown in Fig. 4.
There are three fitting peaks in the measurement range from 250 cm$^{-1}$ to 1000 cm$^{-1}$ centered at about 400–415 cm$^{-1}$ ($\omega_1$), 580–590 cm$^{-1}$ ($\omega_2$), and 770–800 cm$^{-1}$ ($\omega_3$), respectively, as well as a very weak electronic background. The frequencies of the $\omega_1$, $\omega_2$, and $\omega_3$ peaks are in accordance with those observed in the phonon density of states derived from neutron scattering experiments, where different optical contributions have been found around 430, 620, 710, and 780 cm$^{-1}$ [16]. Owing to the simple hexagonal structure (space group $P6_3/mmm$), four optical modes at the $\Gamma$ point of the Brillouin zone are predicted for MgB$_2$: a silent $B\bar{3}g$ mode (at 87.1 meV, $\sim 700$ cm$^{-1}$), the $E_{2g}$ Raman mode (at 174.5 meV, $\sim 600$ cm$^{-1}$), and the infrared active $E_{3u}$ (at 40.7 meV, $\sim 330$ cm$^{-1}$) and $A_{2u}$ (at 49.8 meV, $\sim 400$ cm$^{-1}$) modes, where only the $E_{2g}$ mode is Raman active and strong coupling to the electronic conduction $\sigma$-bands is predicted. In theoretical calculations on the ab initio band structure to describe the EPC between the electronic bands and the phonon $E_{2g}$ mode in MgB$_2$, the frequency of the harmonic $E_{2g}$ mode is located at 515–665 cm$^{-1}$ [17], which is in agreement with $\omega_2$ in this study. The $\omega_1$ and $\omega_3$ peaks are understood to arise from sampling of the phonon density of states (PDOS) due to disorder. The $E_{2g}$ mode is intimately linked to the superconductivity of the MgB$_2$, while the other two modes, especially the $\omega_3$, are responsible for the $T_c$ depression in the chemically doped MgB$_2$ [18].

The superconductivity of MgB$_2$ can be indicated in part by the phonon frequency and lifetime. The dependence of the peak center shift $\Delta\omega_i = \omega_{i,PMF} - \omega_{i,NPMF}$ on the $T_c$ for $\omega_1$, $\omega_2$, and $\omega_3$ is presented in Fig. 5(a), where $\omega_{i,PMF}$ and $\omega_{i,NPMF}$ represent the peak center values of samples sintered with and without PMF. The $E_{2g}$ frequencies for both samples are stable, whereas $\omega_1$ increases and $\omega_2$ decreases, respectively. In the previous studies on the Raman spectra of carbon doped MgB$_2$, the frequencies of $\omega_2$ and $\omega_3$ shifted to higher energy with the increasing carbon substitution for the boron [19], [20], which is different with the results of this research. Although the carbon substitution effect is increased for the CNT doped MgB$_2$ sintered in PMF, the anomalous behavior of $\omega_3$ indicates that the sample possesses stronger EPC than the one sintered without PMF, because of the improved crystallinity in PMF [21].

So far as the phonon linewidths $\Gamma_i$ are concerned, as shown in Fig. 5(b), the $\Gamma_1$ and $\Gamma_3$ are smaller in the high $T_c$ sample, whereas the $\Gamma_2$ is enhanced. The significant broadening of this $\omega_2$ peak arises mainly from the exceptionally strong EPC of the $E_{2g}$ mode with the partially occupied planar boron $\sigma$ bands near the Fermi surface [22]. The EPC intensity and crystal distortion will influence the Raman shift and the linewidth of the Raman scattering, which can give some insight into the competition between the $E_{2g}$ mode and the other modes. Theoretical calculations performed recently by Calandra et al. have demonstrated that the broadened Raman data on MgB$_2$ can be explained if dynamical effects beyond the adiabatic Born-Oppenheimer approximation and electron lifetime effects are included in the phonon self-energy, without invoking anharmonicity [23]. This is consistent with the later harmonic phonon dispersion results obtained from inelastic X-ray scattering [24]. The broad $\Gamma_2$, the softness of $\omega_3$, and the narrow $\Gamma_1$ and $\Gamma_3$ in the high $T_c$ sample indicate that high $T_c$ is apt to exist in less disorder sample.

Although the higher $T_c$ existing in the MgB$_2$ with more C substitution can be explained by the Raman analysis as due to the strong EPC, it is still an open problem why the sample with more C substitution displays more harmonic Raman features. Considering the following reaction:

$$\text{MgI}(s) + 2\text{B}(s) \rightarrow \text{MgB}_2(s)$$

where solid state MgB$_2$ forms on the liquid-solid interface of the Mg-B mixture. The B will be partially replaced by C if there are CNTs on the interface during the reaction. However, it is hard for C to go through the interface to substitute for the B in the crystal. The C substitutions for B occur mostly on the interface, as shown in Fig. 6(a). This phenomenon is consistent with the inhomogeneous nature of C substitution for B, as demonstrated by electron energy loss spectroscopy (EELS) measurements for nano-SiC doped MgB$_2$ [25]. For chemically doped MgB$_2$, the disorder is mainly associated with the crystal distortion and changes in the valence electron. The high C content areas in the matrix show great crystal distortion, because the C-B bond length, about 1.71 Å, is smaller than the B-B bond length (2.8 Å) [26]. At the same time, every C atom offers one more valence electron to the system, which will change the electronic structure and Fermi surface of the crystal. These areas will depress the $T_c$ performance of the surrounding MgB$_2$ as agglomerate inclusions. For the sample processed in 5 T PMF, the C substitution sites are distributed homogenously on the B

![Fig. 4. Normalized Raman spectra with fitted $E_{2g}$ mode ($\omega_2$), PDOS distortion ($\omega_1$ and $\omega_3$), and electronic scattering background for the samples sintered without PMF (a) and in 5 T PMF (b).](image)

![Fig. 5. Dependence of the fitted peak center shift $\Delta\omega_i$ (a), the fitted FWHM (b), and the ratios of the integrated intensities (c) of $\omega_1$, $\omega_2$, and $\omega_3$ on the $T_c$ for the samples sintered with and without 5 T PMF.](image)
plane, because the raw materials and resultant MgB$_2$ crystallites can be mixed by the Lorentz force during the in situ reaction, so that the sintering process is independent of energy-consuming solid-phase diffusions, as shown in Fig. 6(b). Although more C atoms have diffused into the MgB$_2$, the influences on the electronic structure and Fermi surface induced by these dispersive C atoms is weaker, so its superconductivity is better than that of the uneven C substitution sample. Based on the above analysis, the C distribution in the boron planes is an important factor which will determine the Raman feature. The broadened $\Gamma_3'$ in Fig. 5(b) comes from the harmonic behavior of the electronic structure and Fermi surface, which is responsible for the strength of EPC.

IV. CONCLUSION

Summarizing, magnetic field processing technology is a powerful tool to improve the superconductivity performance of CNT doped MgB$_2$ superconductor. The strength of the EPC, which is related to the linewidth of the $E_{2g}$ mode, is the dominant factor that determines the $T_c$ of MgB$_2$. The influence of the PDOS peaks, $\omega_1$ and $\omega_2$, on the EPC strength becomes weak for the sample processed in 5 T PMF. The homogeneously distributed C in the B plane during the in situ reaction is responsible for the more harmonic Raman spectra.

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