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2005 J. Phys.: Condens. Matter 17 3285

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Raman scattering investigation of electron–phonon coupling in carbon substituted MgB_2

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Received 18 February 2005, in final form 25 April 2005

Published 13 May 2005

Online at stacks.iop.org/JPhysCM/17/3285

Abstract

Room temperature Raman scattering measurements have been carried out on well characterized samples of $\text{MgB}_{2-x}\text{C}_x$. The Raman line corresponding to the E_{2g} phonon mode shows progressive hardening from 620 cm^{-1} in pristine MgB_2 to 775 cm^{-1} in the sample with carbon fraction $x = 0.2$. The corresponding line width on the other hand increases from a value of about 220 to 286 cm^{-1} in samples with $x = 0.1$, beyond which it decreases to a value of 167 cm^{-1} for $x = 0.2$. From the average mode frequency and the line width obtained from Raman measurements and taking the values of $N(0)$ obtained from the calculated variation in σ -hole density of states in $\text{MgB}_{2-x}\text{C}_x$, the electron–phonon coupling strength to the E_{2g} phonon, λ_{2g} , is evaluated using Allen’s formula. This remains large for low C fraction, but shows a rapid decrease for $x > 0.10$. Using this value of λ_{2g} appropriately weighted, T_C is obtained from McMillan’s equation. These values are in good agreement with the experimentally measured T_C variation in $\text{MgB}_{2-x}\text{C}_x$.

1. Introduction

The discovery of superconductivity at 39 K in MgB_2 [1] has attracted much attention not only because of the unusual two-gap nature of superconductivity in this system [2], but also because of the possibility of attaining high critical fields [3]. In this connection a vast literature is now accruing on the increase in the critical fields consequent to C substitutions [4, 5], with H_{C2} as large as 32 T. The synthesis of C substituted MgB_2 was much debated. Consequent to several experimental investigations [6–8], there is now a consensus that the T_C and the a -lattice parameter are well established functions of the carbon fraction. Further, the T_C and a -lattice

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parameter show a definite correlation irrespective of the method of synthesis [9–11]. From these experimental results it is now clear that the T_C of MgB_2 with ~ 10 at.% of the B substituted with carbon is 22 K. This decrease in T_C to 22 K is much smaller than that expected from rigid band behaviour. Understanding the T_C dependence and robustness of two-gap superconductivity in carbon doped MgB_2 [12, 13] has motivated several band structure calculations [14–17]; in particular, the effect of electron doping on the σ band has been investigated in [16]. These calculations indicate that for $x = 0.2$ in $\text{MgB}_{2-x}\text{C}_x$ (corresponding to 10 at.% C substitution) the σ -band holes are still present and that for $x = 0.4$ they completely vanish at E_F . It is also suggested that electron–phonon coupling strength mediated by the E_{2g} bond-stretching mode should increase substantially [16] for small C substitutions.

This E_{2g} mode is Raman active [18, 19] and couples strongly with the σ -band holes leading to a high T_C of 39 K in MgB_2 . Thus the role of Raman scattering in understanding superconductivity in MgB_2 is expected to be significant, and such studies have been extensive [20]. The E_{2g} mode in MgB_2 appears at ~ 600 cm^{-1} , which is much lower than in the isostructural, non-superconducting AlB_2 sample wherein it appears at 980 cm^{-1} . This phenomenal softening of the E_{2g} bond stretching mode and excessive broadening (~ 200 cm^{-1}) is understood as largely due to electron–phonon coupling [21]. The E_{2g} mode has also been investigated using inelastic x-ray scattering (IXS) [22], the results of which clearly indicate that the observed broadening of 20–28 meV along the Γ –A line is primarily due to electron–phonon (e–p) coupling and not due to anharmonicity, since the magnitude of the latter is only ~ 1.2 meV at 300 K. Evolution of the Raman mode as a function of pressure up to 15 GPa in pure MgB_2 [23] indicated a large mode Gruneisen parameter. Raman scattering studies have also proven to be useful in studying the phonon behaviour in substituted MgB_2 . Systematic studies on $\text{Mg}_{1-x}\text{Al}_x\text{B}_2$ as a function of x revealed that the E_{2g} phonon frequency softens from 980 cm^{-1} in pure AlB_2 to 600 cm^{-1} in MgB_2 and the corresponding line width increases from 40 cm^{-1} to a value greater than 200 cm^{-1} [24]. Such studies on C substituted MgB_2 are limited. Arvanitidis *et al* reported Raman studies in polycrystalline C substituted MgB_2 samples restricted to a low concentration of $x = 0.08$ [25]. Lee *et al* [26] reported Raman spectra for high carbon composition up to $x = 0.25$, in single-crystalline form. In the present work we study the evolution of the E_{2g} phonon with C substitution in $\text{MgB}_{2-x}\text{C}_x$ for a wide range of composition. Measurements have been carried out on well characterized samples [6, 11]. From the observed frequency and the line width variations of the Raman shift, and the calculated σ -hole density of states, the e–p coupling strength is evaluated as a function of carbon fraction. This variation of e–p coupling is suitably incorporated in the McMillan equation for calculating T_C . The agreement between the measured T_{CS} and those calculated as above is found to be satisfactory.

2. Experimental details

The samples of $\text{MgB}_{2-x}\text{C}_x$ for $x = 0.0$ – 0.06 used in the present investigation have been synthesized at 900 °C, under 50 bar Ar pressure [6], and those with $x > 0.06$ were prepared by reaction of elemental constituents at 1250 °C in sealed Ta tubes [11] and were characterized by measuring the superconducting transition temperatures T_C and lattice parameters. The samples were phase pure and had sharp superconducting transitions. The a -lattice parameters were used to determine the exact C stoichiometry, using the procedure outlined in [4]. T_C was obtained from the temperature of the onset of diamagnetism. T_C versus a -lattice parameter showed a correlation similar to that in single crystals [11]. Raman measurements were carried out on the as-prepared chunks. A 532 nm laser source of power 15 mW was used to excite the Raman line. Scattered light was detected using a CCD based (ANDOR technology) home

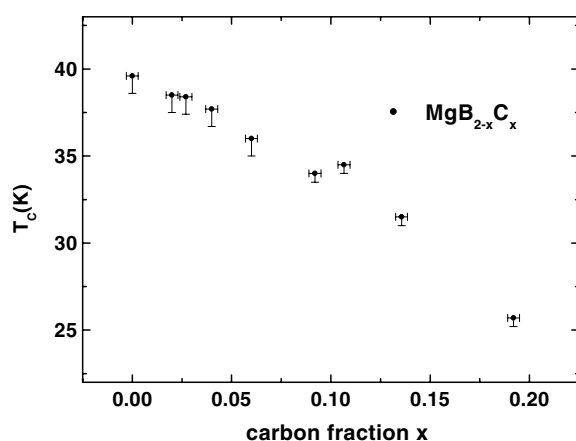


Figure 1. The superconducting transition temperature T_C as a function of the actual carbon fraction, as obtained from Δa - x correlation of [4].

built [27] Raman spectrometer with 600 lines mm^{-1} grating together with a super-notch filter covering the range of 200–1750 cm^{-1} . On each sample several measurements were carried out at different spots. Raman spectra obtained from different regions of the sample were similar, implying a good homogeneity of the sample. The Raman spectrum could be fitted to a Gaussian/Lorentzian line shape. It was noted that for substitutions up to $x = 0.04$ the Lorentzian fits were better, whereas for higher concentrations the fits to the Gaussian line shape was better. In the present work, all the spectra are fitted using a single Gaussian profile, and the parameters from the fit are used for further analysis.

3. Results

T_C , obtained as the onset of diamagnetic signal, for various carbon fractions x is shown in figure 1. The observed T_C dependence on x is in excellent agreement with those reported in the literature [11]. The Raman spectra of some representative samples, after subtracting a linear background, are shown in figure 2. The mode frequency and the linewidth in pristine MgB₂ in the present work are close to those reported by Renker *et al* [21] in polycrystalline samples. The line shape in the pristine sample, however, is nearly symmetric. For higher carbon fraction, the average phonon frequency is obtained by fitting the profile to a single Gaussian, which is also shown as solid line in figure 2. It is clear from the figure that the peak position shifts to a higher wavenumber with increasing C content and the width increases. The variations of the frequency and linewidth as a function of carbon fraction are shown in figures 3(a) and (b) respectively. With increasing carbon fraction, the mode frequency shows an increase for concentrations up to $x = 0.05$, and remains nearly constant over the range $x = 0.06$ – 0.10 . Beyond $x = 0.1$ the frequency increases continuously and has a value of 775 cm^{-1} for $x = 0.2$. The line width gradually increases from 220 cm^{-1} to a maximum value of 286 cm^{-1} at carbon fraction of $x \sim 0.1$ (figure 3(b)), beyond which it shows a precipitous drop to 167 cm^{-1} . This behaviour is qualitatively similar to the earlier single-crystal work, wherein Lee *et al* [24] observed a broad peak for $x = 0.1$, with peak position $\sim 800 \text{ cm}^{-1}$, which narrows considerably for $x = 0.25$ in the non-superconducting sample. Arvanitidis *et al* [25] reported that the spectra could be fitted to two components, one corresponding to the E_{2g} phonon and other due to the peak in the phonon density of states. While the former shows broadening followed by a narrowing with increasing C substitution, the peak due to phonon DOS shows a monotonic increase in width with C substitution. Thus, considering the overall

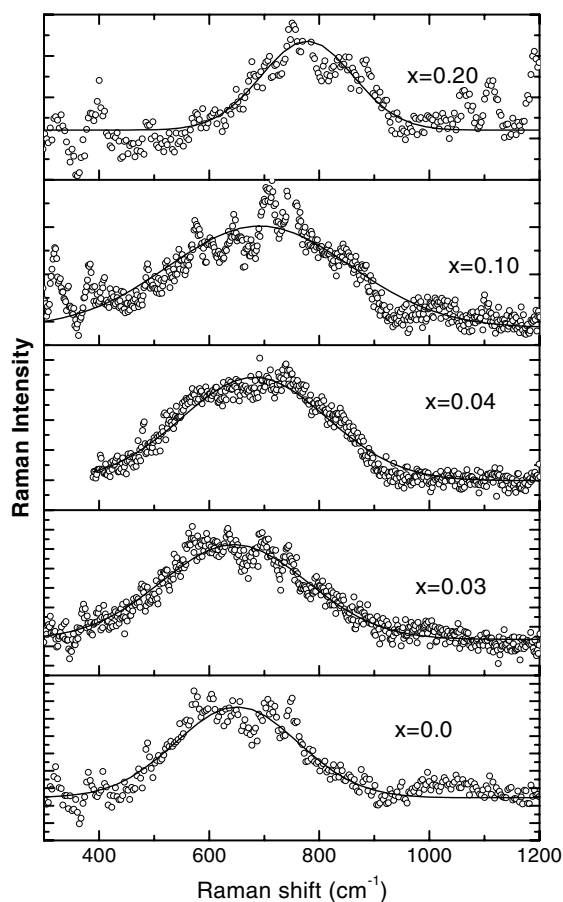


Figure 2. The Raman spectra in $\text{MgB}_{2-x}\text{C}_x$ for the various carbon fractions x . Solid lines are fits to Gaussians.

linewidth dependence on C doping, an initial broadening followed by narrowing is clearly noted in the present work as well as the earlier work [24, 25]. This is qualitatively similar to the behaviour in $\text{Mg}_{1-x}\text{Al}_x\text{B}_2$, wherein line broadening was noted for increasing Al content up to $x = 0.3$ [21], beyond which there is considerable narrowing.

At higher carbon compositions, typically above $x = 0.1$, the Raman spectrum is noted to have relatively sharp bands around 640, 696 and 740 cm^{-1} riding on a broad profile. The positions of these peaks are very close to those in the calculated phonon density of states reported by Osbourn *et al* [28]. Further, impurity phases like MgB_2C_2 lead to strong intensities in the range 1000–1300 cm^{-1} , the absence of which suggests that these peaks are rather due to phonon density of states appearing in the Raman spectrum due to increasing disorder and not from impurity phases.

4. Discussion

Increase in the phonon frequency due to carbon doping has contributions from a decrease in the a -lattice parameter and changes from altered e–p coupling. Variation in mode frequency arising solely from change in a -lattice parameter (brought about by the application of pressure) is shown as a solid line in figure 3(a). This accounts for an increase in the mode frequency from 620 to 675 cm^{-1} for $x = 0.2$. The corresponding increase in line width expected is about

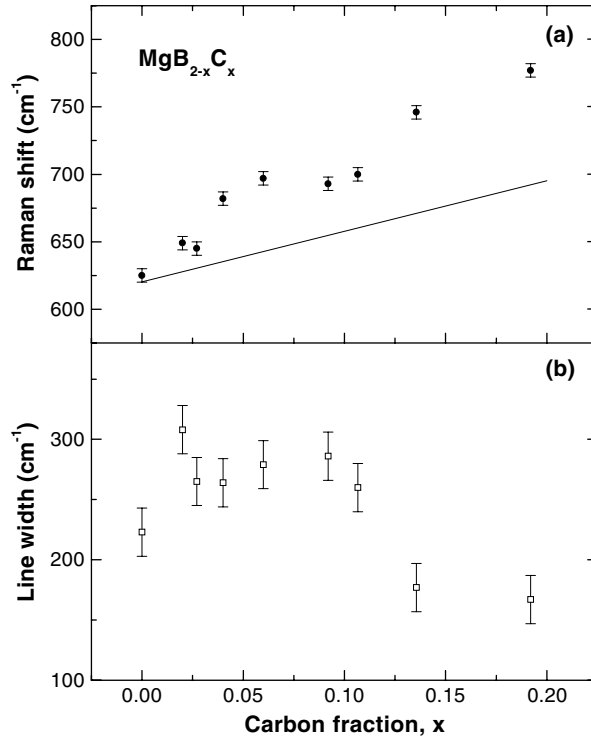


Figure 3. (a) Variation phonon frequency ω with C fraction x in $\text{MgB}_{2-x}\text{C}_x$. The solid line indicates the expected variation due to change in a -lattice parameter based on mode Gruneisen parameter reported in [25]. (b) Variation in the full width at half maximum, γ , with x in $\text{MgB}_{2-x}\text{C}_x$.

10 cm^{-1} . These values are small compared to the changes observed due to carbon substitution, as shown in figures 3(a) and (b), implying that contributions to the changes in γ and ω arise largely due to changes in the electronic structure, namely, due to electron doping rather than due to lattice contraction.

As mentioned in the introduction, it is now widely accepted that the significant softening of the in-plane bond stretching frequency in MgB_2 is attributed to the strong electron–phonon coupling and, consequently, to a high value of the transition temperature T_C . Conversely, an increase in E_{2g} phonon frequency is believed to be correlated to a reduced T_C [25, 26]. A small, but definite, increase in T_C compared to the bulk in strained MgB_2 films grown on SiC substrate [29] is understood along similar lines. Increases in the phonon frequency in carbon-substituted samples in the earlier work [25, 26] were also attributed to a reduced electron–phonon coupling and in turn to a decreased T_C . However, one has to consider the dependence of the e–p coupling strength λ on x in order to understand the T_C dependence on x . Taking a cue from IXS analysis, Allen’s formula [30] is used to relate the line width, γ , to the Raman shift, ω , namely,

$$\gamma = 2\pi\lambda_{2g}N(0)\omega^2 \quad (1)$$

where $N(0)$ is the total density of states at E_F and λ_{2g} is the electron– E_{2g} phonon coupling strength. The quantity γ/ω^2 obtained from the present work is plotted in figure 4, as a function of the carbon fraction x . It can be seen from the figure that γ/ω^2 does not show any significant change over the range $x = 0.0$ – 0.10 , remaining at $\sim 4.5 \text{ eV}^{-1}$; but beyond $x = 0.1$, it drops to

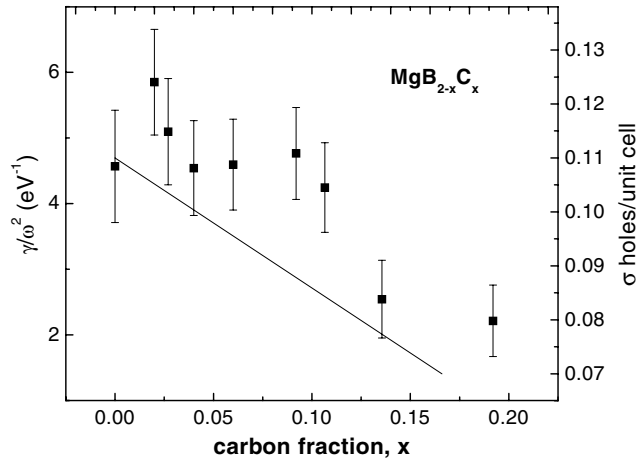


Figure 4. Variation of γ/ω^2 as a function of carbon fraction x in $\text{MgB}_{2-x}\text{C}_x$. The calculated variation [16] in the σ -hole density with x is shown as a solid line.

$\sim 2.0 \text{ eV}^{-1}$. The calculated variation of the number of holes in the sigma band [16] as a function of carbon content, assuming a linear interpolation to be valid for intermediate compositions, is also shown in figure 4 as a solid line.

For pristine MgB_2 the total DOS at E_F is taken as $N(0) = 0.354$ states/eV fu spin, with the contribution from the σ band being 0.15 states/eV fu spin and that from the π band being 0.204 states/eV fu spin [17, 32]. Upon C substitution it is assumed that the π band contribution to the hole DOS $N(0)$ remains constant and that only the σ band contribution to $N(0)$ varies. Taking the cue from the calculation [16] it is argued that the σ -hole DOS is proportional to the number of holes in the σ band. The latter has been calculated for $x = 0$ and 0.167 using a supercell method [16]. Using a linear interpolation to obtain the σ -band contribution to $N(0)$ as a function of C content, the solid line shown in figure 4 is obtained. Adding to this a constant term due to the π band (0.204 states/eV fu spin), we obtain the dependence of $N(0)$ on x .

Knowing γ/ω^2 and $N(0)$ as a function of x , λ_{2g} is evaluated using equation (1). λ_{2g} thus obtained is shown in figure 5, from which it is clear that the electron–phonon coupling strength remains high for small C substitutions up to $x = 0.1$, beyond which it shows a precipitous fall. It is noteworthy that the value of λ_{2g} obtained for pristine MgB_2 , namely 2.04 ± 0.4 , is very close to 2.5 ± 1.1 obtained for the $q = 0.2\Gamma\text{--}A$, E_{2g} phonon from inelastic x-ray scattering measurements [22]. It may be mentioned that the calculations indicated that λ_{2g} would diverge for low carbon substitution, which is however not noted in figure 5. Further, the calculations [16] suggested that there would not be a significant shift expected in the phonon frequency with C substitution. On the other hand, experimental results clearly indicate that there is indeed a significant shift in the peak position, which cannot be fully accounted for from lattice contraction alone, implying that the reduction in hole density does affect the peak position in this system.

It is well known that apart from the electron coupling to the E_{2g} phonon, determined from Allen’s formula, the λ_{tot} that enters McMillan equation has contributions from other phonons as well. So, λ_{tot} arises from E_{2g} phonons and other phonons, namely, $\lambda_{\text{tot}} = \lambda_{2g} + \lambda_{\text{other}}$. Further, to obtain reasonable values of T_C , λ values from E_{2g} and other phonons in pristine MgB_2 is restricted to be 0.4, in accordance with Pickett *et al* [31]. Scaling the λ_{2g} for all C fraction results in the evaluation of λ_{tot} as a function of C content. Using this value of λ_{tot} and

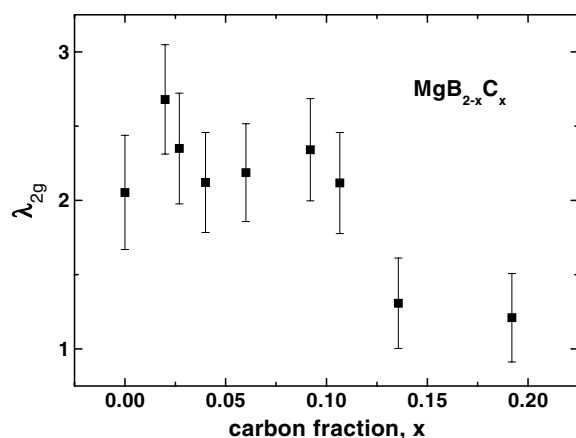


Figure 5. Variation of λ_{2g} with carbon fraction in $\text{MgB}_{2-x}\text{C}_x$.

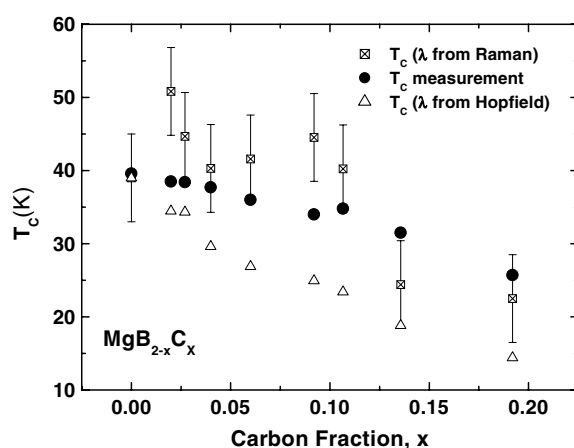


Figure 6. T_C dependence on x in $\text{MgB}_{2-x}\text{C}_x$ calculated from the λ_{2g} variation obtained from Raman data, and from the Hopfield expression. The experimentally measured T_C is also shown for comparison.

$\mu^* = 0.1$ in the McMillan equation, T_C is evaluated for various x and is shown in figure 6. The experimentally measured T_C is also shown in figure 6 for comparison. A large increase in the calculated T_C for the $x = 0.02$ sample is a direct consequence of the rather large linewidth at this composition.

It is also possible to obtain λ_{2g} from the well known Hopfield expression $\lambda_{2g} = N_\sigma(0)\langle I^2 \rangle / M\omega^2$, where $N_\sigma(0)$ is the σ -band hole DOS at E_F , $\langle I^2 \rangle$ the electron–phonon matrix element averaged over the Fermi surface, M the atomic mass and ω the phonon frequency corresponding to the E_{2g} mode. Taking into account the variation of the σ -band hole DOS at E_F and the E_{2g} phonon frequency variation as a function of carbon content x from figure 3, it can be seen from calculations similar to that described earlier that T_C decreases from 39 to 14 K for $x = 0.2$, a reduction much larger than that observed in experiments, as shown in figure 6. On the other hand, λ_{2g} , obtained using Allen’s formula, which incorporates changes in both the line width and the frequency, leads to a T_C variation closer to that observed in $\text{MgB}_{2-x}\text{C}_x$.

5. Summary

Raman scattering measurements were carried out at room temperature in $\text{MgB}_{2-x}\text{C}_x$ samples for $x = 0.0$ – 0.2 . The average phonon frequency increases with C substitution, whereas the

linewidth increases to a maximum for $x = 0.1$, beyond which there is a decrease. The electron- E_{2g} phonon interaction parameter λ_{2g} is extracted using Allen's formula [29]. The value for λ_{2g} thus obtained in pristine MgB_2 is in good agreement with that obtained from x-ray inelastic scattering [24]. By suitably incorporating the $\lambda_{2g}(x)$ variation in λ_{tot} appearing in McMillan's equation, the variation of $T_C(x)$ is calculated, which compares well with the measured T_C in $\text{MgB}_{2-x}\text{C}_x$.

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