Role of the $E_{2g}$ phonon in the superconductivity of MgB$_2$: a Raman scattering study

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Temperature-dependent Raman scattering studies in polycrystalline MgB$_2$ (10 < $T$ < 300 K) reveal that the $E_{2g}$ phonon does not experience any self-energy renormalization effect across the superconducting critical temperature $T_C \approx 39$ K, in contrast with most of the current theoretical models. In the presence of our results, those models must be reviewed. The analysis of the temperature dependence of the $E_{2g}$ phonon frequency yields an isobaric Grüneisen parameter of $|\gamma_{E_{2g}}| \lesssim 1$, smaller than the value of 3.9 obtained from isothermal Raman experiments under pressure. It is suggested that this apparent disagreement can be explained in terms of pressure-induced changes of the topology of the Fermi surface.

PACS numbers: 74.25.Jb;74.25Kc;63.20.Kr
Keywords: inelastic light scattering, superconductors, phonons

MgB$_2$ has attracted much recent interest due to its remarkable physical properties such as: i) relatively high superconducting transition, $T_C = 39$ K, for a binary compound with a simple crystal structure, ii) large and anisotropic coherence lengths, critical fields and current densities, and iii) critical currents that are not limited by grain boundaries (absence of weak link effects).[1]

MgB$_2$ forms in a hexagonal structure with space group $P6/mmm (D_{6h})$. The B atoms are located on a primitive honeycomb lattice consisting of graphite-type sheets. The B$_2$-layers are intercalated with Mg-layers that also form a honeycomb lattice with a Mg atom in the center. For this space group, factor-group analysis predicts four modes at the $\Gamma$ point: $E_u + A_{2u} + E_{2g} + B_{1g}$, where only the $E_{2g}$ mode is Raman-active and the $B_{1g}$ mode is silent. The $E_{2g}$ phonon is a doubly degenerate in-plane B-B bond-stretching mode with nonvanishing Raman tensor elements ($\alpha_{xx} - \alpha_{yy}$) and $\alpha_{xy}$. First principles lattice dynamics calculations indicate that these modes would be observed at 327 cm$^{-1}$($E_u$), 405 cm$^{-1}$($A_{2u}$), 572 cm$^{-1}$($E_{2g}$) and 702 cm$^{-1}$($B_{1g}$).[2]

In analogy with high $T_C$ superconductors (HTS), Hall effect measurements indicate that the charge carriers in MgB$_2$ are holes with a hole density at 300 K of 1.7 – 2.8×10$^{23}$ holes/cm$^3$. In fact, hole-mediated superconductivity has been proposed by An and Pickett for MgB$_2$. [3] These authors attribute the relatively high value of $T_C$ to the strong coupling between holes and the in-plane boron phonon, $E_{2g}$ modes. According to this model, the holes originate in the $\sigma$ ($sp^2$ orbitals) bands due to charge transfer from the $\sigma$ bands to the $\pi$ ($p_z$ orbitals) bands. Based on this model, several papers have discussed the possibility of $E_{2g}$ phonon being a frozen-in mode, strongly coupled to the $\sigma$ electronic bands near the Fermi level.[2][3][4][5] It is claimed that the $E_{2g}$ phonon, due to its rather strong coupling to the $\sigma$ electronic bands, would be highly anharmonic, presenting a very large linewidth. However, Boeri et al [6] pointed out that neither the presence at the Fermi level of the $\sigma$ bands nor their strong coupling to the $E_{2g}$ phonon are sufficient to induce such anharmonic effects, and therefore, the strong anharmonicity would be mainly related to the small value of the $\sigma$ conduction holes Fermi energy ($\approx 0.45$ eV) in the unperturbed crystal. Boeri et al also predicted similar results for heavily hole-doped graphite.

On the other hand, in a perfect harmonic crystal, the equilibrium size would not depend on temperature. Consequently, the phonon frequency would be temperature independent and its linewidth should tend to zero. Hence, it is expected that, for strong anharmonicity, the $E_{2g}$ mode in MgB$_2$ would be very broad and its frequency change strongly with temperature. Isothermal pressure-dependent Raman scattering results and lattice parameter measurements by Goncharov et al [8] have given some evidence for this anharmonic behavior. They have ob-
served at room temperature a very broad (300 cm$^{-1}$) Raman mode at 620 cm$^{-1}$ associated to the E$_{2g}$ mode and an anomalously large mode Grüneisen parameter, $\gamma_{E_{2g}} = 3.9 \pm 0.4$.

The correlation between $T_C$ and the resistivity ratio between room and near-$T_C$ temperatures, known as the Testardi correlation, is an evidence in favor of a dominant electron-phonon mechanism in MgB$_2$.[1] Moreover, the boron isotope effect shows that the boron modes may play a significant role in the MgB$_2$ superconductivity.[10] Besides, $T_C = 39$ K for MgB$_2$ is at the extreme end of $T_C$’s predicted by the BCS theory[11] that would require an electron-phonon coupling (EPC) of $\lambda \approx 1$. However, experimental results[12] give $\lambda \approx 0.6 - 0.7$ while first principle calculations[13, 14] yield an EPC of $\lambda \approx 0.7 - 0.9$. Nevertheless, in these papers there is a consensus about the importance of the E$_{2g}$ phonon in the superconducting mechanism of MgB$_2$. Particularly, Liu et al[2] suggested that the strongest EPC arises along the $\Gamma - A$ line for the E$_{2g}$ mode, and a 12% hardening below $T_C$ at the $\Gamma$ point is predicted. Therefore, the aim and the important contribution of the present work is to study, by means of Raman scattering, the temperature dependence of the E$_{2g}$ mode both below and above $T_C$. Although other groups had performed temperature dependence studies of the Raman spectra of MgB$_2$, e.g. superconducting gap studies by Raman scattering in refs. [14, 17], we present the first systematic investigation of the temperature behavior of the E$_{2g}$ phonon in this compound addressing its possible role in the superconducting mechanisms of MgB$_2$.

Raman spectroscopy is an excellent technique to investigate low-energy elementary excitations, particularly in superconductors. It was one of the first spectroscopic techniques to reveal both the existence of the superconducting gap and its strong coupling to some of the active Raman phonons.[16] In general, for strong electron-phonon coupling, the theoretical models predict that a phonon with the symmetry of the gap and comparable energy should soften or harden below $T_C$, depending on whether the phonon frequency is higher or lower than twice the superconducting energy gap, $2\Delta_0$.[17, 18] Also, the phonon linewidth should change in the superconducting state; phonons with energy below $2\Delta_0$ should sharpen and phonons with energy above $2\Delta_0$ should broaden.[17, 18] These behaviors have been observed in most of the HTS[12, 20, 21]. Besides, the temperature dependence of the phonon frequency and linewidth measured by Raman scattering can give some insight about the anharmonicity of the E$_{2g}$ mode. In general, due to the lattice expansion contribution,[22] the harmonic phonon frequency is temperature-dependent and in the lowest order is given by:

$$\omega(T) = \frac{\omega_0}{2} \left( 1 + e^{-3\beta T_0 \int_0^T \alpha(T')dT'} \right)$$  \hspace{1cm} (1)

where $\gamma$ is the Grüneisen parameter, $\alpha$ is the coefficient of thermal expansion, and $\omega_0 = \omega(T \to 0)$. The linewidth also has a temperature dependence that in the lowest order is given by[22]

$$\Gamma(\omega_0, T) = \Gamma(\omega_0, 0) \left[ 1 + 2n \left( \frac{\omega_0}{\omega} - T \right) \right]$$  \hspace{1cm} (2)

where $\Gamma(\omega, 0)$ is the residual linewidth at $T \to 0$ K and $n(\omega_0, T) = \left( e^{\beta\Delta_0/T} - 1 \right)^{-1}$ the Bose-Einstein factor. Equation 2 represents the decay of the phonon with frequency $\omega_0$ into two others phonons with half frequencies, $\omega_0/2$, and opposite wave vectors.

Our Raman measurements were made on a polycrystalline MgB$_2$ sample prepared in sealed Ta tubes as described previously[23]. X-ray powder-diffraction analysis confirmed single-phase purity and an AlB$_2$-type structure for our MgB$_2$ samples. The transition temperature determined by measuring the real and imaginary components of ac-susceptibility was found to be $T_C \approx 39$ K, as indicated in Figure 1. The collected Raman spectra were dispersed by a Jobin-Yvon (T64000) spectrophotometer and detected with a charge-coupled device (CCD) camera. The scattered signal was polarized with the electric field direction perpendicular to the grating grooves in order to maximize the spectrometer response. The 514 cm line of an Ar$^+$ laser was used as the excitation source. The temperature dependence of the E$_{2g}$ phonon was measured in a pellet of pressed powder using a laser power of 10 mW on a spot of ~100 $\mu$m in diameter. The polycrystalline sample was attached to the cold finger of a temperature controller using a closed-cycle helium cryostat and measured in a near-backscattering configuration. For the laser power used in this experiment we estimate a maximum temperature difference between the sample and thermometer to be $\lesssim 2$ K.

Figure 2 presents a few spectra between 10 – 300 K. Using a lorentzian lineshape and a linear background, the frequency and linewidth of the E$_{2g}$ phonon were extracted and their temperature dependence shown in Figures 3a and 3b, respectively. In contrast with some HTS,[24] the integrated intensity of this peak does not depend on temperature within the accuracy of our measurements. As mentioned above, among the active phonons the E$_{2g}$ mode is considered the main candidate to dominate the electron-phonon coupling.[2, 3, 5, 13] The large EPC between the E$_{2g}$ phonon and the electronic band in the $\Gamma - A$ line led Liu et al[2] to predict a 12% hardening, $\Delta\omega \approx 76$ cm$^{-1}$, of the phonon frequency below $T_C$, which should be easily observable in our Raman experiments. Figure 3a shows that, within the accuracy of our measurements, the phonon frequency does not present any change between the normal and superconducting state, i.e., neither softening nor hardening occurs at $T_C$ and between $T_C$ and room temperature a small hardening of $\approx 2$ cm$^{-1}$ can be observed. Besides, Figure 3b shows that the linewidth presents the expected two-phonon anharmonic decay behavior indicated by the solid line (see discussion below) and no anomalous temperature dependence of the linewidth is observed near $T_C$. 

for this phonon. These results are somewhat surprising in view of several theoretical predictions and what has been observed in most of the HTS.

As pointed out by several authors, the linewidth of this mode is extremely large, indicating strong anharmonicity for this mode. Particularly, Goncharov et al. have shown that the Grüneisen parameter related to the $E_g$ mode is very large, $\gamma_{E_g} = 3.9 \pm 0.4$. Taking into consideration the harmonic frequency $\omega_0 = 631 \text{ cm}^{-1}$, a frequency error bar of $\pm 2 \text{ cm}^{-1}$ for the $E_g$ phonon, the $\gamma_{E_g}$ value obtained by Goncharov, and the thermal expansion coefficient in the $a$ direction $\alpha = 5.4 \times 10^{-6} \text{ K}^{-1}$ measured by Jorgensen et al., the expected temperature dependence of the $E_g$ frequency can be calculated. Using $\gamma_{E_g} = 3.9 \pm 0.4$, we obtain temperature dependence of the $E_g$ frequency illustrated by the area between the two dashed lines in the Figure 3a. These lines were obtained with eq. (1) using the two limiting harmonic frequencies of $633 \text{ cm}^{-1}$ and $629 \text{ cm}^{-1}$. Clearly, the calculated temperature dependence of the $E_g$ frequency is not in agreement with the experimental data. In order to estimate the $\gamma_{E_g}$ value from our data, we present two simulations using eq. (1) for two different values of $\gamma_{E_g} = 1.0$ and 1.0. The area limited by the two dotted lines corresponds to the expected behavior of the $E_g$ frequency as a function of temperature considering $\gamma_{E_g} = 1.0$. Negative Grüneisen parameters are relatively rare. Some of the modes in negative thermal expansion material $\text{ZrW}_2\text{O}_8$ and in RbI at low temperatures are examples of compounds, where they have been found.

Finally, the area corresponding to $\gamma_{E_g} = 1.0$ is represented by the area between the two solid lines in the Figure 3a. $\gamma_{E_g} = 1.0$ is a typical value of Grüneisen parameter for most of the solids. Then, from the comparison between the data and the estimations made for different values, we estimate $\gamma_{E_g} \lesssim 1.0$, in disagreement with the large value obtained by Goncharov et al.

According to our result, the strong anharmonicity of the $E_g$ mode cannot be attributed to a large Grüneisen parameter.

In addition, pressure-induced changes of the topology of the Fermi surface, related to Lifshitz topological electronic transition, were invoked to reconcile the smooth pressure behavior of the $a$, $c$ parameters and the clear anomalous $E_g$ pressure dependence. Those pressure-induced changes in the Fermi surface may also be the explanation for the large difference between our $\gamma_{E_g}$ value and the one obtained by Goncharov et al. The anharmonic effect on the linewidth is shown in Figure 3b as a solid line which was obtained using eq. (2) with $\omega_0 = 631 \text{ cm}^{-1}$ and $\Gamma(\omega_0, 0) = 180 \text{ cm}^{-1}$. Notice that the two-phonon anharmonic decay fits the temperature dependence of the linewidth data quite well.

In summary, our results indicate that the temperature dependence of the frequency and linewidth of $E_g$ mode shows no anomaly at $T_C$, revealing that the involvement of the $E_g$ phonon near the $\Gamma$ point in the electron-phonon mechanism of superconductivity in MgB$_2$ must be revised and probably other $B$-modes, far away from the Brillouin zone center, may be related to the superconducting mechanism in this material. In analyzing the temperature dependence of the $E_g$ frequency, we estimate a Grüneisen parameter of $\gamma_{E_g} \lesssim 1.0$ for this mode, which is in discrepancy with the value estimated from isothermal pressure-dependent Raman scattering experiments. We suggest that this apparent disagreement can be accounted for by considering the pressure-induced changes of the topology of the Fermi surface.

I. ACKNOWLEDGMENTS

This work was supported by the Brazilian Agencies CNPq and FAPESP. Work at LANL was performed under the auspices of the US DOE.

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FIG. 1: Real and imaginary part of ac-susceptibility, $\chi'$ and $\chi''$, taken at $H_{ac} = 1$ Oe and $\nu = 1$ kHz. The superconducting critical temperature obtained was $T_C \approx 39$ K.

FIG. 2: Representative of Raman spectra between 10 – 300 K showing the temperature dependence of the $E_{2g}$ mode.

FIG. 3: Temperature dependence of the frequency (a) and linewidth (b) for the $E_{2g}$ phonon extracted from the Raman spectra in a polycrystalline sample of MgB$_2$. The solids, dotted, and dashed lines in (a) are simulations using eq. (1) as explained in the text. The vertical line indicates $T_C$ value.
Figure 01: The magnetic susceptibility of MgB$_2$ as a function of temperature. The ac magnetic field $H_{ac}$ is 1 Oe and the frequency $\nu$ is 1 kHz. The graph shows the real part $\chi'$ and the imaginary part $\chi''$ of the susceptibility as a function of temperature $T$ (K).
MgB$_2$ ($E_{2g}$)

![Graph showing the Raman shift (cm$^{-1}$) vs. intensity (arb. units) for different temperatures (T(K)).](fig. 2)
MgB$_2$

(a) Phonon Frequency (cm$^{-1}$) vs. T(K)

(b) Linewidth (cm$^{-1}$) vs. T(K)

$\gamma_{E_2}$:
- dotted line: -1.0
- solid line: 1.0
- dashed line: 3.9