Phonons in MgB$_2$ by Polarized Raman Scattering on Single Crystals

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The paper presents detailed Raman scattering study of the unusually broad E$_{2g}$ phonon mode in MgB$_2$ crystal. For the first time, it is shown by the polarized Raman scattering on few-micron-size crystallites with natural faces that the observed broad Raman feature really does obey the selection rules of an E$_{2g}$ mode. Raman spectra on high quality polycrystalline superconducting MgB$_2$ wires reveal a very symmetric E$_{2g}$ phonon line near 615 cm$^{-1}$ with the room temperature linewidth of 260 cm$^{-1}$ only. Additional scattering of different polarization dependence, observed in certain crystallites is interpreted as weighted phonon density of states induced by lattice imperfections.

Recent discovery of superconductivity in the hexagonal magnesium diboride (P6/mmm, Z=1) has motivated numerous experimental and theoretical investigations. Among others, it was claimed that the superconductivity in this compound arises due to the strong electron-phonon coupling. This electron-phonon coupling was found to be particularly strong for the E$_{2g}$ optic phonon mode. In fact, this E$_{2g}$ phonon mode is the only first order Raman active mode in MgB$_2$, so that Raman scattering is a very suitable tool for investigation of this particular phonon mode.

Previous to our investigations, three Raman studies of MgB$_2$ were reported. The paper by Bohnen, Heid and Henken reported Raman spectrum on a 10 micron size crystalline grain from a commercially available powder. The maximum of the observed broad asymmetric peak near 72 meV (580 cm$^{-1}$) corresponds rather well to their harmonic frequencies calculated ab-initio. The unusually large width is ascribed to the predicted strong electron phonon coupling. The second paper by Goncharov et al. is devoted to the evolution of the Raman spectra with applied pressure. Apart from the unusually large positive pressure shift of the frequency, it was found that the Raman spectrum of individual micron size grains is essentially identical with that of the powder. Ambient pressure spectra were fitted by a Gaussian profile with maximum near 620 cm$^{-1}$ and a width (FWHM) of 300 cm$^{-1}$. The origin of the observed signal was questioned but it was concluded that the most probable interpretation is that of first order Raman response from the E$_{2g}$ phonon mode. A subsequent paper by Chen et al. showed the same broad peak (620 cm$^{-1}$) at temperatures of 15 and 45K in Raman spectra taken from polycrystalline MgB$_2$ samples with 0.15-0.3 micron size grains. They performed polarization analysis but no significant difference between the shape and intensity of spectra measured with parallel and antiparallel polarizers was observed, even when using the Raman microprobe. Based on their findings and in contrast to the two previous studies, Chen et al. proposed that the observed broad feature can be interpreted as a disorder induced phonon contribution throughout the Brillouin zone, i.e. a kind of weighted phonon density of states.

The present experiments were carried out using a Renishaw Raman microscope with 514.5 nm (2.41 eV) argon laser excitation. The instrument allows measurements of polarized Raman spectra in back scattering from a spot size down to 1-2 microns in diameter. As a polycrystalline material we have used MgB$_2$ wires with $T_c$=40 K, produced by sealing a boron fiber with a tungsten core and magnesium chips (see Ref. 10 for preparation details and characterization). Microscopic MgB$_2$ single crystals were located on the MgB$_2$ thin films synthetized by ex-situ annealing of boron thin films. Thin boron films with nominal thickness from 100 nm to 200 nm were first deposited on a non-heated, randomly oriented, Al$_2$O$_3$ substrate from a Ta resistive heater in vacuum of $8\times10^{-4}$ Pa. The thin boron film was packed together with magnesium chips into a Nb tube. The Nb tube was inserted into an annular furnace where Ar atmosphere of 3 kPa was maintained during the whole annealing cycle. The furnace temperature was increased from room temperature to 800 °C in one hour, kept for half an hour at 800 °C and subsequently decreased to the room temperature in 5 minutes. The resistance vs. temperature curves (R-T, Fig. 1) show the onset of superconducting state $T_{con}$ near 38 K and zero resistance temperature of about 37 K.

FIG. 1: Resistance versus temperature dependence of the MgB$_2$ thin film
Typical unpolarized Raman spectra taken from polycrystalline wires (Fig. 2, spectrum a) show essentially the same broad feature as those reported earlier. It can be fitted perfectly with a Lorentzian profile at 612 cm\(^{-1}\) with FWHM of 261 cm\(^{-1}\). We have noticed that our peak is somewhat sharper and more symmetrical than that of the previously published spectra. The SEM picture of thin films (Fig. 3) exhibits polycrystalline morphology with single crystal diameter of about 1 \(\mu\)m. Distinct crystallites are oriented more or less randomly. Observation in an optical microscope (reflected light) emphasizes the crystal faces which are parallel to the substrate. Among them, several larger hexagonal or rectangular crystal faces could be identified: two such faces are shown in Figs. 4 and 5. We have assumed that these faces correspond to the high symmetry planes of MgB\(_2\) crystallites, i.e. perpendicular (Fig. 4) and parallel (Fig. 5) to the hexagonal axis. The unpolarized Raman spectra taken from hexagonal faces of two different crystallites are shown in Fig. 2 (spectra b and c). The investigated broad peak is superimposed on a considerable luminescence background of unknown origin, whose intensity differs from crystallite to crystallite. Simultaneously, some finer features are observed mainly on the high frequency side of the investigated peak (see arrows on Fig. 2, spectrum c). Figure 6 shows that the "fine structure" is more pronounced in the polarized Raman spectra with parallel polarizers than in the cross-polarized spectra. The same holds for the luminescence background. This effect, most probably caused by some kind of defects, is discussed in more detail below.

Assuming that the broad peak corresponds to the doubly degenerate E\(_{2g}\) phonon of P6/mmm crystal, the standard Raman selection rules require the allowed scattering to be independent of polarization if both polarization directions are perpendicular to the axis (back scattering from the hexagonal face). If at least one of the polarization directions is parallel to the hexagonal axis, the scattering is forbidden. We have found that the broad

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**FIG. 2:** Unpolarized back scattering Raman spectra. Solid curve (a) for the polycrystalline MgB\(_2\) wire; solid curves (b) and (c) for hexagonal faces of two distinct crystallites; broken curve is the Lorentzian fit of the curve (a). See text.

**FIG. 3:** The SEM micrograph of the MgB\(_2\) thin film.

(from 90 % to 10 %).

**FIG. 4:** Micrograph of a hexagonal MgB\(_2\) crystallite on surface of a rough thin layer as seen in the optical microscope. Bright areas indicate natural crystal faces parallel to the substrate.

**FIG. 5:** Micrograph showing the rectangular MgB\(_2\) crystallite in the optical microscope. See the preceding figure.
FIG. 6: Polarized Raman spectra taken from the hexagonal face of the MgB$_2$ crystallite in Fig. 4 as a function of the angle between its horizontal edge and the incident polarization direction. The spectra at zero angle have no vertical offset.

FIG. 7: Polarized Raman spectra taken from the rectangular face of the MgB$_2$ crystallite in Fig. 5. The arrow shows difference between VV spectrum and interpolated parabolic background due to the luminescence (dashed curve).

peak response actually obeys these rules. Independence of the rotation around the hexagonal axis for both parallel (HH) and crossed (HV) polarization geometry is obvious from Fig. 6. Moreover, the expected extinction of the broad peak in measurements with one or both polarization directions parallel to the hexagonal axis is evident in VV and VH spectra shown in Fig. 6. Here the H and V refer to the horizontal and vertical direction of the polarization of incident or scattered photons with respect to the edges of the rectangular crystalline face shown in Fig. 5. We note that the tacit assumption that the shorter edge is parallel to the hexagonal axis was fulfilled for all of the investigated rectangular crystallites and is further corroborated by our frequent observation of generally oriented MgB$_2$ crystallites with hexagonal plate-like habitus on the same substrate. In addition, the HH spectra of Fig. 6 and Fig. 7 are very similar, despite the fact that they are taken from different crystallites. Our measurements thus confirm the standard selection rules of $E_2^g$ modes in 6/mmm point group for the main peak at 620 cm$^{-1}$.

On the other hand, the additional "fine structure" does not follow the same selection rules as the main peak, namely it does not disappear in VV spectra shown in the Fig. 7. After subtraction of an interpolated smooth parabolic luminescence background, one can obtain a structure indicated by the arrow in the Fig. 7, which somehow reminds of the phonon density of states. It shows five humps at about 300, 400, 600, 750 and 830 cm$^{-1}$, which roughly correspond to the peaks on the reported phonon density of states or Eliashberg function, or at least correspond to the frequency range of the MgB$_2$ phonon spectrum. In fact, a signature of these humps can be identified in most of the displayed spectra (for example, the dip in between of the 300 and 400 cm$^{-1}$ humps is clearly marked in all the spectra shown in Fig. 7). Thus, it is highly probable that this extra Raman signal is related to disorder-induced contribution due to relaxation of the wave vector selection rules. Such or similar mechanism could perhaps also explain why the previous measurements systematically provided asymmetric profiles, steeper on the low-frequency side.

Just after completing our investigation, a new detailed paper on polarized Raman study of 40x30x5 micron size MgB$_2$ crystallite by Martinho et al. appeared in the cond-mat E-print archive. Their surprising observation of complete breakdown of the polarization selection rules of the investigated $E_{2g}$ mode ( at 630 cm$^{-1}$, FWHM 275 cm$^{-1}$) is in flagrant disagreement with our measurements, done with the same excitation wavelength. On the other hand, Martinho et al. made important observation that the phonon linewidth decreases with temperature down to about 180 cm$^{-1}$ at T=15 K, which corroborates the prediction of the giant anharmonicity of the $E_{2g}$ mode. Let us assume that the maximum of the observed $E_{2g}$ Raman line corresponds to the energy difference between the two lowest energy levels in an anharmonic potential for the $E_{2g}$ mode coordinate of a same shape as calculated ab initio by Yildirim et al. In this case the real harmonic frequency corresponding to our best peak frequency of 612 cm$^{-1}$ (76 meV) is merely
about 443 cm\(^{-1}\) (55 meV), which is quite close to the ab initio values given by Kortus et al\(^4\) (470 cm\(^{-1}\)), Yildirim et al\(^7\) (60.3 meV) and not too far from the values of Bohnen, Heid and Henker\(^6\) (66.5 and 70.8 meV for experimental and calculated geometries, respectively).

In conclusion, we have presented a critical review of available Raman studies on phonons in MgB\(_2\) and completed it by more detailed characterization. Our experiments suggest that the observed Raman response consists of a broad but symmetrical phonon E\(_{2g}\) line near 615 cm\(^{-1}\), complemented by a more complicated weaker component reflecting phonon density of states in crystals with defects. An extra component of this type might also explain the asymmetry of the broad E\(_{2g}\) line in the previously published observations. Finally, the E\(_{2g}\) assignment of the principal peak is directly proven by polarization analysis of Raman scattering from oriented MgB\(_2\) microcrystallites.

Acknowledgments

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1. J. Nagamatsu, N. Nakagawa, T. Muranaka, Y. Zenitani and J. Akimitsu, Nature \textbf{410}, 63 (2001).
2. S. L. Bud’ko, G. Lapertot, C. Petrovic, C. E. Cunningham, N. Anderson, and P. C. Canfield, Phys.Rev.Lett. \textbf{86}, 1877 (2001).
3. J. Kortus, I. I. Mazin, K. D. Belashchenko, V. P. Antropov, and L. L. Boyer, Phys.Rev.Lett. \textbf{86}, 4656 (2001).
4. K. D. Belashchenko, M. van Schilfgaarde and V. P. Antropov, cond-mat/0102290.
5. J. M. An and W. E. Pickett, Phys.Rev.Lett. \textbf{86}, 4366 (2001).
6. K.-P. Bohnen, R. Heid, and R. Renker, cond-mat/0103319.
7. T. Yildirim et al., to appear in Phys.Rev.Lett., cond-mat/0103469.
8. A. F. Goncharov et al, cond-mat/0104042.
9. X. K. Chen, M. J. Konstantinović, J. C. Irwin, D. D. Lawrie and J. P. Franck, cond-mat/0104005.
10. A. Pleceník, Š. Beňačka, P. Kůš and M. Grajcar, cond-mat/0104058.
11. R. Osborn, E. A. Goremychkin, A.I. Kolesnikov and D. G. Hinks, cond-mat/0103064.
12. H. Martinho, A. A. Martin, C. Rettori, O. F. de Lima, P. G. Pagliuso, N. O. Moreno and J. L. Sarrao, cond-mat/0105204.