

The Raman Spectra of MgB₂ and Its Potential Impurity Phases

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Introduction The newly discovered BCS-like superconductor MgB₂ [1, 2] has rapidly attracted the interest of the Raman community. Many contributions [3–6] explored the E_{2g} phonon mode of MgB₂ with a predicted strong coupling to the electronic conduction σ -bands [7]. The published Raman spectra of MgB₂ samples both polycrystalline [3] and small single crystals [4, 5] contain mainly the same structures: broad bands extending from 300 to 1600 cm⁻¹. The main peak at ≈ 600 cm⁻¹ is generally associated with the sought E_{2g} mode, but its unusually broad width (≈ 270 cm⁻¹), as well as the presence of other broad peaks in the spectra make the assignment difficult. On the other hand, TEM, X-ray photoemission and diffraction studies [8–10] indicated the presence of impurity phases such as elemental Mg, MgO, B₂O₃, Mg(OH)₂·MgCO₃ [6] and MgB₄ [9]. We investigated these impurity phases and present an analysis of the second-order features in the spectra of MgB₂.

Experimental Results Our samples were prepared by pressing of a commercially obtained powder (Alfa Aesar) into pellets; they revealed a superconductive transition temperature $T_c \approx 38$ K. We took polarized Raman spectra on many points along several lines on the sample. The depolarization ratios ρ were estimated to obtain information about the mode symmetry. The spectrometer slits were set to 5 cm⁻¹ spectral width, and the laser beam was focused to a ≈ 2 μ m spot using microscope optics. We found that a typical spectrum is essentially a combination of the spectra a and b shown in Fig. 1, left. The spectra marked a (parallel and perpendicular scattering geometry) are identified as the true MgB₂ spectra as obtained also by other authors [3–5]. They shall be referred to as the pure-phase MgB₂ spectra in what follows. The spectrum marked b does not have a peak around 600 cm⁻¹, its intensity increases monotonically with the Raman shift below 1200 cm⁻¹ and peaks at ≈ 1370 and 1580 cm⁻¹.

For comparison we measured the Raman spectra of a metallic Mg stripe (a freshly polished and an untreated surface), of MgO, B₂O₃ and Mg(OH)₂·MgCO₃. These spectra are shown in Fig. 1, right. B₂O₃ and Mg(OH)₂·MgCO₃ exhibit sharp lines in their first-order spectra at 500, 600, 807, 883 and at 1122 cm⁻¹, respectively. By comparison we conclude that these potential impurity phases do not contribute to the MgB₂ spectra.

The untreated surface of the Mg stripe consists of dark and light spots as viewed under the microscope. We found them to exhibit two different Raman spectra (Fig. 1, right). Except for three sharp features at 255, 440 and 517 cm⁻¹ the spectra from the light spots on the Mg stripe are identical with spectrum b from Fig. 1, left. The features in spectrum b are thus likely to be due to Mg-containing inclusions in our sample. This partially confirms the results of Refs. [8, 10] where it was found that MgO and metallic Mg are the major impurity phases in MgB₂. We point out, however, that a freshly polished Mg surface and powder MgO reveal an essentially featureless Raman spectrum which suggests a more complicated chemical composition of these impurity phases. The Raman spectra from the dark spots contain broad bands centered at about 380, 560 and 960 cm⁻¹. While the band at 560 cm⁻¹

may be suspected to contribute to the broad E_{2g} line in the pure-phase MgB_2 , it should be associated with the other peaks at 380 and 960 cm^{-1} . As seen in Fig. 1 this is clearly not the case and hence the dark spots of Mg do not contribute to the pure-phase MgB_2 spectrum.

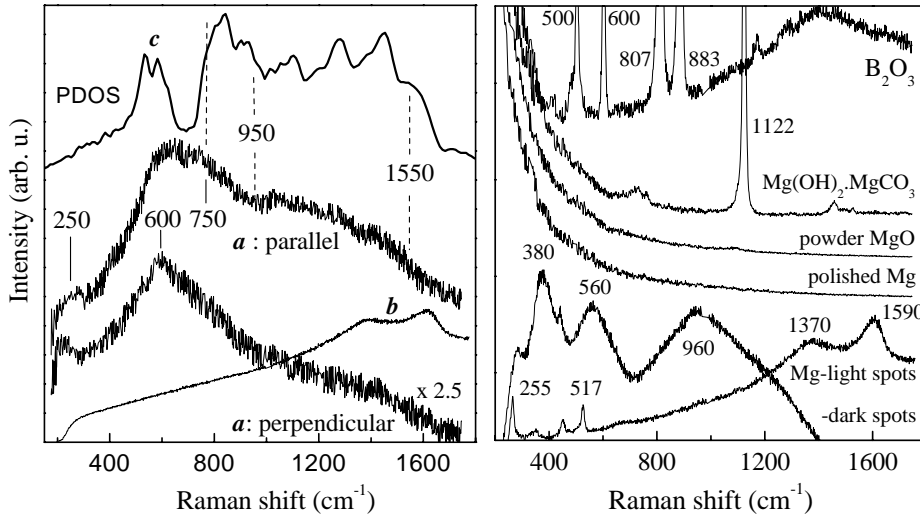


Figure 1: Left: (a) Polarized Raman spectra from pure-phase MgB_2 ; (b) Raman spectrum from an impurity phase in MgB_2 ; (c) phonon density of states of MgB_2 as taken from Ref. [7] and expanded in frequency by a factor of two. Right: Raman spectra of various materials potentially occurring in MgB_2 as impurity phases

The structure of MgB_4 , another potential impurity phase [9], is orthorhombic with 4 formula units per primitive cell and a rich Raman spectrum over a wide frequency range may be expected from this material. Given that all MgB_2 spectra published in the literature so far are sparse in structure, a significant contribution from MgB_4 seems hardly probable.

We now turn to the pure-phase MgB_2 spectra (Fig. 1 left, curves a). In the controversy about the assignment of the E_{2g} mode the authors of Ref. [6] concluded, for instance, that the structure at 600 cm^{-1} does not originate from MgB_2 but rather from a contaminant surface phase with different chemical composition. Our spectroscopic evidence supports, in principle, the presence of other phases in MgB_2 samples. We also measured for the 600 cm^{-1} line a depolarization ratio of $1/3$ incompatible with that of a (nonresonant) E_{2g} mode. Furthermore, the peak intensity of this line appears at slightly different frequencies in parallel and perpendicular scattering geometry ($\Delta\omega \approx 20\text{ cm}^{-1}$). Thus one may suspect that this extremely broad line serves as an envelope for other bands and peaks, including some features from impurity phases or from second-order contribution. On the other hand, the compatibility of the E_{2g} selection rules on single crystals has been reported [5] for the 600 cm^{-1} line. The strong coupling of this mode to the electronic σ -bands and the predicted significant anharmonicity [7] may account for its unusually large linewidth ($\approx 270\text{ cm}^{-1}$). The narrowing of the line upon cooling by a factor of ≈ 1.5 is a further indication that it is an intrinsic MgB_2 feature [4]. Our results show that none of the potential impurity phases investigated reveal features which appear significantly in the pure-phase MgB_2 spectra.

There are two additional weak bands at $\approx 250\text{ cm}^{-1}$ ($\rho \approx 3/4$) and 750 cm^{-1} ($\rho \approx 1/6$) and a broad band ranging from 950 to 1550 cm^{-1} that have similarities to the first- and second-

order maxima in the phonon density of states (PDOS) [7, 11]. For a qualitative comparison we plotted in Fig. 1 the measured PDOS from Ref. [7] expanding it by a factor of two in the frequency axis. In such a plot the features of the PDOS are roughly proportional to the second-order Raman signal. Referring to the phonon dispersion relations calculated in Ref. [7] we assign the bands in our spectra as follows:

(i) The band at 250 cm^{-1} could correspond to a disorder-induced contribution of the acoustic phonon branches which are flat in a large region of the Brillouin zone. The second order of the acoustic phonons possibly contributes to the low-energy side of the E_{2g} peak (compare curves a and c in Fig. 1);

(ii) The band at 750 cm^{-1} falls together with the phonon branches which have E_{1u} and A_{2u} symmetry at the Γ point;

(iii) The band from 950 to 1550 cm^{-1} also corresponds to the PDOS of second-order optical phonon modes.

The assignment to second-order features is corroborated by the determined depolarization ratio of about $1/6$ for the bands (ii) and (iii). This value is consistent with a second-order feature because an overtone always contains the totally symmetric A_{1g} component.

In summary, we have analyzed with Raman spectroscopy several potential impurity phases in MgB_2 samples. Most of them do not have features present in “typical” spectra of MgB_2 . From similarities of the weak structures in the MgB_2 spectra with the calculated phonon density of states we were able to assign most of them to second-order features. The E_{2g} Raman peak at $\approx 600 \text{ cm}^{-1}$ in microcrystalline material appears clearer in perpendicular polarization geometry since it has a larger depolarization ratio than the second-order features.

References

- [1] J. NAGAMATSU, N. NAKAGAWA, T. MURANAKA, Y. ZENITANI, and J. AKIMITSU, *Nature* **410**, 63 (2001).
- [2] S. L. BUDKO, G. LAPERTOT, C. PETROVIC, C. E. CUNNINGHAM, N. ANDERSON, and P. C. CANFIELD, *Phys. Rev. Lett.* **86**, 1877 (2001).
- [3] X. K. CHEN et al., cond-mat/0104005.
A. F. GONCHAROV et al., cond-mat/0104042.
- [4] H. MARTINHO et al., cond-mat/0105204.
- [5] J. HLINKA et al., cond-mat/0105275.
- [6] K. KUNC et al., cond-mat/0105402, submitted to *J. Phys. C*.
- [7] T. YILDIRIM et al., cond-mat/0103469, to appear in *Phys. Rev. Lett.*
- [8] R. P. VASQUEZ et al., cond-mat/0103215, submitted to *Phys. Rev. B*.
- [9] J. Q. LI et al., cond-mat/0104350.
- [10] Y. ZHU et al., cond-mat/0105311.
- [11] R. OSBORN, E. A. GOREMYCHKIN, A. I. KOLESNIKOV, and D. G. HINKS, *Phys. Rev. Lett.* **87**, 017005 (2001).