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Raman Spectra of MgB_2 at High Pressure and Topological Electronic Transition[1]

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Raman spectra of MgB_2 ceramic samples were measured as a function of pressure up to 32 GPa at room temperature. The spectrum at normal conditions contains a very broad peak at ~590 cm^{-1} related to the E_{2g} phonon mode. The frequency of this mode exhibits a strong linear dependence in the pressure region from 5 to 18 GPa, whereas, beyond this region, the slope of the pressure-induced frequency shift is reduced by about a factor of two. The pressure dependence of the phonon mode up to ~5 GPa exhibits a change in the slope, as well as a "hysteresis" effect in the frequency vs. pressure behavior. These singularities in the E_{2g} mode behavior under pressure support the suggestion that MgB_2 may undergo a pressure-induced topological electronic transition.

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The discovery of superconductivity in MgB_2 [1] has initiated a number of studies that are related to the pressure behavior of the crystalline structure, phonon spectrum, and superconductivity transition temperature of this material [2–10]. High-pressure experiments, which traditionally are used to test the structural stability of materials, can also play an important role in the understanding of the superconductivity mechanism. The experimentally observed pressure-induced linear decrease in T_c [6–10] is in general agreement with theoretical estimations based on the BCS theory. Theoretical calculations show that MgB_2 can be treated as a phonon-mediated superconductor with very strong electron–phonon coupling of the in-plane optical E_{2g} phonon mode to the partially occupied planar boron σ bands near the Fermi surface [11, 12]. The strong coupling contributes considerably to the anharmonicity of the Raman-active E_{2g} mode which is manifested by its very broad lineshape, ranging from 460 cm^{-1} to 660 cm^{-1}, according to various calculations [11, 13–15]. The other three phonon modes of MgB_2 with symmetries B_{1g}, A_{2u}, and E_{1u} are harmonic and show insignificant electron–phonon coupling [11].

The first report on Raman scattering in MgB_2 revealed a broad asymmetric peak at ~580 cm^{-1} [16], while subsequent investigations attributed the band at the 615–620 cm^{-1} frequency range to the E_{2g} phonon mode [5, 17]. Recently, Kunc *et al.* [18] have reported Raman spectra of MgB_2 consisting of two broad peaks, which differ considerably from the previously reported Raman results [5, 16, 17], and neither of these was attributed to the E_{2g} phonon mode. The original high-pressure Raman experiment up to 15 GPa has shown a large linear pressure shift of the E_{2g} phonon frequency [5]. Further extension of the pressure range up to 44 GPa has revealed a change in the slope of the linear pressure dependence at ~23 GPa for the isotopically pure $Mg_{10}B_2$ samples [6]. Similar singularities are observed in the dependence of T_c on the relative variation of volume, V/V_0 [6], which exhibits a change in the slope of the linear dependence near the values of V/V_0 corresponding to pressures of ~20 GPa and ~15 GPa for isotopically pure $Mg^{10}B_2$ and $Mg^{11}B_2$ samples, respectively. This behavior of the pressure dependence of T_c was also observed at ~9 GPa for MgB_2 samples prepared from a natural boron-isotope mixture [10]. The observed singularities in the pressure dependence of T_c and E_{2g} phonon frequency [6, 10] were related to the Lifshitz isostructural topological electronic transition [19], since the data available at that time on the pressures dependence of the lattice parameters of MgB_2 did not show any structural phase transition at pressure up to 40 GPa [3, 4]. New high-pressure X-ray results showed that MgB_2 undergoes an isostructural phase transition in the pressure range 26–30 GPa [20].

We measured the Raman spectra of MgB_2 as a function of pressure up to 32 GPa at room temperature. The main goal of our experiments was to study carefully the pressure dependence of the E_{2g} phonon mode and to reexamine possible phase transitions in the MgB_2 system. We believe that the results obtained in the present

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study show new aspects and, in some way, complete the study of the pressure behavior of the E_{2g} phonon mode.

Ceramic samples of MgB_2 were prepared by direct synthesis from constituent elements. The initial materials were amorphous boron powder (natural mixture of isotopes, atomic mass 10.811) and pieces of metallic magnesium, both with a purity greater than 99.9%. The stoichiometric weights of the materials were placed in a molybdenum crucible and heated to 1400°C in a medium-pressure furnace under an Ar-gas pressure of ~12 bar followed by annealing for an hour. During the heating, the synthesis of MgB_2 is assumed to occur at ~900°C. The resulting product was a bronze-colored compact material with a density ~2.23 g/cm^3 and a grain size from 6 to 30 microns. The X-ray powder diffraction pattern of synthesized samples showed the hexagonal MgB_2 (**a** = 3.086 Å and **b** = 3.52 Å) to be the main constituent, with small quantities of MgO and metallic Mg. The transition temperature T_c for the samples used in this study varied between 37.5 and 39 K at normal pressure [10, 21].

Raman spectra were recorded using a triple monochromator (DILOR XY-500) equipped with a CCD liquid-nitrogen cooled detector system. The spectral width of the system was ~8 cm^{-1}, and the 514.5 nm line of an Ar^+ laser with the beam power below 10 mW, measured before the cell, was used for excitation. Small good faceted bronze-colored grains of MgB_2 with a typical size of ~20 μm were selected for Raman measurements. Measurements of the Raman spectra at high pressure were carried out in two independent pressure cycles using a diamond anvil cell (DAC) of the Mao-Bell type [22]. A 4 : 1 methanol–ethanol mixture was used as the pressure-transmitting medium, and the ruby fluorescence technique was used for pressure calibration [23]. The E_{2g} phonon frequency was obtained with an accuracy of about ~10 cm^{-1} by fitting a Gaussian function to the experimental peak after background subtraction. This background was taken as growing linearly, and the reference points used for the subtraction were the minimum (maximum) intensity of the spectrum at its low (high) frequency limits, respectively.

The Raman spectra of the ceramic samples of MgB_2, taken at normal conditions consist of a broad peak centered near ~590 cm^{-1}. This frequency value is lower than the earlier reported frequency of the E_{2g} mode [5, 17]. Probing the ceramic MgB_2 samples with the use of high spatial resolution of the micro-Raman system provided us with the possibility of identifying small crystalline grains of MgB_2, whose Raman spectra represents a typical E_{2g}-mode peak which differs drastically from that of possible inclusions.

The Raman spectra of MgB_2 for various pressures up to ~29 GPa at room temperature are shown in Fig. 1. The initial spectrum at 1.1 GPa (Fig. 1a) contains a broad (FWHM ~ 250 cm^{-1}) peak near ~600 cm^{-1}, which

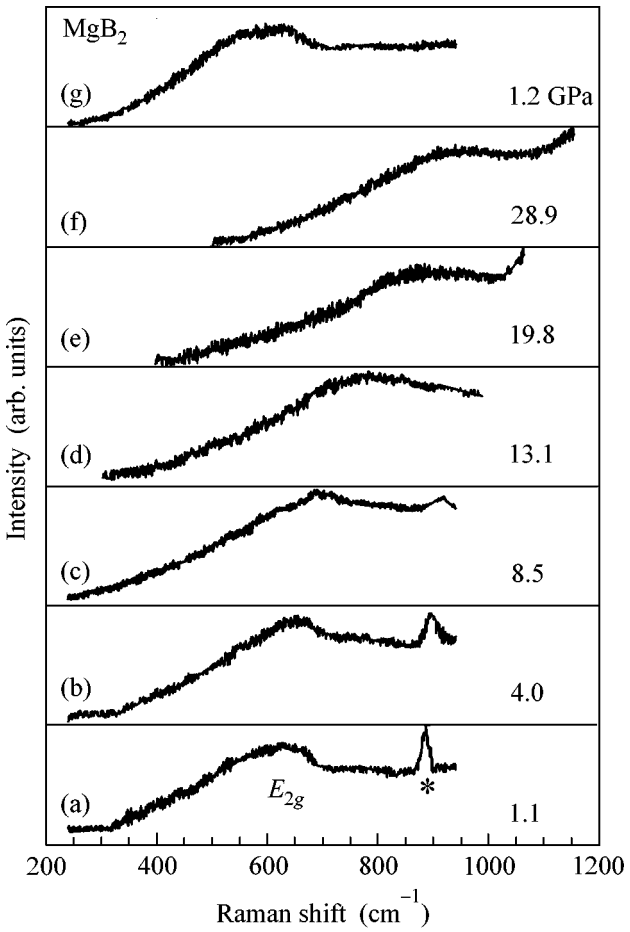

Fig. 1. Raman spectra of MgB_2 for various pressures up to ~29 GPa at room temperature. Asterisk indicates a methanol–ethanol mixture peak.

is assigned to the Raman-active E_{2g} mode. The relatively sharp peak near ~880 cm^{-1} is associated with a methanol–ethanol mixture peak. The intensity of this peak gradually drops with an increase in pressure and vanishes at ~12 GPa upon mixture solidification. When pressure increases, the E_{2g} peak shifts to higher energy (Figs. 1b–1f) and somehow broadens, while its Raman intensity does not change noticeably. The release of pressure down to 1.2 GPa (Fig. 1g) restores the main features of the initial Raman spectrum.

The pressure dependence of the E_{2g}-mode frequency, worked out for various pressure runs, is shown in Fig. 2. The open circles show the data for increasing pressure to ~20 GPa, while the closed circles are related to the decrease of pressure to ~1.2 GPa.

The data marked by open squares are recorded at the subsequent upstroke pressure cycle from ~1.2 GPa to ~32 GPa performed immediately after the release of pressure without disassembling the DAC. The shaded areas near ~5 GPa and ~18 GPa separate the regions where the pressure behavior of the E_{2g}-phonon frequency can be fitted to a linear dependence with

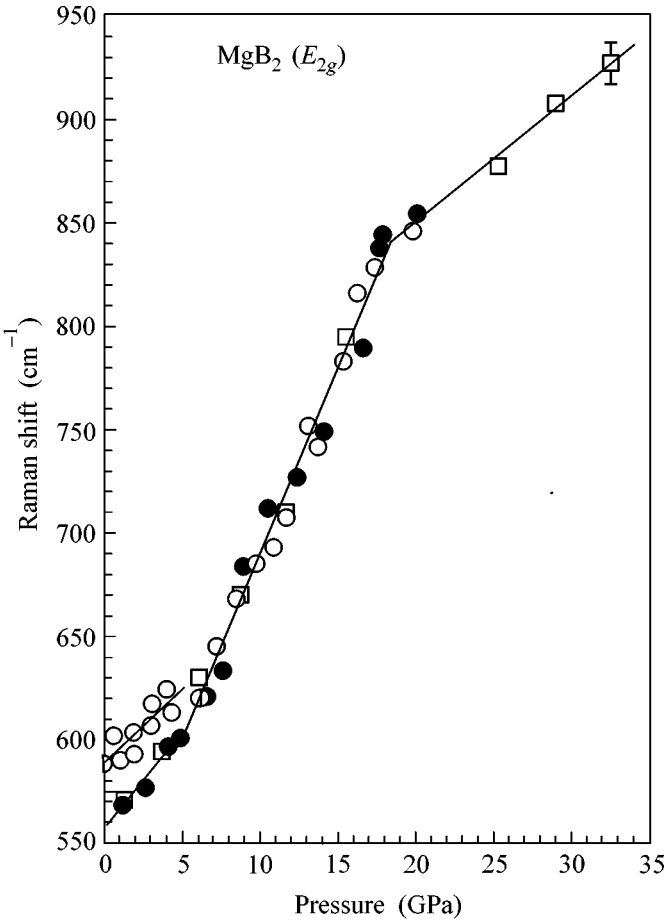

Fig. 2. Pressure dependence of the frequency of the E_{2g} phonon in MgB_2. The open (closed) symbols are related to an increase (decrease) in pressure. The shaded areas show the pressure regions where the changes in the slopes of linear pressure shift were observed.

different slopes $\partial\omega/\partial P$. The largest slope $\partial\omega/\partial P$ = 18 cm^{-1}/GPa, is found for the region $5 \le P \le 18$ GPa, while for $P > 18$ GPa the slope $\partial\omega/\partial P$ is 6 cm^{-1}/GPa. The most intriguing behavior is observed in the pressure region 1 bar–5 GPa, where the route (open cycles in Fig. 2) of the two upstroke pressure cycles (new cell loading) differs from the route of the downstroke (solid cycles in Fig. 2) and upstroke (open squares) cycles without the total release of pressure in the DAC. The slopes $\partial\omega/\partial P$ of both routes are slightly different, ~7 cm^{-1}/GPa for the new loading and ~9 cm^{-1}/GPa for the recycling routes. Note that the spread of experimental data at the E_{2g}-mode frequency is consistent with the accuracy in the peak position determination, which was found to be close to ~10 cm^{-1}.

The pressure dependence of the E_{2g}-mode frequency demonstrates two singularities near ~5 GPa and ~18 GPa. These results are partly correlated with the Raman data obtained by Struzhkin *et al.*, who reported a singularity in the slope of the phonon pressure dependence near ~23 GPa for the isotopic pure $Mg^{10}B_2$ sample and near ~15 GPa in the pressure dependence of T_c for the isotopically pure $Mg^{11}B_2$ sample [6]. Taking into account that the samples in the present investigation were prepared from a natural mixture of boron isotopes, we believe that the singularity near ~18 GPa has the same origin as those observed in [6] for isotopically pure samples. As for the singularity at ~5 GPa, it seems to be a new result revealed by recording the spectra with small steps of pressure increase in this interval.

The experimental data for the pressure dependence of the E_{2g}-phonon mode are seemingly in contradiction with the X-ray data on MgB_2. Although the Raman data show distinct singularities in their pressure dependence, the pressure dependences of the *a* and *c* parameters of the hexagonal lattice are smooth and do not show any structural phase transition in the pressure region up to 12 GPa [2, 3, 5–6]. Furthermore, the X-ray results of Bordet *et al.* [4], extended to higher pressure, indicated the absence of any structural phase transitions up to ~40 GPa. However, Sun Li-Ling *et al.* [20] observed an isostructural phase transition in the pressure region 26–30 GPa accompanied by a substantial change in the unit-cell volume, while their Raman results also showed some anomalies in the E_{2g}-mode pressure behavior, the most significant of them being the appearance of a band splitting at ~30 GPa. A possible explanation for these discrepancies in the pressure behavior of MgB_2 may be related to the Lifshitz topological electronic transition [19] associated with the pressure-induced changes in the topology of a Fermi surface. In such a transition, the electron density of states at the Fermi level, as well as the electron dynamics, possess some specific features which lead to anomalies of the electron thermodynamic and kinetic characteristics. The band structure calculations for MgB_2 [11, 12] show splitting of the planar boron σ bands along the Γ–A line near the Fermi surface, which creates the conditions for the Lifshitz-type transition under high pressure. Tissen *et al.* [10] have suggested that MgB_2 undergoes the Lifshitz topological electronic transition, and this explains the cusp in the pressure dependence of T_c near 9 GPa. The same suggestion has been used to explain the changes in the slopes of the linear pressure dependences of the E_{2g}-phonon frequency and superconducting transition temperature T_c for isotopically pure $Mg^{11}B_2$ and $Mg^{10}B_2$ samples [6]. We believe that the manifestation of the electronic topological transition in the pressure dependence of the E_{2g}-phonon mode may be related to the strong electron–phonon coupling of this mode to the planar boron σ bands.

Concerning the singularity in the E_{2g}-phonon pressure dependence near ~5 GPa, we believe that this may be related to some transformation of the initial ceramic material associated with a trend towards phase homogenization under high pressure. It seems that the recovered material is more homogeneous, because its pres-

sure response and the E_{2g}-phonon frequency is lower than that of the starting material; therefore, the investigation of T_c for a high-pressure-treated ceramic sample might be interesting. In any case, we think that, in order to clarify this suggestion, further experiments with high-quality crystalline samples are necessary.

Finally, we would like to address the difference in the E_{2g}-phonon frequency reported in various Raman studies at normal conditions [5, 6, 16–18]. We think that its origin may be related to the difference in the stoichiometry of ceramic samples. For example, recent publication [21] indicates that the ceramic samples, in fact, have various stoichiometries, $Mg_{1-x}B_2$ with $0 \le x \le 0.2$, and the superconducting transition temperature T_c varies accordingly from 37 to 39 K.

In conclusion, the pressure dependence of the E_{2g} phonon-mode frequency measured as a function of pressure up to 32 GPa shows two singularities near ~5 and ~18 GPa. The singularity at ~5 GPa may be related to the pressure-induced homogenization of ceramic samples, while the singularity at ~18 GPa may be related to a Lifshitz topological electronic transition [19].

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