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Raman spectra of MgB_2 at high pressure and topological electronic transition

K. P. Meletov[1)], *M. P. Kulakov, N. N. Kolesnikov, J. Arvanitidis*[+], *G. A. Kourouklis*[+]

Institute of Solid State Physics RAS, 142432 Chernogolovka, Moscow reg., Russia

[+]*Physics Division, School of Technology, Aristotle University of Thessaloniki, GR-540 06 Thessaloniki, Greece*

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Raman spectra of the 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 $\sim 590\,cm^{-1}$ 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 related to the pressure behavior of the crystalline structure, phonon spectrum and superconductivity transition temperature of this material [2 – 10]. The high pressure experiments, which traditionally are used to test the structural stability of materials, can play also an important role in the understanding of the superconductivity mechanism. The experimentally observed pressure-induced linear decrease of 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 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 an insignificant electron-phonon coupling [11].

The first report on Raman scattering in MgB_2 revealed a broad asymmetric peak at $\sim 580\,cm^{-1}$ [16], while subsequent investigations attributed the band at the 615–620 cm^{-1} frequency region 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 one was attributed to the E_{2g} phonon mode. The initial 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 revealed the change in the slope of the linear pressure dependence at $\sim$ 23 GPa for the isotopically pure $Mg^{10}B_2$ samples [6]. Similar singularities are observed in the dependence of T_c vs. relative variation of volume, V/V_0, [6], which exhibits change in the slope of the linear dependence near the values of V/V_0 corresponding to pressures of $\sim$ 20 GPa and $\sim$ 15 GPa for $Mg^{10}B_2$ and $Mg^{11}B_2$ isotopically pure samples, respectively. This behavior in the pressure dependence of T_c was also observed at $\sim$ 9 GPa, for MgB_2 samples prepared from 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 a Lifshitz isostructural topological electronic transition [19], since the available, at that time, data on the pressure dependence of the lattice parameters of MgB_2 did not show any structural phase transition with 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 have measured the Raman spectra of MgB_2 as a function of pressure, up to 32 GPa, at room temperature. The main goal in our experiments was to study carefully the pressure dependence of E_{2g} phonon mode and to reexamine possible phase transitions in MgB_2 system. We believe that the results obtained in the present study

[1)] e-mail:mele@issp.ac.ru

show new aspects and complete somehow the study of the pressure behavior of the E_{2g} phonon mode.

Ceramic samples of MgB_2 were prepared by direct synthesis from the constituent elements. The initial materials were amorphous boron powder (natural mixture of isotopes, atomic mass 10.811) and pieces of metallic magnesium, both better than 99.9% purity. The stoichiometric weights of materials were placed in molybdenum crucible and heated up to 1400 °C into the medium-pressure furnace under Ar-gas pressure of $\sim$ 12 bar followed by annealing there for an hour. During the heating, the synthesis of MgB_2 is believed to occur at $\sim$ 900 °C. The resulting product was a bronze-color compact material with density $\sim 2.23\,g/cm^3$ and grain size from 6 to 30 microns. X-ray powder diffraction pattern of synthesized samples showed the hexagonal MgB_2 ($\mathbf{a} = 3.086$ Å and $\mathbf{b} = 3.52$ Å) to be the main constituent, with small quantities of MgO and metallic Mg. The transition temperature T_c for the samples used in the present 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 $\sim 8\,cm^{-1}$ and the 514.5 nm line of an Ar^+ laser with beam power below 10 mW, measured before the cell, was used for excitation. Small good facetted bronze-colored grains of MgB_2 with typical size of $\sim 20\,\mu m$ 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 Mao-Bell type [22]. The 4:1 methanol-ethanol mixture was used as 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 $\pm 10\,cm^{-1}$ by fitting a Gaussian function to the experimental peak after background subtraction. This background was taken as growing up 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 ceramic samples of MgB_2, taken at normal conditions, consist of a broad peak centered near $\sim 590\,cm^{-1}$. This frequency value is lower than the earlier reported frequency value of the E_{2g} mode [5, 17]. Probing the ceramic MgB_2 samples, using high spatial resolution of the micro-Raman system, gave us the possibility to identify small crystalline grains of MgB_2 whose Raman spectra represents the typical E_{2g} mode peak which differs drastically from that of possible inclusions.

The Raman spectra of the MgB_2 for various pressures up to $\sim$ 29 GPa and at room temperature are shown in Fig.1. The initial spectrum at 1.1 GPa (Fig.1a)

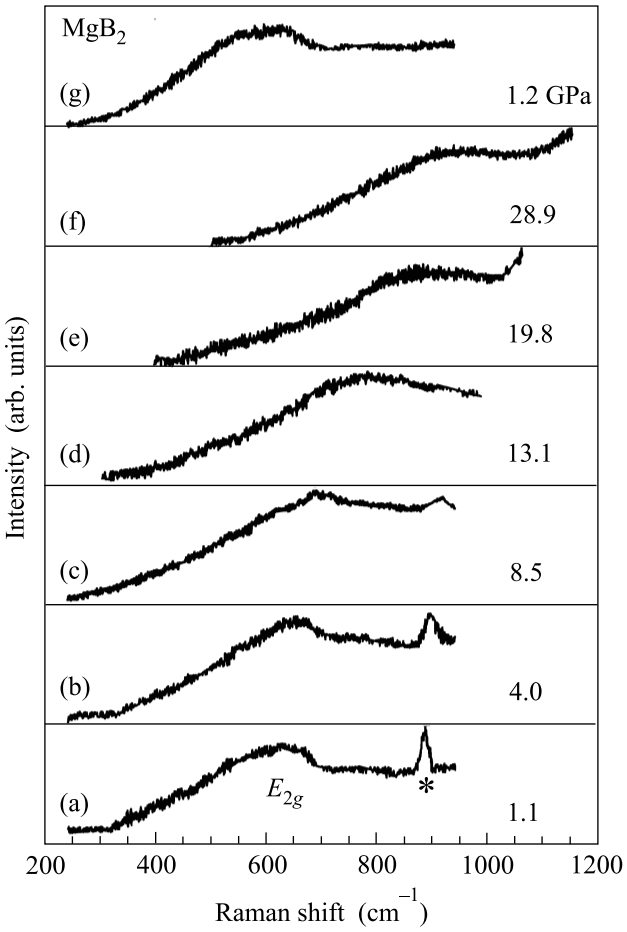

Fig.1. Raman spectra of the MgB_2 for various pressures up to $\sim$ 29 GPa and room temperature. Asterisk indicates a methanol-ethanol mixture peak

contains the broad (FWHM $\approx 250\,cm^{-1}$) peak near $\sim 600\,cm^{-1}$ related to the Raman active E_{2g} mode. The relatively sharp peak near $\sim 880\,cm^{-1}$ is associated with a methanol-ethanol mixture peak. The intensity of this peak gradually drops with the increase of pressure and vanishes at $\sim$ 12 GPa upon mixture solidification. When pressure increases the E_{2g} peak shifts to higher energy (Fig.1b-f) 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 up to $\sim$ 20 GPa, while the closed circles are related to the decrease of pressure down to $\sim$ 1.2 GPa.

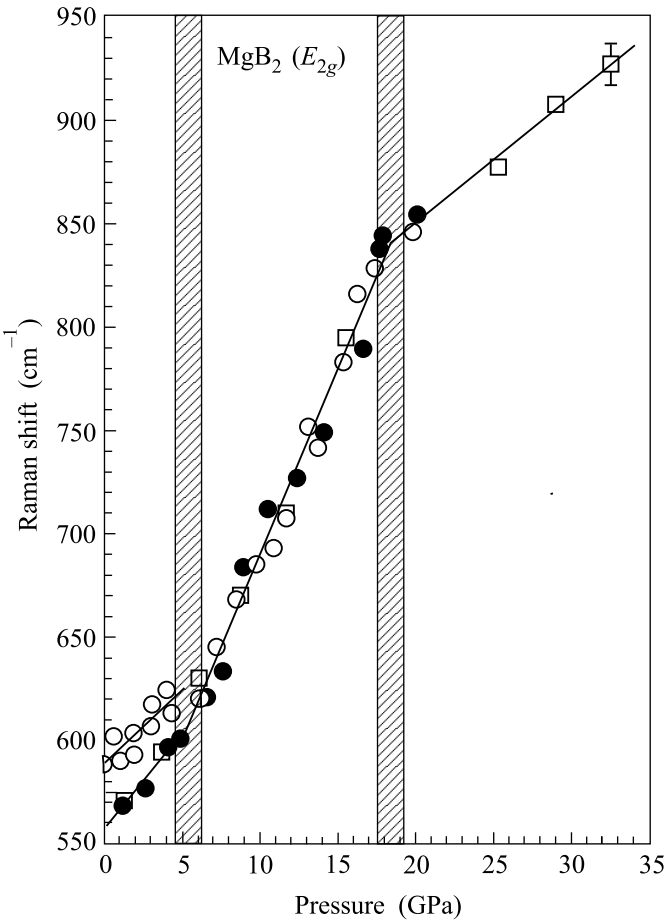

Fig.2. Pressure dependence of the frequency of E_{2g} phonon in MgB_2. The open (closed) symbols are related to the increase (decrease) of pressure. The shaded areas show the pressure regions where the changes in the slopes of linear pressure shift were observed

The data marked by open squares are recorded at the subsequent upstroke pressure cycle from $\sim$ 1.2 GPa to $\sim$ 32 GPa performed immediately after the release of pressure without disassembling of the DAC. The shaded areas near $\sim$ 5 GPa and $\sim$ 18 GPa separate the regions where the pressure behavior of E_{2g} phonon frequency can be fitted to a linear dependence with different slopes $\partial\omega/\partial P$. The largest slope $\partial\omega/\partial P = 18\,\mathrm{cm}^{-1}/\mathrm{GPa}$ is found for the region $5 \leq P \leq 18$ GPa, while for $P > 18$ GPa the slope $\partial\omega/\partial P$ is $6\,\mathrm{cm}^{-1}/\mathrm{GPa}$. The most intrigue 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, $\sim 7\,\mathrm{cm}^{-1}/\mathrm{GPa}$ for the new loading and $\sim 9\,\mathrm{cm}^{-1}/\mathrm{GPa}$ for the recycling routes. Note that the spread out of experimental data on the E_{2g} mode frequency is consistent with the accuracy in the peak position determination, which was found to be close to $\pm 10\,\mathrm{cm}^{-1}$.

The pressure dependence of the E_{2g} mode frequency demonstrates two singularities near $\sim$ 5 GPa and $\sim$ 18 GPa. These results are partly correlated with the Raman data obtained by Struzhkin et al., which have been reported a singularity in the slope of the phonon pressure dependence near $\sim$ 23 GPa for the isotopic pure $Mg^{10}B_2$ sample and near $\sim$ 15 GPa in the pressure dependence of T_c for the isotopic pure $Mg^{11}B_2$ sample [6]. Taking into account that the samples in the present investigation were prepared from natural mixture of boron isotopes we think that the singularity near $\sim$ 18 GPa has the same origin as those observed in [6] for isotopic pure samples. As for the singularity at $\sim$ 5 GPa, it seems to be a new result revealed by recording the spectra for 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 dependencies 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 $\sim$ 40 GPa. However, Sun Li-Ling et al. [20] observed an isostructural phase transition in the pressure region 26–30 GPa accompanied with a substantial change in the unit cell volume, while their Raman results showed, also, some anomalies in the E_{2g} mode pressure behavior, with the most significant being the appearance of a band splitting at $\sim$ 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 of the topology of the Fermi surface. In such a transition the electron density of states on the Fermi level as well as the electron dynamics, possess some peculiar features, which lead to anomalies of the electron thermodynamic and kinetic characteristics. The band structure calculations for the MgB_2 [11, 12] show the splitting of the planar boron σ bands along the $\Gamma-A$ line near the Fermi surface, which creates the conditions for a Lifshitz-type transition under the application of high pressure. Tissen et al. [10] have suggested that MgB_2 undergoes the Lifshitz topological electronic

transition to explain the cusp in the pressure dependence of the T_c near 9 GPa. Later the same suggestion has been used to explain the changes in the slopes of the linear pressure dependencies of the E_{2g} phonon frequency and superconducting transition temperature T_c for isotopic 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 to phase homogenization under high pressure. It seems that the recovered material is more homogeneous as far as its pressure response and the E_{2g} phonon frequency is lower than that of the starting material, therefore, an investigation of the 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 the 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, a recent publication [21] indicates that the ceramic samples in fact have various stoichiometries, $Mg_{1-x}B_2$ with $0 \leq x \leq 0.2$, and superconducting transition temperature T_c varies accordingly from 37 K 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 GPa and ~ 18 GPa. The singularity at ~ 5 GPa may be related to the homogenization of ceramic samples induced by pressure, while the singularity at ~ 18 GPa may be related to a Lifshitz topological electronic transition [19].

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