Infrared absorption in superconducting MgB$_2$

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Abstract

Infrared absorption measurements in the range of 125 to 700 cm$^{-1}$ have been carried out as a function of temperature up to 5 K in MgB$_2$. The absorption spectrum is characterised by a broad band centred at 485 cm$^{-1}$, with shoulders at 333 and 387 cm$^{-1}$. Studies on the temperature dependence of absorption, indicate that these modes initially harden with the lowering of temperature, and this trend is arrested at $\sim 100$ K, below which they soften. Further, in the case of the mode at 333 cm$^{-1}$, there is a distinct softening associated with the superconducting transition at 39 K. The implications of these experimental results in the context of superconductivity in MgB$_2$ are discussed.

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I. INTRODUCTION

The recent discovery of superconductivity$^1$ at 39 K in the binary intermetallic MgB$_2$, having a simple hexagonal structure consisting of alternating honeycomb layers of B and closed packed layers of Mg, has evoked a widespread interest. Initial experiments suggest
that the superconductivity in this system arises due to phonon-mediated interaction, as supported by experiments on isotope effect\(^\text{4}\), measurements on the superconducting gap by tunnelling\(^\text{5}\) and optical spectroscopy\(^\text{6}\), as also the decrease of \(T_c\) with the application of pressure\(^\text{7}\). There have been several theoretical calculations\(^\text{8}\)–\(^\text{10}\) that emphasise the importance of electron-phonon coupling, though alternative mechanisms\(^\text{11}\) for superconductivity have also been proposed. Electronic structure calculations in MgB\(_2\) indicate that Mg is completely ionised and the bands at the Fermi level are derived from \(\sigma\) orbitals of boron. There are four distinct zone centre vibrational modes: a silent mode \(B_{1g}\), the doubly degenerate Raman mode, \(E_{2g}\), and two infrared active modes of \(A_{2u}\) and \(E_{1u}\) symmetry. While there is a general agreement with regard to electronic structure and vibrations, the details differ, both with respect to the calculated frequencies and the relative importance of these modes with respect to superconductivity in the system. For example, in the calculations of An and Pickett\(^\text{11}\), using the deformation potential approach, it is the \(E_{2g}\) mode that is shown to have a dominant coupling with the electrons, whereas in the calculations of Kong et al.\(^\text{12}\), the electron phonon interaction is spread over all the modes. Inelastic neutron scattering experiments measuring the vibrational density of states\(^\text{13}\)–\(^\text{15}\) indicate acoustic modes at less than 40 meV and peaks in the phonon density of states at 54, 78, 89 and 97 meV corresponding to the optic modes. Raman scattering measurements\(^\text{16}\)–\(^\text{18}\) indicate a mode at \(\sim 600\) cm\(^{-1}\), which is characterised by very large width \(\sim 200\) cm\(^{-1}\), indicative of strong electron phonon interaction.

In this paper, results of infrared absorption measurements on superconducting MgB\(_2\), covering a spectral range of 125 - 700 cm\(^{-1}\), in which the optic modes are predicted to exist, are reported. In addition supportive experiments have also been carried out in the mid infrared range, upto 2000 cm\(^{-1}\). Based on these experiments and comparison with theoretical calculations\(^\text{17}\)–\(^\text{19}\), the optic modes of MgB\(_2\) are identified. From studies on the temperature dependence of infrared absorption, it is seen that the optic modes show an interesting temperature variation in that the hardening behaviour at low temperatures is arrested below 100 K, below which they soften. In addition, the IR mode at 333 cm\(^{-1}\) shows
a distinct softening below $T_c$.

**II. EXPERIMENTAL DETAILS**

The MgB$_2$ sample used in the present experiments was prepared from Mg (99.99 %) powder of 50 mesh and B (99.98 %) powder of 325 mesh. The starting materials were thoroughly mixed and put in Ta tube that was sealed in Ar atmosphere. This was subsequently sealed in a quartz tube that was heat treated at 1223 K for 2 hours. After cooling down to room temperature, the polycrystalline lumps were crushed using agate mortar and pestle and subsequently used for experimentation. X-ray diffraction measurements were carried out using Cu-K$_\alpha$ radiation in the Bragg-Brentano geometry. AC susceptibility measurements were carried out with a mutual inductance bridge and lock-in amplifier, using a dipstick cryostat operating in the 4 to 300 K range. The diamagnetic signal corresponding to the sharp superconducting transition at 39 K, and the results of the x-ray diffraction measurements are shown in Fig.1. The diffraction pattern of MgB$_2$ can be indexed to hexagonal structure (P6/mmm) with lattice parameters: $a=3.0864$ Å and $c=3.5253$ Å, in agreement with earlier studies. The diffraction pattern of crystalline $\beta$ rhombohedral boron is also shown, and it is seen that boron peaks are not discernable in the diffraction pattern of MgB$_2$. However, there are a few peaks that could be associated with MgO, whose concentration is estimated to be $\sim 1\%$. From the powder ac-susceptibility measurements, using Pb powder as standard, the superconducting volume fraction was estimated to be 75%.

Infrared absorption measurements were carried out on finely ground MgB$_2$ sample pelletized along with KBr, using a BOMEM -DA8 spectrometer operating with a resolution of 2 cm$^{-1}$. Measurements in the range of 125 - 700 cm$^{-1}$ were carried out using a mylar beam splitter and a DTGS detector. Experiments in the mid infrared range of 400 to 2000 cm$^{-1}$ have been carried out using the combination of KBr beam splitter and MCT detector. To study the temperature variation of IR modes, the sample was mounted inside a JANIS continuous flow cryostat in which temperature variation of 300 to 5 K could be achieved.
III. RESULTS AND DISCUSSION

Fig. 2 shows the IR absorbance of MgB$_2$ in the range of 300 to 650 cm$^{-1}$. The region below 300 cm$^{-1}$ is suppressed, as it is dominated by KBr absorption. The absorption spectrum in MgB$_2$ is characterised by a broad band centred at 485 cm$^{-1}$ with shoulders at 333, 387 cm$^{-1}$. Further sharp features are also noted at 542, 592 and 633 cm$^{-1}$. The latter modes match with those of $\beta$ rhombohedral boron\cite{19}, whose absorption spectrum is also shown. The occurrence of these modes, while the x-ray diffraction pattern does not indicate the presence of any B (cf. Fig. 1), points to the activation of B-like modes in MgB$_2$ due to disorder (see below). Information on the frequencies, widths and intensity of the various phonon modes have been obtained by fitting the absorption curves to a sum of Gaussians and a linear background. The resulting fits along with the components is shown in the right panel of Fig. 2, for the two representative temperatures of 297 K and 5 K.

Factor group analysis predicts for MgB$_2$ (space group P6/mmm, z=1) B$_{1g}$ + E$_{2g}$ + E$_{1u}$ + A$_{2u}$ zone centre optic modes, of which E$_{1u}$ and A$_{2u}$ are IR active and E$_{2g}$ is Raman active. There have been several calculations of these mode frequencies\cite{6,7,9,14} with a general agreement. Kortus et al\cite{6} have calculated the two IR active modes of E$_{1u}$ and A$_{2u}$ symmetry to be at 320 and 390 cm$^{-1}$ respectively and a Raman mode of E$_{2g}$ symmetry at 470 cm$^{-1}$. In the calculations of Kong et al\cite{8}, carried out using LMTO method, the infrared modes are at 335 and 401 cm$^{-1}$ and the Raman mode is at 585 cm$^{-1}$. Yildrim et al\cite{14} have calculated the infrared modes to be $\omega$(E$_{1u}$) = 40.7 meV, $\omega$(A$_{2u}$) = 49.8 meV and the Raman mode $\omega$(E$_{2g}$) = 74.5 meV. Comparing these theoretical calculations\cite{6,7,9,14} with our experimental results, we identify the absorption features at 333 and 387 cm$^{-1}$ with E$_{1u}$ and A$_{2u}$ infrared modes.

As for the absorption band centred at 485 cm$^{-1}$, we first note that it is different from the Raman mode identified to be at 560 cm$^{-1}$ in the experiments by Bohnen et al\cite{15} and at 620 cm$^{-1}$ in the experiments of Chen et al\cite{16}, and Goncharov et al\cite{17}. In all these experiments, the Raman mode is observed to be very broad $\sim$ 200 cm$^{-1}$. Chen et al\cite{16} have suggested
that this broad feature arises due to disorder which relaxes the momentum selection rule resulting in phonons in the entire Brillouin zone being sampled in the Raman experiment. Taking cue from this, we note that the broad feature at 485 cm\(^{-1}\), observed in the present infrared absorption experiments (cf. Fig.2) can be associated with the peak in the phonon density of states at \(\sim 54\) meV, that is seen in the theoretical calculations and neutron scattering experiments\(^{12,14}\). In effect the broad absorption band centred at 485 cm\(^{-1}\) arises due to sampling of the phonons in this energy range over the entire Brillouin zone. The exact nature of disorder that is being invoked to account for the absorption spectrum is not clear at present, but could be off-stoichiometry or disorder in the arrangement of layered structure. We reiterate that the present infrared absorption measurements have been carried out on a sample characterised by sharp x-ray diffraction pattern and superconducting transition (cf. Fig.1).

The results of additional infrared absorption experiments in MgB\(_2\), carried out over an extended range upto 2000 cm\(^{-1}\), are shown in Fig.3. The absorption spectrum is characterised by a linear background with broad humps centred at 485, 1040, 1442 and 1635 cm\(^{-1}\). While the band at 1040 cm\(^{-1}\) matches with crystalline B (also shown), we discount the possibility of attributing this feature in MgB\(_2\) to the presence of a second phase of B in our sample, since our x-ray diffraction pattern does not indicate the presence of unreacted B. To substantiate this, we also show in Fig. 3b the absorption spectrum of superconducting MgB\(_2\) synthesised from amorphous B. This is also characterised by an absorption band at 1040 cm\(^{-1}\), a feature that is absent in the starting amorphous B. This could not have arisen due to crystallisation of amorphous B itself, a process that is known\(^2\) to occur only beyond 1500 K. From these studies, as also several control infrared and x-ray diffraction experiments on MgB\(_2\) samples in which intentionally crystalline B has been added, and studies\(^2\) on Cu doped MgB\(_2\), we infer that the absorption spectrum of MgB\(_2\) shown Fig.3, viz., as characterised by a linear background with broad bands centred at 485, 1040, 1442 and 1635 cm\(^{-1}\) is intrinsic to the system. We note that the absorption bands occurring at 1040, 1442 and 1635 cm\(^{-1}\) are beyond the range of optic phonons predicted by theoretical calculations\(^6\)–\(^9\). This
once again points to the important role of disorder in this system which may be activating the high frequency B-like modes\textsuperscript{19} in MgB\textsubscript{2}. We also note that these high frequency features appear like replication of the absorption band at 485 cm\textsuperscript{-1} and hence may be due to combination modes. The relatively large intensity of these combination modes could be due to the large anharmonicity, which has been shown to exist\textsuperscript{14} in this system.

**IV. TEMPERATURE DEPENDENCE OF IR ABSORPTION**

The temperature dependence of IR absorption in the range of 300-650 cm\textsuperscript{-1} has been followed across the superconducting transition. Fig.4 summarises the results on the temperature variation of the frequencies and widths of the phonon features at 333, 387 and 485 cm\textsuperscript{-1}. These are seen to harden initially with the lowering of temperature, but this trend is arrested at \( \sim 100 \) K, below which they soften. An anomalous variation is also noticed in the widths, in that they increase with the lowering of temperature. In contrast, it is seen from Fig.5 that the phonon modes at 542, 592 and 634 cm\textsuperscript{-1}, which are B-like modes(cf. Fig.2), indicate a regular behaviour, viz., a hardening of the modes and a decrease in phonon width with the lowering of temperature.

The observed softening of the mode frequencies below \( \sim 100 \) K in Fig.4 point to a structural anomaly. While the presence of an incipient structural instability is well known in the case of strong electron phonon coupled superconductors\textsuperscript{22}, this is not clearly established in the case of MgB\textsubscript{2}. In fact the experiments by Jorgensen et al\textsuperscript{18} on the variation of lattice parameters of MgB\textsubscript{2} with temperature, down to 11 K, indicate only a continuous decrease in the a and c axis parameters with no anomalies. At the same time, experiments on the suppression of superconductivity with small decrease in c-parameter, obtained by Al doping\textsuperscript{23}, is indicative of the fact that MgB\textsubscript{2} is near a structural instability. The present infrared absorption measurements, which shows softening of the phonon modes suggest that there could be a minor increase in c axis parameter below \( \sim 100 \) K. This calls for further detailed structural investigations using techniques such as EXAFS.
In the case of mode at 333 cm$^{-1}$, there is also a distinct softening below $T_c$. While the underlying reason for this behaviour is not clear, we would like to point out that in the experiments of Jorgensen et al\textsuperscript{18}, a distinct increase in the Debye-Waller factor, $U_{33}(B)$, has been observed below $T_c$. This increase in the thermal factor of B along the $z$ axis may have a bearing on the softening of the optic mode, observed in the present investigations. Earlier neutron diffraction measurements by Sato et al\textsuperscript{13} indicated an anomalous behaviour of a mode at 17 meV, subsequently discounted in other experiments\textsuperscript{14}. In the studies by Yildrim et al\textsuperscript{14}, no substantial changes in the phonon density of states has been observed with the lowering of temperature from 200 to 7 K. While this is contrary to the present observations, this may be pointing to the sensitivity of infrared absorption measurements to pick up small changes in the mode frequencies with the lowering of temperature. We also note that while we have seen a small softening of the 333 cm$^{-1}$ mode, there is no corresponding change in the width, which is expected to be modified with the appearance of electronic energy gap in the superconducting phase\textsuperscript{24}.

V. CONCLUSIONS

To summarise, through infrared absorption measurements, optic modes in MgB$_2$ have been identified. Infrared modes are seen at 333 and 387 cm$^{-1}$, in accordance with theoretical calculations\textsuperscript{6–9}. While the present experiments have been carried out on MgB$_2$ sample characterised by sharp diffraction peaks and superconducting transition, it is noted that the infrared absorption shows broad features that can be accounted by invoking disorder and the consequent relaxation of momentum selection rule. The broad band centred at 485 cm$^{-1}$, has been identified with the peak in the phonon density of states and additional broad features corresponding to combination modes are also seen in the present experiments. In effect, the measured absorption spectrum is an indication of the phonon density of states as sampled by the infrared absorption. These optic modes in the far infrared range exhibit interesting temperature dependence involving a softening below $\sim$ 100 K. The implications
of this on a possible structural anomaly needs to be investigated.

It is seen that the infrared modes at 333 and 387 cm$^{-1}$ are characterised by a widths of \( \sim 40 \text{ cm}^{-1} \), which is considerably smaller than the width of the Raman mode \( \sim 200 \text{ cm}^{-1} \). This may be taken as an evidence for the strong electron phonon interaction with the $E_{2g}$ mode, as has been suggested by theoretical calculations. However, given that in this system disorder and dispersion effects seem to play a considerable role, to dileneate the electronic contribution to the width and to estimate the electron phonon interaction from the measured widths, using Allen formula, experiments need to be carried out on single crystals of MgB$_2$. This will also help to clarify the possible role, if any, of disorder on the superconductivity in MgB$_2$.

VI. ACKNOWLEDGEMENTS

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FIG. 1. X-ray diffraction pattern of MgB$_2$ indexed to hexagonal P6/mmm structure. The impurity lines due to MgO are indicated by asterix. Also shown is the diffraction pattern of crystalline B to indicate that no B features are discernable in the diffraction pattern of MgB$_2$. The inset shows the superconducting transition at 39 K.
FIG. 2. Panel (a) shows the absorption spectrum of MgB$_2$ at 297 and 5 K respectively. Also shown are the absorption spectra of the crystalline B. Panel (b) shows the fits of the absorption spectrum at 297 K and 5 K in terms of sum of six Gaussians and a linear background.
FIG. 3. Mid-infrared absorption spectrum of superconducting MgB$_2$ (a) synthesised from crystalline B, and (b) from amorphous B. For comparison, the absorption spectra of the starting amorphous and crystalline B are also shown. The absorption spectrum of MgB$_2$ is characterised by broad absorption bands at 485, 1040, 1442 and 1635 cm$^{-1}$.
FIG. 4. Temperature dependence of the frequency and width of the modes at 333, 387 and 485 cm\(^{-1}\). The lines are guide to the eye, and the arrow corresponds to the superconducting transition. Notice the softening of the infrared modes below \(\sim 100\text{K}\) and a distinctive softening below \(T_c\) for the 333 cm\(^{-1}\) mode.
FIG. 5. Temperature dependence of the frequency and width of the modes at 542, 594 and 634 cm$^{-1}$. In contrast to the modes shown in Fig. 4, these show a regular hardening behaviour with the lowering of temperature. The filled squares are the mode frequency and width for crystalline B. The lines are guide to the eye.
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