Vibrational Modes in LiBC: Theory Compared with Experiment

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The search for other superconductors in the MgB$_2$ class currently is focussed on Li$_{1-x}$BC, which when hole-doped (concentration $x$) should be a metal with the potential to be a better superconductor than MgB$_2$. Here we present the calculated phonon spectrum of the parent semiconductor LiBC. The calculated Raman-active modes are in excellent agreement with a recent observation, and comparison of calculated IR-active modes with a recent report provides a prediction of the LO–TO splitting for these four modes, which is small for the B-C bond stretching mode at $\sim 1200$ cm$^{-1}$, but large for clearly resolved modes at 540 cm$^{-1}$ and 620 cm$^{-1}$.

I. INTRODUCTION

The discovery of MgB$_2$ with $T_c \sim 40$ K [1] has led to the search of related materials that may show superconductivity. An important feature required for strong electron-phonon coupling in this class of materials is that the B-C bonding $\sigma$ bands need to be partially unfilled as in MgB$_2$, which is not the case in AlB$_2$. [2] Several isostructural transition metal diborides exist, [3] but their electronic structures are entirely different and not conducive to high temperature superconductivity.

The theoretical work since January 2001 [2,11–15] has clarified much about the cause of the high $T_c$ in MgB$_2$: strongly covalent-bonding states, normally fully occupied, are driven to the Fermi level ($E_F$) by the chemistry of MgB$_2$, and the resulting hole carriers are exceedingly strongly coupled to the bond stretching modes. This “covalent” coupling is what drives the critical temperature from zero (or near) to 40 K.

II. METHOD OF CALCULATION

The phonon energies and EP matrix elements have been obtained from linear response theory, [16] as implemented in Savrasov’s full-potential linear muffin-tin orbital code. [17,18] A double-$\kappa$ basis was sufficient, since the atoms only have open $s$ and $p$ shells. A dense grid of Q points was chosen (a 16,16,4 grid giving 90 Q points in the irreducible wedge). For k-space integration a finer 32,32,8 grid was used, together with an adaptive tetrahedron integration scheme. The code was used previously for MgB$_2$ by Andersen’s group. [13] These Q meshes and k-point meshes were chosen to deal with Fermi surface effects in the hole-doped (hence metallic) material, and should be more than sufficient for the semiconducting phase that we discuss here. The effects of doping on the phonon spectrum are reported elsewhere. [6]

The frozen phonons were calculated using one of two methods. The linearized augmented plane method as implemented in the WIEN97 package [19] and the full potential local orbital (FPLO) code [20,21] were used. Calculational details were described previously. [4,6] The masses used were, in a.m.u.: Li, 6.94; B, 10.81; C, 12.01, and the experimental lattice constants $a=2.75\AA$, $c=7.058\AA$ were used.
III. CALCULATED PHONON FREQUENCIES AT Q=0

The results for all eighteen branches along high symmetry directions in the hexagonal Brillouin zone are shown in Fig. 2. We concentrate here on the Q=0 modes that are most accessible to experimental probes. According to the code [22] SMODES1.2.4 that calculates the eigenmodes for an arbitrary crystal structure and Q point, the Γ point modes in LiBC (P6\textsubscript{3} mmc, #194 in the International Tables) decompose as 3A\textsubscript{2u}+2B\textsubscript{2g}+1B\textsubscript{1u} (6 modes) polarized along the c axis, and 3E\textsubscript{1u}+2E\textsubscript{2g}+E\textsubscript{2u} (12 modes) polarized in the basal plane. The 2E\textsubscript{2g} modes are Raman active, while IR activity involves the 2A\textsubscript{1g} modes. [9] (A different convention for designating the B\textsubscript{1g} and B\textsubscript{2g} symmetry labels was used in Ref. [10]. We use the convention used by the SMODES code.) We go through the modes calculated using linear response theory individually in increasing frequency (given in cm\textsuperscript{-1}).

- \(\omega=0\): A\textsubscript{2u} and E\textsubscript{1u}, acoustic modes.
- \(\omega=171\): E\textsubscript{2g}, B-C layers sliding against each other
- \(\omega=289\): B\textsubscript{2g}, B-C layers beating against each other, motion along the c axis
- \(\omega=306\): E\textsubscript{2u}, Li layers sliding against each other
- \(\omega=352\): E\textsubscript{1u}, Li layers sliding against the B-C layers
- \(\omega=422\): A\textsubscript{2u}, Li layers beating against the B-C layers, motion along the c axis
- \(\omega=540\): B\textsubscript{1u}, Li layers beating against each other, motion along the c axis
- \(\omega=802\): A\textsubscript{1g}, B-C puckering mode, all B atoms move oppositely to all C atoms, Li sites become inequivalent
- \(\omega=821\): B\textsubscript{2g}, B-C puckering mode, B moves with C atoms above/below it, Li sites remain equivalent
- \(\omega=1194\): E\textsubscript{1u}, B-C bond stretching mode, the two layers are out-of-phase
- \(\omega=1204\): E\textsubscript{2g}, B-C bond stretching mode, layers in phase

As expected, the lower frequency modes \(\omega < 600\) cm\textsuperscript{-1} involve “rigid” layer displacements (B and C displacements differ somewhat, but are parallel for these modes). The puckering (B-C bond bending) modes lie at 811±10 cm\textsuperscript{-1} = 100 meV, and both in-phase and out-of-phase bond-stretching modes are at very high frequency (1200 cm\textsuperscript{-1} = 149 meV).

IV. CHECKS USING THE FROZEN PHONON METHOD

During the progress of our studies we have made various checks on the results of the linear response calculations by using the (reliable but tedious) frozen phonon method for selected modes. Here we briefly describe these results, which serve to verify the linear response results and provide some indication of the precision of our methods. Each of the methods is subject to its own numerical approximations, and hence uncertainties. For example, the frozen phonon method requires the fitting of a discrete set of E(u) (energy versus displacement) values to a functional form, followed by use of the quadratic term, whereas the linear response method does not, but is more sensitive to choice of basis set, for example.

Symmetry lowering from the ideal P6\textsubscript{3} mmc space group observed in Raman scattering spectra [10] suggested a puckering of the B-C rings and change of crystal symmetry to the P\textsupersym\textsubscript{3}1 space group, which would imply an instability of the flat B-C layer to such a puckering displacement. Calculation of the energy change versus displacement for this buckling mode indicated not only no instability, but a rather hard phonon with frequency of 788 cm\textsuperscript{-1}, within 2.5% of the linear response result of 802 cm\textsuperscript{-1}. This result is consistent with the tight-binding model of Ramirez et al. [23] for a single B-C layer coupled to ionic charges representing the rest of the crystal, which gave a stable flat (unpuckered) layer. Another possibility that may account for this observed symmetry lowering would be layer stacking faults (B above B and C above C). Such faults would provide another distinct type of Li site, in much the same way that occurs for the (proposed) frozen puckering mode. Further experimental work will be necessary to clarify this question.

Frozen phonon evaluations of the E\textsubscript{2g} bond-stretching mode were carried out using both the FPLO and LAPW
codes. The results (1167 cm\(^{-1}\) and 1145 cm\(^{-1}\), respectively) are 4\% lower than the linear response result. However, some of this discrepancy is due to neglect of coupling of this mode with the lower frequency \(E_{2g}\) mode. (The “frozen phonon” we chose assumed the B and C displacement amplitudes were inversely proportional to their masses.) This neglected coupling would increase the frequency, improving agreement with the linear response value.

V. COMPARISON WITH EXPERIMENT

Raman active \(E_{2g}\) modes are observed at 170 and 1176 cm\(^{-1}\). [10] The harder mode is surely the bond-stretching mode, calculated to lie at 1204 (linear response) and 1145, 1167 cm\(^{-1}\) by the two independent FP calculations discussed above (which, as noted there, are known to be slight underestimates). Thus the linear response value is too large by 2\%. The 170 mode arises from the B-C “shear” mode (Li layers are fixed) [9] and is indistinguishable from the calculated 171 cm\(^{-1}\).

The excellent agreement for the bond-stretching mode implies that anharmonicity must be negligible for LiBC. Several groups have calculated the harmonic frequency of the Raman-active mode in MgB\(_2\), finding results in the range 490 – 550 cm\(^{-1}\). The peak in the observed Raman spectrum occurs at 600 cm\(^{-1}\), which has been interpreted to mean that anharmonicity of this mode in MgB\(_2\) is considerable. [14,15] Boeri et al. have demonstrated that this anharmonicity is due to the metallic nature, and to the proximity of the Fermi level to the \(\sigma\) band edge. [24] Hence, appreciable anharmonicity is not expected to be present in the undoped LiBC material. We have found, in hole-doped Li\(_{1-x}\)BC, that this anharmonicity again arises, and this work will be reported elsewhere.

IR absorption measurements, performed with samples and geometry such that all modes are likely to be seen, identify broad but reasonably well defined peaks centered at 540, 620, and 1180 cm\(^{-1}\), and a shoulder in the 680-800 cm\(^{-1}\) region that could be fit to a IR mode. The harder mode is surely the bond-stretching mode, \(E_{2g}\), \(\omega_{\text{calc}} = 306\), \(\omega_{\text{exp}} = 620\) (implying an unexpectedly large LO-TO splitting of 315 cm\(^{-1}\)), since it would imply a large \(Z^*\) for the Li ion. The last, and lowest, mode is the B-C layer beating mode, \(\omega_{\text{calc}} = 289\), \(\omega_{\text{exp}} = 540\). This large LO-TO splitting of 250 cm\(^{-1}\) implies large \(Z^*\) for the B and/or C atoms for \(\hat{c}\) axis displacement.

VI. SUMMARY

The linear response phonon calculations are in quite close agreement with the Raman scattering identifications of Hlinka et al. [10] seen in \(zy\) polarization. The symmetry lowering inferred from scattering in \(xx\) polarization remains unclear. Comparison of the calculations with the IR microscope results of Pronin et al. [9] for the lower frequency IR modes suggest large \(Z^*\) for the Li and B (and perhaps C) ions for \(\hat{c}\) axis displacements, while the lack of any significant LO-TO splitting for the bond-stretching mode suggests negligible \(Z^*\) for \(a-b\) plane displacement of B and C.

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