Vibrational modes in LiBC: theory and experiment

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Abstract

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 and 620 cm^{-1}.
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1. 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 σ 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.

Some of the present authors have proposed [4] that hole-doped LiBC, which was reported by Wörle et al. [5], should be a member of the MgB_2 class of superconductors and would have an even higher T_c if it is doped to $x > 0.3$ [4,6]. Several other groups have now reported the undoped, semiconducting LiBC compound [7–10] and have reported characterization by X-ray diffraction, infrared (IR) absorption, and Raman spectroscopy.

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 (Fig. 1).

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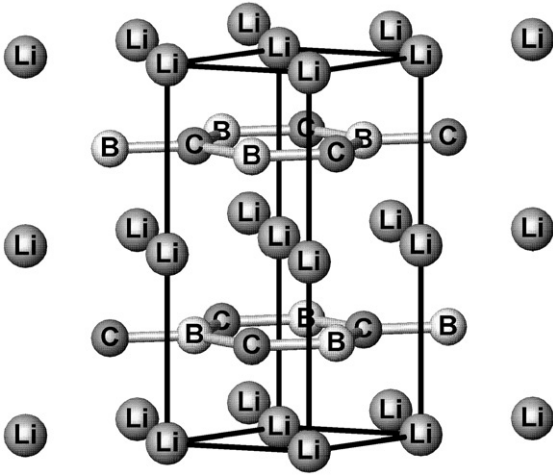
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Fig. 1. Crystal structure of LiBC. The graphene structure of the B–C layers is a direct generalization of the B layers of MgB_2, and the Li atoms reside on the Mg site of MgB_2. The unit cell contains two formula units because B and C alternate in position along the $\hat{c}$-axis (i.e. the two B–C layers are connected by a 120° screw axis).

2. 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-κ 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 $a = 2.75$ Å, $c = 7.058$ Å were used.

3. Calculated phonon frequencies at $Q = 0$

The results for all 18 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] SMODES.1.2.4 that calculates the eigenmodes for an arbitrary crystal structure and Q point, the Γ point modes in LiBC ($P6_3/mmc$, #194 in the International Tables) decompose as $3A_{2u} + 2B_{2g} + 1B_{1u}$ (6 modes) polarized along the $\hat{c}$-axis, and $3E_{1u} + 2E_{2g} + E_{2u}$ (12 modes) polarized in the basal plane. The $2E_{2g}$ modes are Raman active, while IR activity involves the $2A_{2u}$ and $2E_{1u}$ modes [9]. (A different convention for designating the B_{1g} and B_{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^{-1}.)

- $\omega = 0$: A_{2u} and E_{1u}, acoustic modes
- $\omega = 171$: E_{2g}, B–C layers sliding against each other
- $\omega = 289$: B_{2g}, B–C layers beating against each other, motion along the $\hat{c}$-axis
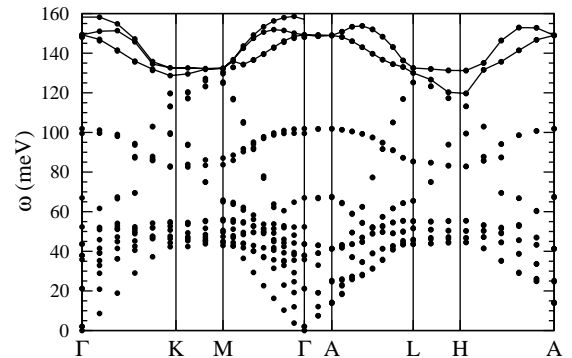

Fig. 2. Phonon spectrum of semiconducting LiBC, calculated using linear response methods as described in the text. The bond-stretching modes are connected by solid lines.

- $\omega = 306$: E_{2u}, Li layers sliding against each other
- $\omega = 352$: E_{1u}, Li layers sliding against the B–C layers
- $\omega = 422$: A_{2u}, Li layers beating against the B–C layers, motion along the $\hat{c}$-axis
- $\omega = 540$: B_{1u}, Li layers beating against each other, motion along the $\hat{c}$-axis
- $\omega = 802$: A_{2u}, B–C puckering mode, all B atoms move oppositely to all C atoms, Li sites become inequivalent
- $\omega = 821$: B_{2g}, B–C puckering mode, B moves with C atoms above/below it, Li sites remain equivalent
- $\omega = 1194$: E_{1u}, B–C bond stretching mode, the two layers are out-of-phase
- $\omega = 1204$: E_{2g}, B–C bond stretching mode, layers in phase.

As expected, the lower frequency modes $\omega < 600$ cm^{-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^{-1} = 100 meV, and both in-phase and out-of-phase bond-stretching modes are at very high frequency (1200 cm^{-1} = 149 meV).

4. 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 $P6_3/mmc$ space group observed in Raman scattering spectra

[10] suggested a puckering of the B–C rings and change of crystal symmetry to the $P\bar{3}m1$ 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^{-1}, within 2.5% of the linear response result of 802 cm^{-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_{2g} bond-stretching mode were carried out using both the FPLO and LAPW codes. The results (1167 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.

5. 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 cm^{-1} 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 σ 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 around 700 cm^{-1} [9]. Comparison of calculations with IR measurements is problematic unless the dynamical effective charges Z^* are calculated, which we have not yet done. All of our calculations neglect the accompanying macroscopic electric field which gives the LO–TO splitting. Since the calculations agree so well with data for the Raman modes, we will interpret the difference $\omega_{exp} - \omega_{calc}$ as the LO–TO splitting for the mode, and we will only know of difficulties if this difference is negative.

The observed 1180 cm^{-1} mode is surely the E_{1u} B–C bond stretching mode, calculated to lie at 1194 cm^{-1}. The agreement implies that the LO–TO splitting for this mode is very small (it cannot be negative, of course). The best identification of the experimental "shoulder" mode at ~ 700 cm^{-1} is with the calculated A_{2u} B–C puckering mode at 802 cm^{-1}, which indicates a problem either with the identification of this shoulder with an IR-active mode, or a problem with the calculation; further experimental study will be required to resolve this discrepancy. The next lower calculated mode is the E_{1u} Li sliding mode, $\omega_{calc} = 306, \omega_{exp} = 620$ (implying an unexpectedly large LO–TO splitting of 315 cm^{-1}), and it would imply a large Z^* for the Li ion. The last, and lowest, mode is the B–C layer beating mode, $\omega_{calc} = 289, \omega_{exp} = 540$. This large LO–TO splitting of 250 cm^{-1} implies large Z^* for the B and/or C atoms for $\hat{c}$-axis displacement.

6. Summary

The linear response phonon calculations are in quite close agreement with the Raman scattering identifications of Hlinka et al. [10] seen in xy 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.

Note added in proof

The symmetry lowering discussed in Section 4 has been found to be sample history dependent; see Ref. [10].

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