PHYSICAL REVIEW B **69**, 052506 (2004)

Lattice dynamics of LiBC

B. Renker,[1] H. Schober,[2] P. Adelmann,[1] P. Schweiss,[1] K.-P. Bohnen,[1] and R. Heid[1]
[1]*Forschungszentrum Karlsruhe, Institut für Festkörperphysik, P.O. Box 3640, D-76021 Karlsruhe, Germany*
[2]*Institut Laue-Langevin, Boîte Postale 156 X, F-38042 Grenoble Cedex, France*

(Received 2 October 2003; published 27 February 2004)

We have investigated the lattice dynamics of LiBC at various annealing temperatures. Experimental Raman and inelastic neutron-scattering results are confronted with density-functional calculations. The excellent agreement between experiment and theory indicates that we have attained a high level of understanding for LiBC, which by its structure is closely related to superconducting MgB_2. We will show that annealing of the sample is insufficient to cause Li deficiency and thus produce the expected superconductivity.

DOI: 10.1103/PhysRevB.69.052506 PACS number(s): 74.25.Kc, 63.20.Kr, 78.70.Nx, 71.20.Lp

The simple binary compound MgB_2 has attracted considerable attention because of its exceptional superconducting properties. A strong coupling of holes in the B $2p$ σ bands to high-frequency boron in-plane phonon modes meets the BCS requirements for a transition temperature as high as 40 K.[1,2] A most prominent experimental manifestation of this coupling is the extreme broadening of the E_{2g} mode in the Raman spectrum.[2,3] With respect to structural peculiarities LiBC provides a comparable system to MgB_2. B and C atoms alternately occupy the sites within the hexagonal sheets. Charge neutrality is restored by replacing Mg^{+2} by Li^+. A doubling of the unit cell along the hexagonal axis occurs due to an interchange of B and C atoms in neighboring planes[4]. While the stoichiometric compound is an insulator with completely filled σ bands, there have been recent theoretical speculations that hole doping of these bands can be achieved for LiBC compounds with Li deficiencies in the range of 25%, resulting in transition temperatures as high as 120 K, i.e., largely exceeding those of MgB_2.[5] So far no convincing experimental evidence for superconductivity could be established.[6,7] In this context, it is most interesting to investigate the lattice dynamics of this particular compound and to compare it with our previous results for MgB_2 and AlB_2.

LiBC has been synthesized following a procedure which is described in detail in Ref. 4. In view of our neutron-scattering experiments we have used isotope pure ^{7}Li metal together with amorphous ^{11}B and graphite powders. The mixed components were pressed into pellets wrapped into a Ta foil and annealed in a closed Nb tube at 1500 °C for 3 h. The final product was homogeneous and consisted of yellow shining crystallites with clean faces and metallic luster. Hexagonal shaped platelets with diameters of up to 200 μm and 20 μm in thickness could be found and were chosen for optical measurements and structural analysis on a four circle diffractometer. Additional x-ray powder diffraction gave no indications of any spurious phases. The hexagonal space group $P6_3$/mmc which had been found before was confirmed for all of our samples. In order to achieve the desired hole doping, part of our samples were annealed in dynamic vacuum up to temperatures of 1370 K where clear signatures of a disintegration of the crystallites were observed. There was evidence from single-crystal structure analysis and surface sensitive Raman-scattering investigations performed on the same specimens that a homogenous doping by Li deficiency could not be obtained. Li losses were restricted to the surface and finally resulted in a destruction of the $P6_3$/mmc structure. Preparations where some of the Li^+ was replaced by bigger Na^+ ions did not change this result. However, with

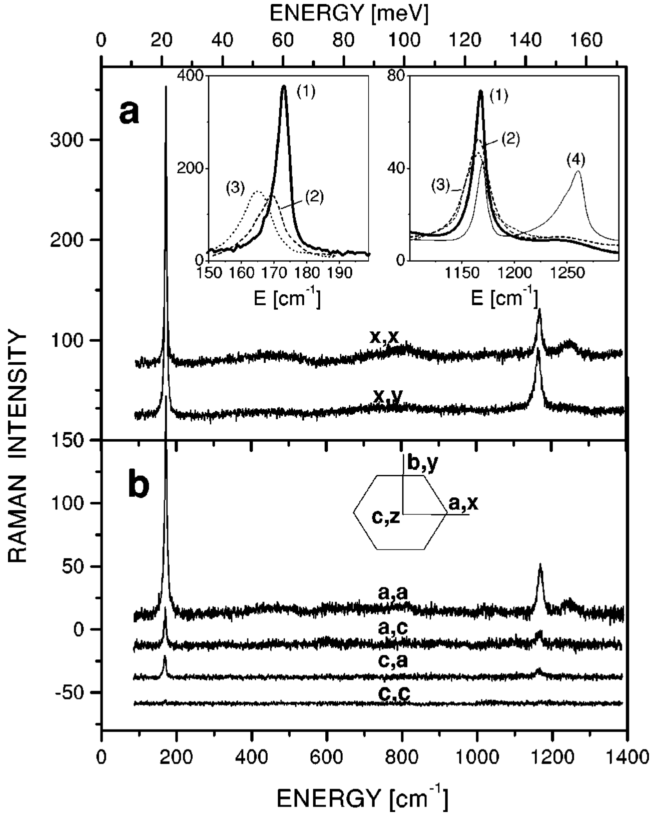

FIG. 1. Observed Raman signals from a LiBC single crystal in backscattering configuration. Part (a): scattering from the hexagonal plane. The small contribution near 1240 cm^{-1} in the polarized spectrum is not allowed for $P6_3$/mmc symmetry and is attributed to structural defects (see text). Results for the treated materials are shown by the inserts: (1) as prepared LiBC, (2) LiBC annealed at 1270 K, (3) $Li_{0.95}Na_{0.05}BC$, (4) severely damaged LiBC crystal by laser heating. Part (b): scattering from the ac plane; the lettering above the spectra marks the polarization vectors of the incoming and outgoing light. In agreement to the selection rules strong Raman signals are only observed if both polarization vectors are contained within the hexagonal plane.

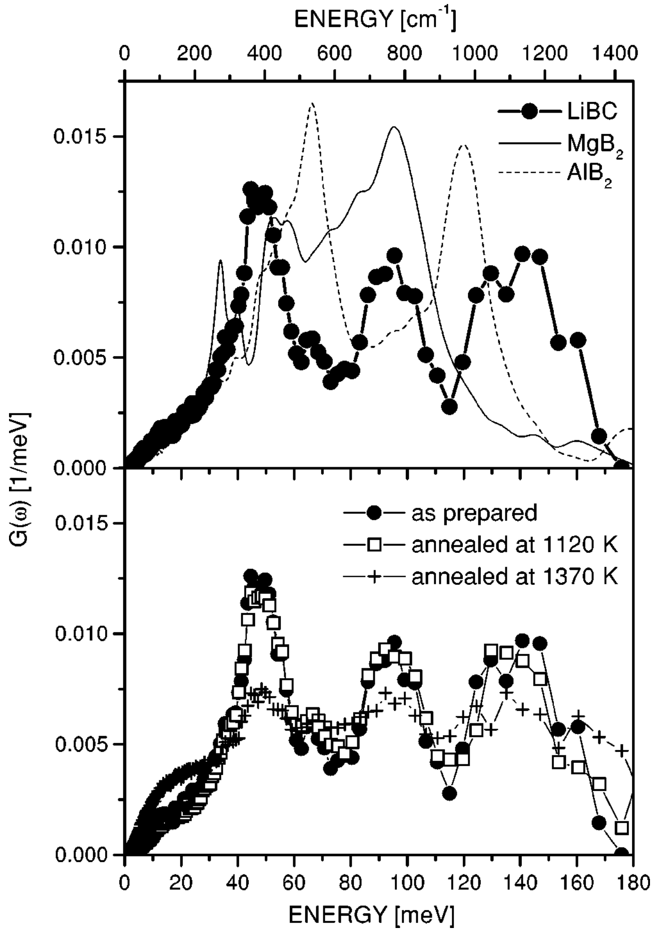

FIG. 2. Generalized phonon densities of states for samples of LiBC measured by inelastic neutron scattering. Upper part: Result for as prepared LiBC at 300 K in comparison to MgB_2 and AlB_2. Lower part: No peak shifts occur on heating even at 1370 K. Heating at $T \geqslant 1370$ K causes a decomposition of the sample as it can be seen from a progressively washing out of characteristic structures. For a hole doped sample a significant down shift of the high-energy peak would have been expected.

respect to the higher vacuum pressure only 5% of the amount of Li were replaced by Na. All of our samples—the as prepared, the annealed, and the Na doped ones—proved to be nonsuperconducting above 4 K.

For inelastic neutron-scattering (INS) measurements the microcrystalline powders were filled into flat pockets of $2 \times 3 \times 0.3$ cm^3 made from Al foil. Measurements were performed at 300 K on the time-of-flight spectrometers IN6 (incoming energy 4.7 meV) and IN4 (incoming energy 39.4 meV) at the HFR in Grenoble (France) in the upscattering mode. A generalized phonon density of states $G(\omega)$ was obtained from the sum of scattering spectra recorded over a large angular range from 10° to about 120°. The IN6 and IN4 $G(\omega)$ coincide well above 10 meV indicating that the incoherent approximation works very well. Only small coherence effects are observed in the IN6 data below 10 meV due to the fact that the Q space is less extensively sampled with the longer wavelength neutrons at these small energy transfers. Multiphonon contributions were removed via a self-consistent calculation procedure.[8]

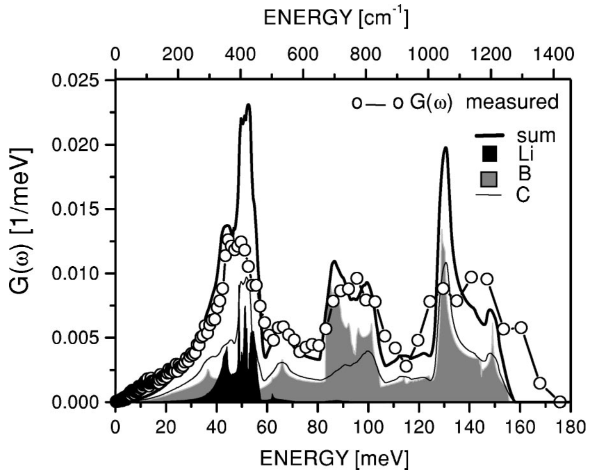

FIG. 3. The calculated generalized phonon density of states compared to the measured result for pristine LiBC. Marked are contributions of the different atoms.

The factor group analysis for LiBC yields $2A_{2u}+2B_{1g}+B_{2u}+2E_{1u}+2E_{2g}+E_{2u}$ zone-center optic modes where only the two E_{2g} modes are Raman active. The latter modes should be observable for all configurations with polarization vectors of the incoming and the reflected light within the hexagonal plane. Zero intensity is expected if one of these vectors is parallel to the crystallographic c axis. The spectra shown in Fig. 1 prove that this is essentially the case. In particular we do not observe additional strong and sharp lines at 546 cm^{-1} and 830 cm^{-1} which have been reported by Hlinka *et al.*[9] and which was the reason to propose the lower symmetric space group $P\bar{3}m1$ for LiBC.

These authors conclude on a particular "puckering" of hexagonal BC planes.[9] We have never observed these lines although we have noticed that the background spectrum may depend on details of the sample preparation. A broader contribution around 1270 cm^{-1} which occurs in the polarized spectra is also observed in our measurements. It is not allowed as a one phonon contribution. Its intensity when compared to the allowed line at 1167 cm^{-1} is sample dependent and increases for samples which were annealed at higher temperatures as shown by the insert. This line is attributed to structural defects although its origin is not fully understood. X-ray-diffraction measurements on the same crystallites which investigate the whole volume however did not give evidence for similar strong changes. It is concluded that defects which are created by Li evaporation mainly exist on the surface.

We have annealed part of our samples at 800 °C, 1000 °C, and 1100 °C for $\geqslant 3$ h in dynamic vacuum in order to reduce the Li content. Structural changes within the Li sheets which provide a coupling between neighboring BC planes are expected to show up in the sliding frequency at 171 cm^{-1} whereas an enhanced electron-phonon coupling should give rise to a strongly anharmonic behavior of the in-plane E_{2g} mode. Little changes are observed in the Raman spectra up to about 1000 K when Li starts to evaporate. For the sample which was annealed at 1270 K we observe a

TABLE I. Calculated Γ point frequencies in meV (cm^{-1}).

sym	ω	Elongations
E_{2g} (R)	21.8 (176)	E_{2g}, BC planes slide against each other Li at rest
E_{2u}	37.3 (301)	Li layers slide against each other
B_{1g}	39.5 (319)	symmetric vibration of BC layers along c
E_{1u} (IR)	43.9 (T) (354) 47.4 (L) (382)	Li layers slide against BC layers
A_{2u} (IR)	56.7 (T) (457) 69.9 (L) (563)	Li layers vibrate against BC layers along c
B_{2u}	67.9 (548)	Li layers vibrate against each other along c
A_{2u} (IR)	101.5 (T) (819) 104.2 (L) (840)	B and C sublattices move against each other along c, Li not at rest
B_{1g}	104.5 (843)	symmetric vibration of BC layers along c, Li at rest
E_{1u} (IR)	140.9 (T) (1136) 152.7 (L) (1231)	B-C bond stretching mode, odd displacement of BC layers
E_{2g} (R)	142.0 (1145)	B-C bond stretching mode, even displacement of BC layers

small but significant downshift of the sliding frequency. A larger shift is observed for a sample of nominal $Li_{0.95}Na_{0.05}BC$. For the B-C stretching mode at 1167 cm^{-1}, however, we register still smaller relative shifts which let us conclude that possible changes in the electronic system are negligible. These results proved to be reproducible on different crystallites and are shown in detail by the inserts in Fig. 1. Thus neither a dramatic softening nor a huge line broadening as observed for MgB_2 (Refs. 2,3) occur. In view of the high frequency of the E_{2g} in plane mode LiBC resembles much more the compound AlB_2. However, our investigations so far failed to give evidence for a homogeneous reduction of the Li concentration in the entire crystal—a prerequisite for a hole doping and the expected down shift of the E_{2g} mode frequency. In a recent paper hole doping of $Li_{1-x}BC$ with $x \leqslant 0.37$ according to the observed weight losses is reported.[10] The samples, however, also remained semiconducting.

Further results are obtained by inelastic neutron scattering which can access all excitations in the entire Brillouin zone and which in difference to Raman-scattering probes the whole volume of the crystallites. Figure 2 shows the generalized phonon density of states $G(\omega)$ which for all of our results is normalized to one. The 300 K result for LiBC is shown in comparison to earlier data obtained for MgB_2 and AlB_2.[2,3] The spectrum consists of three main peaks. Hard B and C in-plane and out-of-plane modes are grouped around 150 meV and 100 meV, respectively. Modes where neighboring BC sheets slide against each other as well as vibrations of the weaker bonded Li ions contribute to the lowest peak around 50 meV. It can be seen that the upper two peaks of LiBC group nicely around a corresponding line of AlB_2 at 120 meV. A significantly softer spectrum was observed for superconducting MgB_2 which in part is due to the spectacular softening of B-B in-plane vibrations.

We have studied in detail whether such frequency shifts occur for the annealed samples. A phonon softening is predicted by theory for hole doped samples due to Li deficiency.[5] It can be seen from Fig. 2 that no distinct shift in peak positions occurs. Rather the observed changes can be related to a progressive disintegration of LiBC crystallites. The shoulder at 160 meV gains significantly in intensity for the annealed samples. This feature agrees well with the "forbidden" line at 1270 cm^{-1} in the Raman spectrum. The 1370 K spectrum shows a strong increase in intensity at low frequencies which is typical for an amorphous system. At the same time the well pronounced original structure in the phonon spectrum is washed out. Even for the severely damaged sample (the 1370 K spectrum) no significant shift in frequency of the peaks around 90 meV and 130 meV occurs. In the original paper of Wörle *et al.*[4] there was hope that the $P6_3/mmc$ structure was stable for samples with $Li_{1-x}BC$ with $x \leqslant 0.25$. We find, however, that the structure breaks down for Li deficiencies and conclude that Li diffusion within the sheets is negligible. Similar results have been found by other authors.[6,7]

A detailed analysis of the lattice dynamics is obtained from density-functional calculations which could successfully explain peculiarities in the spectra of various diborides.[2,3,11] For LiBC a direct comparison of theoretical predictions to the measured Raman and INS results allows for a critical check of such first principles calculations. The density-functional theory provides an accurate and parameter free analysis of the electronic structure and of the bonding properties. Our calculations which correspond to those performed for other diborides[11] are based on a perturbational approach using the mixed basis pseudopotential method and provide information on the phonon frequencies and electron-phonon coupling within the whole Brillouin zone. Pseudopotentials for Li and C (Ref. 12) were constructed according to Hamann-Schlüter-Chiang, whereas for B a Vanderbilt-type potential was chosen. Our calculations apply to stoichiometric LiBC and the structure $P6_3/mmc$ which assumes a regular stacking of hexagonal BC planes and sheets of Li ions sitting on the corner of trigonal prisms. It can be seen from Fig. 3 that a very high level of correspondence to the experimental $G(\omega)$ is reached. All distinct maxima correspond to similar features in the experimental spectrum. The high-frequency shoulder at 160 meV seen in the experimental spectrum is not reproduced by the calculation, which supports our interpretation as a defect induced contribution. It can be seen from the partial density of states that the Li modes overlap with B and C vibrations. Our theoretical phonon dispersion curves are in reasonable agreement with those obtained recently by a linear-response calculation within a linear-muffin-tin-orbitals approach.[13,14]

In Table I we have listed all 15Γ-point frequencies for undoped LiBC ordered with increasing energies. It can be seen that the correspondence of the calculated E_{2g} frequencies to the measured Raman lines at 171 cm^{-1} and 1167 cm^{-1} is quite good. A significant feature of a very strong electron-phonon coupling in MgB_2 was the drop of the E_{2g} in-plane mode at Γ well below the B_{1g} out-of-plane mode which does not occur for pristine LiBC. For the infrared active modes (A_{2u} and E_{1u} symmetry), the calculation predicts large LO-TO splittings of almost 100 cm^{-1} for the modes at 457 cm^{-1} and 1136 cm^{-1}, and much smaller ones for the remaining two. The same behavior has been found in a recent linear-response calculation using a plane-wave pseudopotential approach[15] and recent experimental work by Hlinka *et al.*[16,17]

In conclusion, we have investigated the lattice dynamics of LiBC which is closely related to that of the diborides. The present density-functional calculations provide a very satisfying description of the measured phonon density of states and Raman data. Hole doping by Li evaporation should have an important influence on the transport properties and the electron-phonon coupling as well. We have measured the phonon spectra for a series of samples which were annealed at appropriate temperatures in order to cause the desired doping. However, we do not find any spectral shifts. Our results let us believe that only a very modest quantity of Li can be evaporated from the surface of the crystals and that diffusion within the Li sheets is negligible. Annealing at high temperatures in vacuum causes an increase in amorphous contributions at the expense of crystalline LiBC. A replacement of Li^+ by bigger Na^+ might favor diffusion within the Li sheets. However, the considerably higher vacuum pressure of Na sets limits for such replacements. For a sample of nominally $Li_{0.95}Na_{0.05}BC$ a significant down-shift of 8 cm^{-1} of the 171 cm^{-1} Raman line is observed but still no signatures for an enhanced electron-phonon coupling.

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