Electronic and optical properties of LiBC

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LiBC, a semiconducting ternary borocarbide constituted of the lightest elements only, has been synthesized and characterized by x-ray powder diffraction, dielectric spectroscopy, and conductivity measurements. Utilizing an infrared microscope the phonon spectrum has been investigated in single crystals. The in-plane B-C stretching mode has been detected at 150 meV, noticeably higher than in AlB2, a non-superconducting isostructural analog of MgB2. It is this stretching mode, which reveals a strong electron-phonon coupling in MgB2, driving it into a superconducting state below 40 K, and is believed to mediate predicted high-temperature superconductivity in hole-doped LiBC [H. Rosner, A. Kitaigorodskiy, and W. E. Pickett, Phys. Rev. Lett. 88, 127001 (2002)].

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The discovery of phonon-mediated superconductivity in MgB2 with a superconducting transition temperature of \(T_c \approx 40\) K (Ref. 4 has triggered enormous interest in similar layered compounds. MgB2 consists of graphite-like boron layers with the Mg ions intercalated in between. The B-B bonding \(\sigma\)-bands reveal a two dimensional character and are strongly coupled to the in-plane stretching mode, consistent with a phonon-mediated BCS type pairing mechanism. In Raman and neutron scattering experiments an extremely strong reorganization of this stretching mode has been unambiguously demonstrated. The authors found that the in-plane boron vibration in MgB2 is shifted to 70 meV, while in the isostructural but non-superconducting AlB2 it is located at 123 meV. From the averaged phonon density and the electron-phonon coupling the superconducting transition temperatures can be estimated and the theoretical estimates using a strong electron-phonon coupling deduced superconducting transition temperatures of the correct magnitudes. Similar layered compounds have been theoretically investigated, 5 and a superconducting transition temperature of \(T_c \sim 120\) K has been predicted for hole-doped LiBC by Rosner et al. 6

Since the mid 80's LiBC was a subject of only a few experimental studies. 5 It reveals the same structure as MgB2, but with the planar hexagonal boron layers replaced by B-C layers, with the B and C atoms alternating both within the layer and along the c direction. LiBC has \(P6_{3}mnm\) symmetry with \(a = 0.275\) nm and \(c = 0.7058\) nm. 5 The stoichiometric compound is insulating. From band structure calculations a gap of at least 1 eV has been deduced for the pure compound and it has been shown that on hole doping, induced by Li-deficiency, the \(\sigma\) bands significantly contribute to the Fermi level and are strongly coupled to the B-C stretching mode. 6

In this work we synthesized powder and single crystalline LiBC, characterized the samples by x-ray powder diffraction, determined the dielectric constant and the conductivity as function of temperature, and measured the optical properties in the far-infrared and mid-infrared range. Besides the interesting question of the phonon renormalization in hole-doped compounds, which should be the subject of further studies, it certainly also is highly interesting to investigate a ternary compound synthesized from the lightest elements only.

LiBC was synthesized from the elements at 770 K with subsequent annealing at 1770 K in sealed niobium ampoules with open molybdenum crucibles inside. The molybdenum crucibles, 5 mm diameter and approximately 50 mm length, have been filled in an argon box with commercially available lithium, boron, and carbon with a lithium excess of 300% compared to the stoichiometric ratio. This excess is necessary to provide a high lithium vapor pressure in the ampoule. The carbon and boron powders were preliminarily annealed in vacuum. The Mo crucibles have been placed in Nb ampoules, the latter sealed by argon welding. It is known, that molybdenum does not react with any of the components, while it can not hold high pressures at high temperatures. Due to this fact an additional niobium ampoule is necessary. The use of a Nb ampoule only is impossible since niobium reacts with boron. This sample preparation technique has been developed in the groups of R. Nesper (Zürich) and H. G. von Schnering (Stuttgart), and is described in detail in Refs. 8,9,10. The ampoules have been heated up to 770 K with a rate 100 K/hour, held at 770 K during one hour, then heated up to 1770 K with 200 K/hour, held one more hour at this temperature, and finally cooled down with a rate of approximately 150 K/hour. Faster cooling seems to support the growth of crystals of larger size. After removing the extra lithium the product consists of mainly yellow golden powder. Some crystals can be quite large reaching the size of \(0.5 \times 0.5 \times 0.01\) mm³. One of these platelets is shown in Fig. 3. The hexagonal morphology is clearly indicated by the terraced ideal hexagon shown in the in-

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The dc-resistivity of a single-crystalline sample was measured using a standard four-point technique in the range $3 \, K < T < 300 \, K$. Using a coplanar contact geometry the electrical field was directed parallel to the B-C layers. The contacts were prepared by silver paint. Due to the ill-defined geometry of the rather small sample, the absolute values of the resistivity should be taken as a rough estimate only. As is shown in Fig. 2 the temperature dependence of the resistivity exhibits semiconducting characteristics, however, only with a rather small overall change of about a factor of three in the investigated temperature range. It does not follow a thermally activated behavior, $\rho \propto \exp(E/T)$. Also the prediction of the variable range hopping model, $\rho \propto \exp(B/T^{1/4})$, which often can be applied for hopping conduction of localized charge carriers, does not work for LiBC. Instead, in a rather broad temperature range the resistivity can be phenomenologically described by a power law, $\rho \propto T^{-n}$, as demonstrated in the double-logarithmic representation in the inset of Fig. 2 revealing an exponent $n \approx 0.23$. However, we are not aware of any theoretical model that could explain such a power law behavior.

In addition, the dielectric properties of the platelet-shaped samples were measured in sandwich geometry, i.e. with the field directed perpendicular to the B-C layers. The measurements were performed for frequencies $10^6 \leq \nu \leq 2 \times 10^9$ Hz employing a reflectometric technique, described in detail in Ref. 12. Fig. 3 shows the frequency dependence of the dielectric constant $\varepsilon'$ and the conductivity $\sigma'$ for three temperatures. $\varepsilon'(\nu)$ exhibits a step-like decrease with the point of inflection close to 300 MHz, $\sigma'(\nu)$ an increase with a shoulder near the same frequency. Such a behavior could be indicative of a dipolar relaxation process, but as the existence of dipolar entities in LiBC is unlikely, a non-intrinsic origin of the observed relaxation-like features seems to be more reasonable. Thus we ascribe this behavior to Maxwell-Wagner type contributions of the interface between sample and contacts. As demonstrated in detail in Ref. 13, then the intrinsic response is revealed at high frequencies only, when the contact resistance is bridged by the contact capacitance acting like a short at high frequencies. From Fig. 3 close to 1 GHz we read off a value of $\varepsilon' \approx 35$, which smoothly saturates towards higher frequencies and is nearly temperature independent. From the frequency dependence of $\sigma'(\nu)$ in the intrinsic region at $\nu > 300$ MHz a plateau, followed by a further increase, can be suspected, which would be indicative of hopping conduction of localized charge carriers. Measurements at even higher frequencies are necessary to corroborate this conjecture. Within this picture the plateau represents the intrinsic dc conductivity, which can be read off as $\sigma_d \approx 10^{-2} \, \Omega^{-1} \, \text{cm}^{-1}$, showing a weak temperature dependence only. Thus the dc resistivity perpendicular to the BC planes seems to be more than two orders of magnitude higher than the measured dc resistivity parallel to the planes (cf. Fig. 2) indicating a strong anisotropy of the electrical transport properties.

The measurements of the optical reflectivity were carried out using the infrared microscope Bruker IFS 66v, which was connected to a Fourier-transform infrared

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**FIG. 1:** Photograph of a LiBC crystalline sample. (1) shows an example of the area investigated in the infrared experiments. The inset (2) shows a magnification of a little terrace on the sample surface with a perfect hexagonal shape.

**FIG. 2:** Temperature dependence of the dc resistivity of LiBC, measured with the field parallel to the BC planes using four-point contact configuration. The inset shows the same data in a double-logarithmic representation, the line demonstrating an approximate $T^{-n}$ power-law behavior with $n \approx 0.23$. 
plane-parallel samples, the samples were tilted by a small angle to eliminate multiple reflections from the opposite sides of the sample. The measurements carried out on flat surfaces of as-grown single crystals at temperatures. The measurements were performed using a two-point contact configuration with the electric field directed parallel to the B-C planes.

In order to eliminate multiple reflections from the opposite sides of the plane-parallel samples, the samples were tilted by a small angle (approximately 10°) to the normal incidence. Using the infrared microscope we were able to focus on a small fraction of the LiBC platelets with the best flatness compared to surrounding areas. An example of such an investigated area is shown in Fig. 1.

The reflectivity as obtained from the infrared measurements is shown in Fig. 4. We observe three well-defined peaks in the spectrum at 540, 620, and 1180 cm⁻¹, and assign them to the infrared active phonons. A large shoulder at 700 cm⁻¹ most likely represents the forth optical phonon. It should be noted that the quasi-periodic variation of \( R \), visible in the spectra, is the residual influence of the multiple reflections inside the sample, which could not be completely removed by tilting the sample. This interference pattern is most clearly seen in the spectra measured closer to the normal incidence. These oscillations make a much more pronounced fringes. These oscillations make a significant contribution to the reflectivity.

The inset in Fig. 4 shows the dielectric permittivity \( \varepsilon' \) calculated from the fit of the reflectivity spectrum. Since the description of the reflectivity is not perfect, the data for \( \varepsilon' \) are subject to large errors. However, we would like to stress that \( \varepsilon' \approx 15 \) in the terahertz regime is not too far from \( \varepsilon' \approx 35 \) as measured at 1 GHz, having in mind that the intrinsic value still is not quite reached at this frequency. The remaining difference most likely is due to a relative large uncertainty in the determination of the crystal thickness, which affects the absolute values of \( \varepsilon' \) in the dielectric measurements.

The group analysis for LiBC \( (P6_3/mmc, D^{4}_{6h}) \) yields the following modes at the \( \Gamma \)-point: \( 3A_{2u} + 2B_{1g} + B_{2u} + 3E_{1u} + E_{2u} + 2E_{2g} \), four of which are optical infrared-active modes \( (2A_{2u} \text{ and } 2E_{1u}) \). The four modes observed in our measurements most likely represent these infrared-active phonons. Although the reflectance was measured from quite plane sample surfaces, which are supposed to be mostly parallel to the B-C planes, we believe that a significant amount of the out-of-plane response is also present in our measurements. The tilted geometry further increases the out-of-plane contribution.

If one compares the observed absolute values of the phonon frequencies in LiBC with those observed and calculated for aluminum diboride \( ALB_2 \), one immediately finds a close similarity. In both compounds there is a very high frequency phonon, which is a Raman-active \( E_{2g} \) mode in \( ALB_2 \) at \( \sim 980 \) cm⁻¹ \( (123 \) meV) and the mode at \( 1180 \) cm⁻¹ \( (\sim 150 \) meV) in our measurements of LiBC. We assign this mode to the \( E_{1u} \) infrared-active phonon. Due to the doubling of the unit cell in LiBC compared to \( ALB_2 \), the stretching Raman-active \( E_{2g} \) mode of the B-B hexagons transforms into two modes in LiBC: \( E_{3g} \) and \( E_{1u} \). The latter is infrared-active, its displacement pattern is shown in Fig. 2. The \( E_{2g} \) mode in \( ALB_2 \) has been shown to soften considerably on doping this compound with Mg, which is accompanied by the onset of supercon-

![FIG. 3: Frequency dependence of the real parts of the dielectric constant \( \varepsilon' \) and ac conductivity \( \sigma' \) of LiBC for three temperatures. The measurements were performed using a two-point contact configuration with the electric field directed parallel to the B-C planes.](image)

![FIG. 4: Reflectivity of a LiBC crystal in the far- and mid-infrared range. The vertical arrows mark the phonon positions. The dashed line is a fit of the experimental spectra with four Lorentz oscillators. The inset shows the dielectric permittivity calculated from the fit of the reflectivity data. The displacement pattern of the B-C stretching infrared-active mode is shown in the upper left corner.](image)
ductivity in Mg$_{1-x}$Al$_x$B$_2$ (Ref. 4). This softening is believed to result from the electron-phonon renormalization driving the superconductivity in magnesium diboride.

The three other infrared modes in LiBC have lower frequencies and are situated quite close to each other, resembling again the situation in AlB$_2$, where two infrared-active modes are supposed to exist in the range of 300 to 500 cm$^{-1}$ (Refs. 3, 4). The moderate upward shift in the frequencies of the observed modes in LiBC compared to the modes in AlB$_2$ is due to the fact that LiBC consists of lighter elements. Concluding this section, we mention that we have extended the infrared measurements up to approximately 1 eV and found no indication of the onset of an interband transition, demonstrating that the band gap is substantially larger than 1 eV. In the LDA calculations of Rosner et al., valence and conduction bands are separated by 1 eV. By Wörle et al. (Ref. 4) band gaps between 2.5 and 4.2 eV have been calculated.

In conclusion, we have synthesized the ternary borocarbide LiBC, characterized it by x-ray diffraction, and performed dc resistivity and dielectric measurements on single crystals. The dc resistivity demonstrates semiconducting temperature characteristics with strong anisotropy of $\rho_{||}/\rho_{\perp} \geq 100$. Infrared spectroscopy on single crystals utilizing an infrared microscope reveals four infrared-active phonon modes, consistent with point-group symmetry considerations. The high-frequency mode at 150 meV can be ascribed to the B-C stretching mode. It is this phonon mode that is expected to drive phonon-mediated superconductivity in hole-doped LiBC at temperatures substantially higher than in MgB$_2$ (Ref. 7). The next step is to follow the softening of this in-plane mode as a function of Li deficiency.

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