Prediction of High T\textsubscript{c} Superconductivity in Hole-doped LiBC

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(November 1, 2018)

The layered lithium borocarbide LiBC, isovalent with and structurally similar to the superconductor MgB\textsubscript{2}, is an insulator due to the modulation within the hexagonal layers (BC vs. B\textsubscript{2}). We show that hole-doping of LiBC results in Fermi surfaces of B-C \textit{p\textsubscript{r}} character that couple very strongly to B-C bond stretching modes, precisely the features that lead to superconductivity at T\textsubscript{c} \approx 40 K in MgB\textsubscript{2}. Comparison of Li\textsubscript{0.5}BC with MgB\textsubscript{2} indicates the former to be a prime candidate for electron-phonon coupled superconductivity at substantially higher temperature than in MgB\textsubscript{2}.

The discovery of \~40 K superconductivity in MgB\textsubscript{2} has led to a resurgence of interest in layered compounds that are metallic, or may be made metallic by doping. MgB\textsubscript{2} itself is, to date, a unique system, one that a number of studies of the electronic structure confirm contains strongly covalent bonds similar to graphite yet is a good metal with strong electron-phonon (EP) coupling. A variety of evaluations of the EP coupling indicates that it is strong enough to account for superconductivity in the 40 K range, and the observed B isotope shift of T\textsubscript{c} confirms that pairing is due to phonons. So far, attempts to make related, nearly iso-electronic diborides with the same structure have been fruitless. Be “diboride” (actually BeB\textsubscript{2.75}) forms a complex compound distinct from the MgB\textsubscript{2} type structure that has been presumed for several band structure studies. Ca, Sr, and Ba have resisted incorporation into the MgB\textsubscript{2} structure. Al can be alloyed in, resulting in a decrease in T\textsubscript{c} and a subsequent collapse of superconductivity altogether. Alloying with monovalent ions for Mg should increase T\textsubscript{c} (based on rigid band concepts) but attempts to do this also have been unsuccessful.

A closely related compound that has not received attention since the discovery of MgB\textsubscript{2} is LiBC. Although apparently straightforward to make, it has been studied very little to date. Its structure can be derived from the “fully intercalated graphite” structure of MgB\textsubscript{2} by Mg \rightarrow Li, and B\textsubscript{2} \rightarrow BC, with the hexagonal BC layers alternating so that B is nearest neighbor to C along the \textit{c} axis as well as within the layer. Like the compound CuBC suggested by Mehl et al. \cite{19}, it is isovalent with MgB\textsubscript{2}: Li has one less valence electron than Mg, but C has one more than B. The main features of the electronic structures, which are dominated by in-plane B-B and B-C bonding respectively, should be expected to have strong similarities. LiBC is insulating, however, with a gap that (we show below) arises from the replacement B\textsubscript{2} \rightarrow BC, and not from the alternating stacking. An important feature of Li\textsubscript{x}BC is that the Li content can be varied within the same crystal structure: while this system forms stoichiometrically (x=1), the Li content can be reduced and a structural change was seen only for \textit{x}=0.24. \cite{16}

Ramirez et al. \cite{18} have presented semi-empirical Hartree-Fock (INDO) results for a (BC)\textsuperscript{−} layer representing LiBC in the absence of interlayer coupling. They obtained a band gap of 4.3 eV (acknowledged to be an overestimate due to neglect of correlation), with its minimum value at the K point of the Brillouin zone between bonding and antibonding \textit{\pi} (\textit{p\textsubscript{\pi}}) bands. B and C character of the bands were not distinguished in their results. The \textit{\sigma} bands (\textit{sp\textsubscript{\textit{p}}}) however lie above the \textit{p\textsubscript{\textit{\pi}}} valence bands in a region around the \Gamma point. Albert included LiBC in a discussion of Li borocarbides, most of which are structurally very different from LiBC.

In this paper we present results for the electronic structure and EP coupling of Li\textsubscript{x}BC (x = 0.5, 0.75, 1.0) and compare it with that of MgB\textsubscript{2}. We determine that once it is hole-doped, the states at the Fermi level include \textit{\sigma} bands with cylindrical \textit{\sigma} Fermi surfaces that are strongly coupled to the B-C bond-stretching mode (more strongly than in MgB\textsubscript{2}). At x \approx 0.5, the density of states (DOS) N(E\textsubscript{F}) is comparable to that of MgB\textsubscript{2} while the EP coupling is much stronger. These features suggest that hole-doped LiBC is a very favorable candidate for superconductivity, possibly at much higher temperature than in MgB\textsubscript{2}.  

![Crystal structure of LiBC](image)

FIG. 1. Crystal structure of LiBC, a direct generalization of that of MgB\textsubscript{2}, showing the alternating layers of hexagonal BC. Li ions lie in the interstitials.

The layered structure of LiBC, pictured in Fig. 1, has been determined by Wörle et al. \cite{13} from golden hexag-
and 1.73 a.u. (B and C) were used. Atomic sphere radii of 3.00 a.u. (Li) were taken into account to increase the completeness of the basis set. The spatial extension of the basis orbitals, at the basis set. The spatial extension of the basis orbitals, was chosen as the basis set. All lower lying states were treated as core states. The Li 2p and 3d states as well as the B and C 3d states were taken into account to increase the completeness of the basis set. The spatial extension of the basis orbitals, controlled by a confining potential \( \frac{e^2}{r_{0}^2} \) (r/r0)4, was optimized to minimize the total energy. In addition, the LMTO-47 code [22] was used for the virtual crystal calculations and to obtain the deformation potentials that we report. Li(2s, 2p, 3d), B (2s, 2p, 3d) and C (2s, 2p, 3d) states, respectively, were chosen as the basis set. The Li 2p and 3d states as well as the B and C 3d states were taken into account to increase the completeness of the basis set. The spatial extension of the basis orbitals, controlled by a confining potential \( \frac{e^2}{r_{0}^2} \) (r/r0)4, was optimized to minimize the total energy. In addition, the LMTO-47 code [22] was used for the virtual crystal calculations and to obtain the deformation potentials that we report. Atomic sphere radii of 3.00 a.u. (Li) and 1.73 a.u. (B and C) were used.

**Stoichiometric Compound.** The band structure of LiBC (observed structure) along high symmetry lines in the Brillouin zone (BZ) is shown in Fig. 2(a). Valence bands are separated from conduction bands by a calculated gap of 1.0 eV, with the valence band maximum occurring at \( \Gamma \), and the conduction band minimum occurring at H. As in other semiconductors, this LDA value is likely to be an underestimate of the experimental gap. It will be shown below that the band structure of LiBC is closely related to that of MgB2, so the first question to address is the origin of the band gap at the Fermi level in LiBC, with the two possibilities being the alternating stacking of B-C layers along the \( c \) axis, and the alternation of B and C within the layer itself.

This question is answered by performing two calculations, one for an isoelectronic virtual crystal “LiB2,” where B is an average atom between B and C with nuclear charge Z=5.5, and another for an alternative LiBC structure in which the stacking of layers along the \( c \) axis is A-A stacking rather than the observed A-B stacking. (This is the structure for CuBC considered by Mehl et al. [19].) These results are also shown in Fig. 2(b)-(c). The bands of LiB2 are isomorphic to those of MgB2, as expected, as it is structurally identical and chemically similar. The bands look different from those normally shown for MgB2 because we have used a doubled cell (along \( c \)) to allow direct comparison with the bands of LiBC. The \( \sigma \) and \( \pi \) bands (see below) appear twice due to BZ folding, with the former separated by only a few tenths of eV due to their layered character (\( s - p_{s} - p_{y} \)) and the latter (\( p_{z} \)) separated by 3-4 eV around and below the Fermi level \( E_{F} \).

The A-A stacking of BC layers [Fig. 2(b)] produces a substantial change of the electronic structure: it does not change the separation of the valence and conduction bands, but it does change \( k_{z} \) dispersion sufficiently that the gap disappears – it becomes a semimetal with a calculated band overlap of 1.7 eV. The calculated total energy of the A-B stacking is lower than A-A stacking (at constant structure, the experimental one) by 35 meV per formula unit, consistent with the observed A-B stacking.

To understand the electronic structure of LiBC and its similarity to that of MgB2 more clearly, we display

![FIG. 2. Band structures of: (a) LiBC in the observed structure; (b) LiBC in fictitious A-A stacking structure, where additional \( k_{z} \) dispersion produces a semimetallic band structure; (c) LiB2, the virtual crystal analog; (d) Li_{0.5}BC in virtual crystal approximation; (e) C \( \sigma \)-fatbands; (f) B \( \sigma \)-fatbands; (g) C \( \pi \)-fatbands; (h) B \( \pi \)-fatbands.](image-url)
in Fig. 2(e)-(h) the “fatbands” plots showing C and B \(\sigma\) and \(\pi\) character. The \(\sigma\) bands are as in MgB\(_2\), with C character concentrated more heavily at the bottom of the bands (-6 to -8 eV below the gap) because the on-site energies \(\varepsilon_s\) and \(\varepsilon_p\) are lower for C than for B. The gap in LiBC, also evident in the DOS plots in Fig. 3, lies between bonding and antibonding combinations of \(\pi\) bands that are forced by symmetry in MgB\(_2\) to connect, and thus enforce metallicity. The bonding \(\pi\) bands have a preponderance of C \(p_z\) character, while the antibonding bands just above the gap are more strongly B \(p_z\) in character. The ionic character of the B-C layer compared to B-B helps to push the \(\pi\) character downward with respect to the \(\sigma\) character, resulting in a larger proportion of \(\sigma\) character \([N_{\sigma}(\varepsilon)]\) than in MgB\(_2\), a point of some importance below.

Substoichiometric \(\text{Li}_x\text{BC}\). In a band semiconductor such as LiBC, heavy hole doping will make \(\text{Li}_x\text{BC}\) metallic. If the \(\sigma\) bands can be populated by a sufficient density of holes, then by analogy with MgB\(_2\) the system should become superconducting, and perhaps a very good superconductor. There are at least two crucial questions. First, can the Fermi level be moved far enough into the valence bands to give a value of \(N(E_F)\) large enough to be interesting — comparable to that of MgB\(_2\), say? Second, are these \(\sigma\) states strongly coupled to the B-C bond stretching modes as they are in MgB\(_2\)?

We have used supercells (doubled within the layers) to study the \(x = 0.5\) and \(x = 0.75\) concentrations. For the \(x = 0.5\) case, two configurations were studied to assess the effect of the placement of missing Li atoms. In both configurations half of the Li atoms were removed from each layer, in one case along a line parallel to the \(c\) axis, and in the other case in staggered positions. The differences are very minor. In Fig. 4 the resulting DOS of these systems are compared with those for \(x = 1\). The Fermi level moves into the valence band, as it must, and the behavior in the region of the gap and Fermi level is not far from rigid band. It is noteworthy that it is the \(\sigma\) bands that are occupied first as holes are doped in [Fig. 2(a)]. The value of \(N(E_F) = 0.68\) eV\(^{-1}\) at \(x = 0.5\) is nearly equal to that of MgB\(_2\).

**Estimation of \(T_c\).** EP coupling (strength \(\lambda\)) in MgB\(_2\), which drives its superconductivity, is dominated by coupling of B-B bond stretching modes to the \(\sigma\) cylinder sheets of Fermi surface. \({\lambda} = \text{3, 10, 13}\) We calculate the deformation potential of these states for the zone-center B-C bond stretching mode in Li\(_{0.5}\)BC to be \(D = 18.5\) eV/\(\AA\), more than 40% larger than in MgB\(_2\) (where it is 13 eV/\(\AA\) \([9]\)), resulting from the stronger B-C bonding compared to B-B. We calculate \(\omega_{E_{2g}} = 68\) meV for Li\(_{0.5}\)BC. We can obtain a realistic estimate using \(\lambda \approx N_{\sigma}(E_F) D^2/4\mu\omega^2\) and scaling from calculated quantities and experimental \(T_c\) for MgB\(_2\). Defining the ratio \(R(K) = K_{\text{Li}_{0.5}\text{BC}}/K_{\text{MgB}_2}\) of any property \(K\), our calculations give \(R(N_{\sigma}) = 1.3\), \(R(D^2) = 2.0\), and \(R(\omega_{E_{2g}}) = 1.17\), finally giving \(R(\lambda) = 2.1\) as the enhancement of \(\lambda\) in Li\(_{0.5}\)BC compared to that of MgB\(_2\).

The value of \(\lambda\) in MgB\(_2\), averaged over four groups who have done extensive calculations, \([10, 13]\) is 0.82±0.08. The enhancement of 2.1 (above) gives \(\lambda \approx 1.75\) for Li\(_{0.5}\)BC. We obtain \(T_c\) from the Allen-Dynes equation \([29]\) with a single frequency; choosing \(\mu^* = 0.09\) with our calculated \(\omega = 58\) meV (similar to \([12, 13]\)) and \(\lambda = 0.82\) gives \(T_c = 39\) K for the reference material MgB\(_2\), as observed. Using the same \(\mu^*\), our calculated value \(\omega_{E_{2g}} = 68\) meV, and \(\lambda = 1.75\) gives \(T_c \approx 115\) K for \(x = 0.5\). Variation with \(x\) should be dominated by the \(\sigma\) DOS \(N_{\sigma}(E_F(x))\), and in Fig. 5 we plot the calculated \(T_c(x)\) assuming other quantities are constant to give an idea of the rapidity of the variation of \(T_c(x)\). This estimate indicates that \(T_c\) should be higher than 40 K for \(x \geq 0.25\). This estimate neglects multiband effects which are substantial for MgB\(_2\), \([28]\) but our purpose of illus-
trating the likely value of $T_c$ relative to MgB$_2$ should be reasonable. Even if our method of estimating $T_c$ overoptimistic, Li$_x$BC should still be an impressive superconductor.

To gather these results together: we have shown that in comparison to MgB$_2$, the material Li$_x$BC, $x \sim 0.5$, has (i) the hole-doped $\sigma$ states at $E_F$ that are crucial in MgB$_2$, (ii) $N(E_F)$ is comparable to that of MgB$_2$, (iii) an $E_{2g}$ deformation potential of the $\sigma$ bands that is over 40% larger than in MgB$_2$, and (iv) the $E_{2g}$ mode frequency is similar to that in MgB$_2$. In combination, these results strongly suggest a coupling strength perhaps as high as $\lambda \simeq 1.75$, and a superconducting critical temperature that could be more than twice as high as in MgB$_2$ for $x = 0.5 \pm 0.2$.

We thank J. M. An for calculation of the phonon frequency of Li$_{0.5}$BC. This work was supported by National Science Foundation Grant DMR-9802076, and by the Deutscher Akademischer Austauschdienst.

FIG. 5. Calculated $T_c$ versus hole concentration, but accounting only for the $x$ dependence of $N_\sigma(E_F)$. The curve is based on the model described in the text that is pegged to reproduce MgB$_2$ exactly with $\lambda = 0.82$, $\mu^* = 0.09$, $\omega = 58$ meV. The inset shows the $\lambda$ dependence of $T_c$ for MgB$_2$ (calculated $\omega = 58$ meV) and Li$_{0.5}$BC (calculated $\omega = 68$ meV).

According to Wörle et al. the hole doping we have treated has already been achieved, but measurements at reduced temperature were not made. In the event that doping is difficult, LiBC (being a semiconductor) seems to be a prime candidate for field-effect doping (FED) to achieve superconductivity. FED has already been reported to produce (1) $T_c = 52$ K in field-effect hole-doped C$_60$ and at $T_c = 117$ K in expanded C$_{60}$ and (2) at 14 K in a ladder cuprate and 89 K in an “infinite layer” cuprate. Not only do these studies establish the capabilities of the FED technique, they demonstrate that phonon-coupled superconductivity (as in the fullerenes) can produce very high values of $T_c$, as we are suggesting here for Li$_x$BC.

EP coupling of the strength that we obtain for Li$_x$BC must raise the question of the associated lattice instability that will ultimately occur. In MgB$_2$ the $E_{2g}$ mode remains stable although it acquires a very large width and no doubt is renormalized downward strongly by the large coupling to the $\sigma$ states. In weakly coupled AIBo$_2$ the $E_{2g}$ is $123$ meV. With its much stronger coupling, Li$_x$BC provides the opportunity to approach and perhaps encounter the associated instability. We are currently calculating $\omega_{E_{2g}}(x)$ to study this instability; note however that suppose that a (say) 20% lower frequency actually leads to a higher $T_c$ in this regime, because the larger value of $\lambda$ more than compensates the decrease in energy/temperature scale. Raman and inelastic neutron spectroscopy will be very informative in revealing the response of the lattice to this large EP coupling.

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