

Prediction of High T_c Superconductivity in Hole-Doped LiBC

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(Received 6 November 2001; published 6 March 2002)

The layered lithium borocarbide LiBC, isovalent with and structurally similar to the superconductor MgB_2 , is an insulator due to the modulation within the hexagonal layers (BC vs B_2). We show that hole doping of LiBC results in Fermi surfaces of B-C $p\sigma$ character that couple very strongly to B-C bond stretching modes, precisely the features that lead to superconductivity at $T_c \approx 40$ K in MgB_2 . Comparison of $\text{Li}_{0.5}\text{BC}$ with MgB_2 indicates the former to be a prime candidate for electron-phonon coupled superconductivity at substantially higher temperature than in MgB_2 .

DOI: 10.1103/PhysRevLett.88.127001

PACS numbers: 74.25.Jb, 74.25.Kc, 74.70.Ad

The discovery of ~ 40 K superconductivity in MgB_2 [1] has led to a resurgence of interest in layered compounds that are metallic or may be made metallic by doping. MgB_2 itself is, to date, a unique system, one that a number of studies of the electronic structure [2–9] 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 [3,4,10–13], and the observed B isotope shift of T_c [14] confirms that pairing is due to phonons. So far, attempts to make related, nearly isoelectronic diborides with the same structure have been fruitless. Be “diboride” (actually $\text{BeB}_{2.75}$) forms a complex compound [15] distinct from the MgB_2 -type structure that has been presumed for several band structure studies [5,6,9]. Ca, Sr, and Ba have resisted incorporation into the MgB_2 structure. Al can be alloyed in, resulting in a decrease in T_c and a subsequent collapse of superconductivity altogether. Alloying with monovalent ions for Mg should increase T_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_2 is LiBC. Although apparently straightforward to make [16], it has been studied very little to date [17]. Its structure [16,18,19] can be derived from the “fully intercalated graphite” structure of MgB_2 by $\text{Mg} \rightarrow \text{Li}$, and $\text{B}_2 \rightarrow \text{BC}$, with the hexagonal BC layers alternating so that B is nearest neighbor to C along the \hat{c} axis as well as within the layer. Like the compound CuBC suggested by Mehl *et al.* [20], it is isovalent with MgB_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 $\text{B}_2 \rightarrow \text{BC}$, and not from the alternating stacking. An important feature of Li_xBC 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 $x = 0.24$ [16].

Ramirez *et al.* [19] have presented semiempirical Hartree-Fock (INDO) results for a $(\text{BC})^-$ 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 π (p_z) bands. B and C character of the bands was not distinguished in their results. The σ bands ($sp_x p_y$ hybrids), however, lie above the $p\pi$ valence bands in a region around the Γ point. Albert included LiBC in a discussion [21] of Li borocarbides, most of which are structurally very different from LiBC.

In this Letter, we present results for the electronic structure and EP coupling of Li_xBC ($x = 0.5, 0.75, 1.0$) and compare it with that of MgB_2 . We determine that once it is hole doped, the states at the Fermi level include σ bands with cylindrical σ Fermi surfaces that are strongly coupled to the B-C bond-stretching mode (more strongly than in MgB_2). At $x \approx 0.5$, the density of states (DOS) $N(E_F)$ is comparable to that of MgB_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_2 .

The layered structure of LiBC, pictured in Fig. 1, has been determined by Wörle *et al.* [16] from golden hexagonal platelets (and red in transmission, hence insulating) to be $P6_3/mmc$ (D_{6h}^4 , No. 194), $a = 2.752 \text{ \AA}$, $c = 7.058 \text{ \AA} = 2 \times 3.529 \text{ \AA}$. This structure is similar to that of MgB_2 , except that a is 9% smaller; the interlayer spacing is nearly identical. The BC layers are stacked in alternating fashion, so there is no B-B or C-C bonding in the structure. To expose the effects of alternating (A - B) versus primitive (A - A) stacking of the layers, we also consider the A - A stacking, which has space group $P\bar{6}m2$ (D_{3h}^1 , No. 187).

We have used two electronic structure methods. A full-potential nonorthogonal local-orbital scheme [22] was used to obtain accurate band structures and the total energies that we report. $\text{Li}(2s, 2p, 3d)$, $\text{B}(2s, 2p, 3d)$, and $\text{C}(2s, 2p, 3d)$ states, respectively, were 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

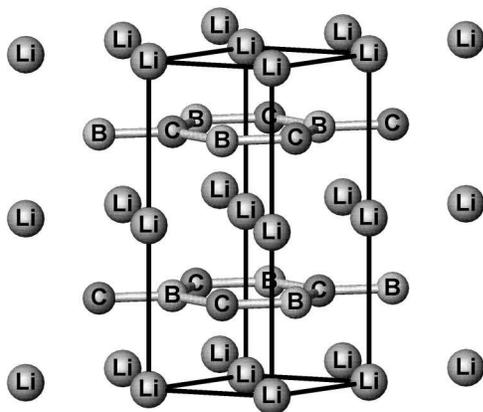


FIG. 1. Crystal structure of LiBC, a direct generalization of that of MgB_2 , showing the alternating layers of hexagonal BC. Li ions lie in the interstices.

were taken into account to increase the completeness of the basis set. The spatial extension of the basis orbitals, controlled by a confining potential [23] $(r/r_0)^4$, was optimized to minimize the total energy. In addition, the LMTO-47 code [24] was used for the virtual crystal calculations and to obtain the deformation potentials that we report below. 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 Γ , and the conduction band minimum occurring at H. As in other semiconductors, this local density approximation value is likely to be an underestimate of the experimental gap. It is shown below that the band structure of LiBC is closely related to that of MgB_2 , 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 \hat{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 “ LiB_2 ,” where \mathcal{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 \hat{c} axis is A-A stacking rather than the observed A-B stacking. (This is the structure for CuBC considered by Mehl *et al.* [20].) These results are also shown in Figs. 2(b) and 2(c). The bands of LiB_2 are isomorphic to those of MgB_2 , as expected, as it is structurally identical and chemically similar. The bands look different from those normally shown for MgB_2 because we have used a doubled cell (along \hat{c}) to allow direct comparison with the bands of LiBC. The σ and π 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 ($s - p_x - p_y$) 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 MgB_2 more clearly, we display in Figs. 2(e)–2(h) the “fatbands” plots showing C and B σ and π character. The σ 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 ε_s and ε_p are lower for C than for B. The gap in LiBC, also evident in the DOS plots in Fig. 3, lies between

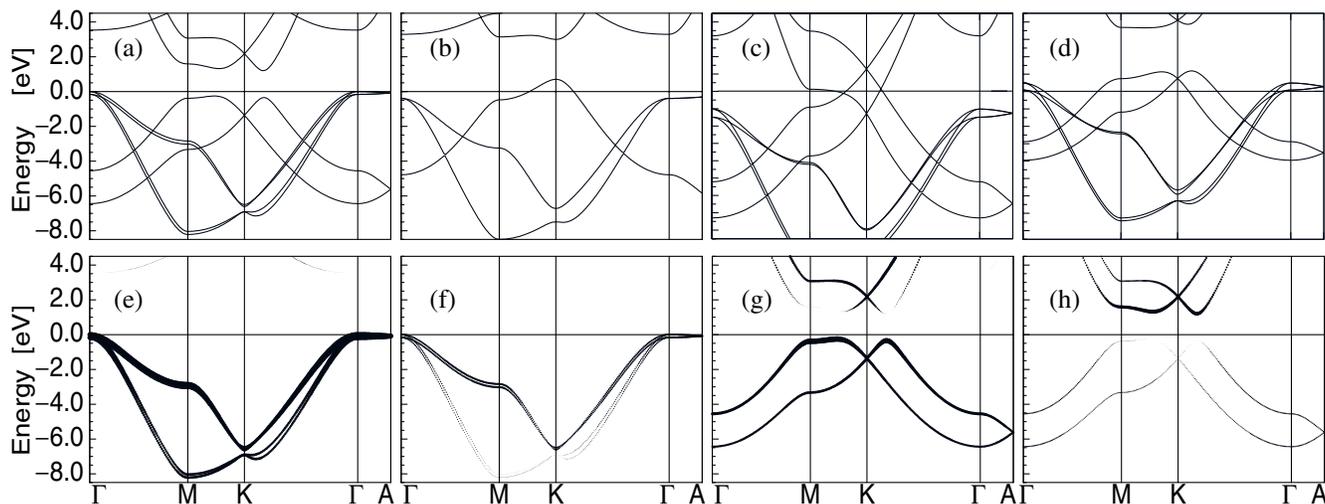


FIG. 2. Band structures of (a) LiBC in the observed structure; (b) LiBC in fictitious A-A stacking structure, where additional k_z dispersion produces a semimetallic band structure; (c) LiB_2 , the virtual crystal analog; (d) $\text{Li}_{0.5}\text{BC}$ in virtual crystal approximation; (e) C $p\sigma$ “fatbands”; (f) B $p\sigma$ fatbands; (g) C $p\pi$ fatbands; and (h) B $p\pi$ fatbands.

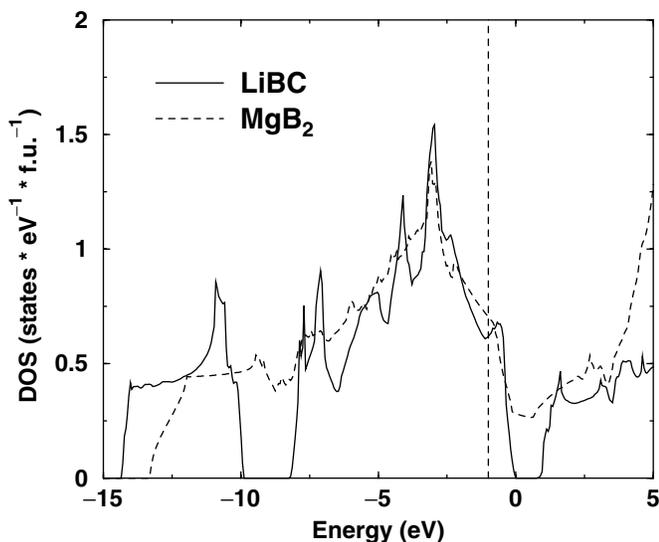


FIG. 3. The density of states of LiBC (solid line) compared to that of MgB₂ (dashed line, with the vertical line denoting the Fermi level); the gaps arise from in-plane (B-C) modulation. The main valence band peaks have been aligned to illustrate the similarity.

bonding and antibonding combinations of π bands that are forced by symmetry in MgB₂ to connect and thus enforce metallicity. The bonding π 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 π character downward with respect to the σ character, resulting in a larger proportion of σ character [$N_\sigma(\epsilon)$] than in MgB₂, a point of some importance below.

Substoichiometric Li_xBC.—In a band semiconductor such as LiBC, heavy hole doping will make Li_xBC metallic. If the σ bands can be populated by a sufficient density of holes, then by analogy with MgB₂ 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, say, of MgB₂? Second, are these σ states as strongly coupled to the B-C bond stretching modes as they are in MgB₂?

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 \hat{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 σ bands that are occupied first as holes are doped in [Fig. 2(a)]. The value of $N(E_F) = 0.68 \text{ eV}^{-1}$ at $x = 0.5$ is nearly equal to that of MgB₂.

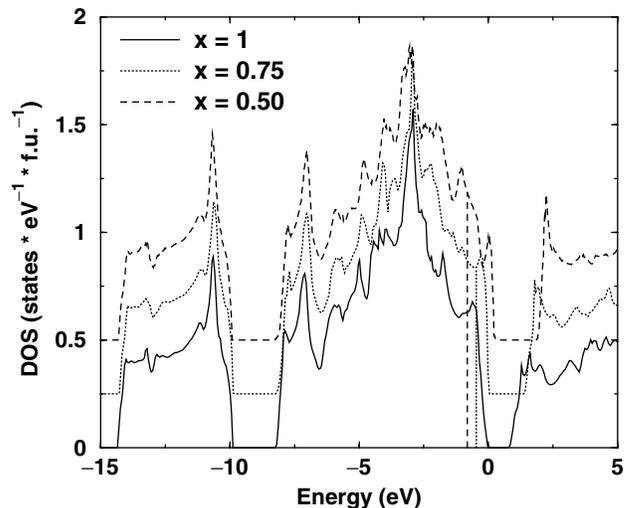


FIG. 4. Densities of states of Li_xBC, for $x = 1, 0.75,$ and $0.50,$ displaced upward consecutively for clarity. The $x = 0.50$ curve is averaged over two possible supercells (see text). The main valence band peaks have been aligned (but the gaps also remain aligned), so the Fermi level (vertical lines) moves downward, roughly in rigid band fashion, as hole doping proceeds.

Estimation of T_c .—EP coupling (strength λ) in MgB₂, which drives its superconductivity, is dominated by coupling of B-B bond stretching modes to the σ cylinder sheets of Fermi surface [3,4,10–13]. We calculate the deformation potential of these states for the zone-center B-C bond stretching mode in Li_{0.5}BC to be $\mathcal{D} = 18.5 \text{ eV}/\text{\AA}$, more than 40% larger than in MgB₂ (where it is $13 \text{ eV}/\text{\AA}$ [3]), resulting from the stronger B-C bonding compared to B-B. We calculate $\omega_{E_{2g}} = 68 \text{ meV}$ for Li_{0.5}BC. We can obtain a useful estimate using [3] $\lambda \propto N_\sigma(E_F)\mathcal{D}^2/M\omega^2$ and scaling from calculated quantities and experimental T_c for MgB₂. Defining the ratio $\mathcal{R}(K) = K_{\text{Li}_{0.5}\text{BC}}/K_{\text{MgB}_2}$ of any property K , our calculations give $\mathcal{R}(N_\sigma) = 1.3$, $\mathcal{R}(\mathcal{D}^2) = 2.0$, and $\mathcal{R}(\omega_{E_{2g}}) = 1.17$, finally giving $\mathcal{R}(\lambda) = 1.8$ as the enhancement of λ in Li_{0.5}BC compared to that of MgB₂.

The value of λ in MgB₂, averaged over four groups who have done extensive calculations [10–13], is 0.82 ± 0.08 . The enhancement of 1.8 (above) gives $\lambda \approx 1.5$ for Li_{0.5}BC. We obtain T_c from the Allen-Dynes equation [25] with a single frequency; choosing $\mu^* = 0.09$ with our calculated $\omega = 58 \text{ meV}$ (similar to [10–13]) and $\lambda = 0.82$ gives $T_c = 39 \text{ K}$ for the reference material MgB₂, as observed. Using the same μ^* , our calculated value $\omega_{E_{2g}} = 68 \text{ meV}$, and $\lambda = 1.5$ gives $T_c \approx 100 \text{ K}$ for $x = 0.5$. Variation with x should be dominated by the σ 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 $T_c(x)$ and the value of x required for high T_c . 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 MgB₂ [26], as well as variation of $\omega_{E_{2g}}$ with x , but our purpose of illustrating the likely value of T_c relative to MgB₂ should be reasonable. Even

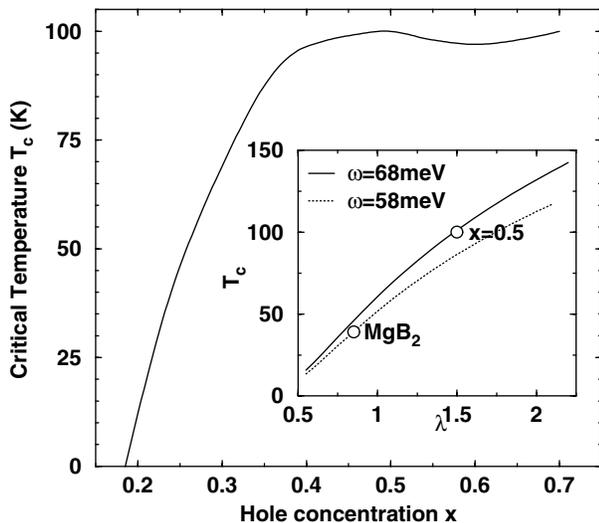


FIG. 5. Calculated T_c versus hole concentration, but accounting only for the x dependence of $N_\sigma(E_F)$. The curve is based on the model described in the text that is pegged to reproduce MgB_2 exactly with $\lambda = 0.82$, $\mu^* = 0.09$, $\omega = 58$ meV. The inset shows the λ dependence of T_c for MgB_2 (calculated $\omega = 58$ meV) and $\text{Li}_{0.5}\text{BC}$ (calculated $\omega = 68$ meV).

if our method of estimating T_c is overoptimistic, Li_xBC should still be an impressive superconductor.

According to Wörle *et al.* [16] 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} [27] and (2) at 14 K in a ladder cuprate and 89 K in an “infinite layer” cuprate [28]. 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_xBC .

EP coupling of the strength that we obtain for Li_xBC 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 [11] and is renormalized downward strongly [29] by the large coupling to the σ states. (In weakly coupled AlB_2 $\omega_{E_{2g}} = 123$ meV [11].) With its much stronger coupling, Li_xBC provides the opportunity to approach the associated instability with continuous variation of x . We are currently calculating $\omega_{E_{2g}}(x)$ to study this instability; note however that supposing a (say) 20% lower frequency actually leads to a higher T_c in this regime, because the larger value of λ more than compensates the decrease in energy/temperature scale. The variability of Li concentration will also allow the study of nonadiabatic behavior as E_F crosses the σ band edge, a regime that has proven inaccessible in MgB_2 .

In conclusion, we have shown that in comparison to MgB_2 , the material Li_xBC , $x \sim 0.5$, has (i) the hole-doped

σ 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 σ 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 suggest, for $x = 0.5 \pm 0.2$, a coupling strength as much as 80% larger than in MgB_2 and a superconducting critical temperature that could be more than twice as high.

We thank J.M. An for calculation of the phonon frequency of $\text{Li}_{0.5}\text{BC}$. This work was supported by National Science Foundation Grant No. DMR-0114818 and by the Deutscher Akademischer Austauschdienst.

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