Hole-doped, High-Temperature Superconductors $Li_xBC$, $Na_xBC$ and $C_x$ : A Coherent-Potential-Based Prediction

Prabhakar P. Singh

Department of Physics, Indian Institute of Technology, Powai, Mumbai-400076, India

(March 22, 2022)

Using density-functional-based methods, we show that the hole-doped $Li_xBC$ and $Na_xBC$ in $P6_3/mmc$ crystal structure and $C_x$ in graphite structure are capable of showing superconductivity, possibly with a $T_c$ much higher than that of MgB$_2$. We use full-potential methods to obtain the optimized lattice constants $a$ and $c$, coherent-potential approximation to describe the effects of disorder, Gaspari-Gyorffy formalism to obtain the electron-phonon coupling constant $\lambda$, and Allen-Dynes equation to calculate $T_c$ as a function of hole concentration in these alloys.

PACS numbers: 74.25.Jb, 74.70.Ad

The search for new MgB$_2$-like superconductors [1] has proved to be elusive so far, in spite of intense experimental effort. The difficulty in finding new materials with superconducting properties similar to that of MgB$_2$ [3] may partly be due to the delicate nature of interaction responsible for superconductivity (SC) [3,8]. In MgB$_2$, the relatively high superconducting transition temperature, $T_c$, of 39 K is achieved through a coming together of various aspects of phonon-mediated electron-electron interaction, such as (i) strong in-plane $B – B$ covalent bonding [0,3], (ii) electron and hole-like cylindrical Fermi sheets along $\Gamma$ to $A$ [1,5], (iii) a strong coupling of the $\sigma$ states to the in-plane $B – B$ bond-stretching mode [4,5] including an-harmonic effects [5,6], (iv) $B_{p(x,y)}$ contribution to the total density of states (DOS) at the Fermi energy, $E_F$, and the total DOS at $E_F$ [4,5], and others.

Most of the experimental as well as theoretical efforts have used layered and metallic materials as the starting point to obtain materials with above-mentioned electronic properties leading to high-temperature SC but without success. It may be that we have to follow a different route to obtain new MgB$_2$-like superconductors with high $T_c$. Such an alternative route is provided by hole-doping of the layered but semiconducting or insulating materials [3].

With the aim of developing materials with MgB$_2$-like electronic properties, we have studied how hole-doping can be used to tailor the electronic structure of $Li_xBC$, $Na_xBC$ and $C_x$ alloys. In particular, it turns out that the hole-doping makes $Li_xBC$, $Na_xBC$ and $C_x$ alloys similar to MgB$_2$ in more ways than one, making these alloys promising candidates for showing high-temperature SC.

In the following, we present the results of (i) fully-relaxed, full-potential electronic structure calculations for $LiBC$ and $NaBC$ in $P6_3/mmc$ crystal structure and $C$ in graphite structure, using density-functional-based methods, (ii) charge-self-consistent, coherent-potential-based electronic structure calculations for the hole-doped $Li_xBC$, $Na_xBC$ and $C_x$ alloys, and (iii) the calculations of $T_c$ in hole-doped $Li_xBC$, $Na_xBC$ and $C_x$ alloys with $x$ ranging from 1 to 0.2 (hole concentration is equal to $(1-x)$).

For full-potential calculations, we have used ABINIT code [1] based on pseudopotentials and planewaves, and optimized the lattice constants $a$ and $c$ of $LiBC$, $NaBC$ and $C$. The effects of hole doping in $Li_xBC$, $Na_xBC$ and $C_x$ alloys have been studied using Korringa-Kohn-Rostoker coherent-potential approximation in the atomic-sphere approximation (KKR-ASA CPA) method [1,2]. For calculating $T_c$ as a function of $x$ in $Li_xBC$, $Na_xBC$ and $C_x$ alloys, we have used the Gaspari-Gyorffy formalism [4] to evaluate the electron-phonon (EP) coupling constant $\lambda$, and Allen-Dynes equation [4] to calculate $T_c$.

Based on our calculations, described below, we find that the hole-doped $Li_xBC$ and $Na_xBC$ and $C_x$ are capable of showing SC, possibly with a $T_c$ as high as $\sim 105K$ for $Li_{0.5}BC$ [3], $\sim 106K$ for $Na_{0.6}BC$ and $\sim 60K$ for $C_{0.4}$. Such a high $T_c$ in these alloys becomes possible partly because the hole-doping modifies the electronic structure, discussed in terms of the density of states and spectral function along $\Gamma$ to $A$ direction, and brings it closer to that of MgB$_2$.

Before describing our results in detail, we provide some of the computational details. The structural relaxation of $LiBC$, $NaBC$ and $C$ was carried out by the molecular dynamics program ABINIT as described in Ref. [1]. The charge self-consistent electronic structure of $Li_xBC$, $Na_xBC$ and $C_x$ alloys as a function of $x$ has been calculated using the KKR-ASA CPA method. We have used the CPA rather than a rigid-band model because CPA has been found to reliably describe the effects of disorder in metallic alloys [1,2], including MgB$_2$ alloys [3]. We parametrized the exchange-correlation potential as suggested by Perdew-Wang [6] within the generalized gradient approximation. The Brillouin zone (BZ) integrations for charge self-consistency and the DOS calcu-
The total density of states calculated at the optimized lattice constants using the ABINIT program. For comparison the DOS for MgB₂ has been doubled. The vertical dashed line indicates $E_F$.

**TABLE I.** The calculated lattice constants $a$ and $c$ in atomic units. The experimental lattice constants are shown in the parentheses.

| Compound  | $a$       | $c$       |
|-----------|-----------|-----------|
| LiBC      | 5.16 (5.202) | 13.24 (13.342) |
| NaBC      | 5.25      | 15.62     |
| C         | 4.63 (4.650) | 12.62 (12.649) |
| MgB₂      | 5.76 (5.834) | 6.59 (6.657) |

The changes were carried out using 1215 and 4900 $k$-points in the irreducible part of the BZ, respectively. For DOS (spectral function) calculation, we added a small imaginary component of 1 (2) $m_Ry$ to the energy. The lattice constants for $Li_xBC$, $Na_xBC$ and $C_x$ alloys as a function of $x$ were kept fixed to the values given in Table I. To reduce ASA-related errors in open structures we introduced empty spheres. The Wigner-Seitz radii for Li and Na were slightly larger than that of B and C. The maximum $l$ value used was $l_{max} = 2$.

The $\lambda$ was calculated using Gaspari-Gyorffy formalism with the potentials of $Li_xBC$, $Na_xBC$ and $C_x$ obtained with the KKR-ASA CPA method. Subsequently, the variation of $T_c$ with $x$ was calculated using Allen-Dynes equation. The average value of phonon frequency $\omega_{ln}$ for MgB₂ was taken from Ref. [3], while the value of $\mu^*$ was kept fixed at 0.09.

First, we discuss the changes brought about by hole-doping in the various aspects of the electronic structure of $Li_xBC$, $Na_xBC$ and $C_x$ alloys in terms of (i) total DOS, (ii) partial B and C $p$-contributions to the total DOS at $E_F$, and (iii) spectral function along $\Gamma$ to $A$ evaluated at $E_F$. Then we describe the calculated $T_c$ for these alloys as a function of hole concentration, which is the main result of the present work.

We show in Fig. 1 the total DOS for $LiBC$, $NaBC$ and $C$ alloys calculated using the ABINIT program at the optimized lattice constants as given in Table I. For comparison we also show the DOS for MgB₂ obtained as described in Ref. [5]. The compound NaBC has a higher $c/a$ than LiBC primarily because of the larger Na atoms. The difference in $c/a$ ratio leads to significant changes between the electronic structure of $LiBC$ and $NaBC$. By comparing the DOS of $LiBC$, $NaBC$ and $C$ with MgB₂, it is clear that if $E_F$ can be moved suitably inside the valence band then the DOS at $E_F$ in these alloys can be made comparable to the DOS at $E_F$ in MgB₂. One of the ways of moving the $E_F$ inside the valence band is through hole-doping, as described next.

The changes in the electronic structure of $Li_xBC$, $Na_xBC$ and $C_x$ alloys as a function of $x$ has been studied for $x$ ranging from 1 to 0.2. We find that with increasing hole concentration $E_F$ moves inside, as expected, and consequently these alloys become metallic. As an example, we show in Fig. 2 the total DOS of $Li_{0.5}BC$, $Na_{0.5}BC$ and $C_{0.5}$ alloys, calculated as described earlier. From a comparison with the DOS of MgB₂, calculated using the same approach and also shown in Fig. 2, it is clear that the DOS around $E_F$ in $Li_{0.5}BC$, $Na_{0.5}BC$ and $C_{0.5}$ alloys are comparable to that of MgB₂. Our calculation shows that the hole concentrations of 50% - 80% are ideal for matching the total DOS of $Li_xBC$, $Na_xBC$ and $C_x$ alloys with that of MgB₂. Knowing the importance of the total DOS as well as the in-plane $Bp$-contribution to the total DOS at $E_F$ in MgB₂, the alloys $Li_xBC$, $Na_xBC$ and $C_x$ alloys are most suitable for hole-doping. The changes brought about by hole-doping in the various aspects of the electronic structure of $Li_xBC$, $Na_xBC$ and $C_x$ alloys as a function of $x$ were calculated using the ABINIT program at the optimized lattice constants as given in Table I.
Na$_x$BC and C$_x$ will be good candidates for showing SC only if the B and C $p$-contributions to the total DOS at $E_F$ are comparable to that of MgB$_2$.

In Fig. 3 we compare the $p_x(y)$ contributions of B and C to the total DOS around $E_F$ with the corresponding contribution from MgB$_2$. The $Bp_x(y)$ contribution in Li$_{0.5}$BC is almost identical to that of MgB$_2$, while the $Cp_x(y)$ contribution is slightly higher, indicating a strong $B-C$ covalent bonding. In Na$_{0.5}$BC the $Bp_x(y)$ contribution is slightly lower than that in MgB$_2$. Thus a further increase in hole concentration will enhance the $p_x(y)$ contribution to the total DOS. On the other hand in the case of C$_{0.5}$ the $Cp_x(y)$ DOS is identical to that of the $Bp_x(y)$ contribution in MgB$_2$.

For Li$_x$BC, Na$_x$BC and C$_x$ alloys to remain in the contention for showing MgB$_2$-like superconducting properties, a favorable matching of the total DOS and the partial $Bp_x(y)$ and/or $Cp_x(y)$ contributions to the total DOS at $E_F$ must be followed by similarities in the Fermi surfaces of these hole-doped alloys with that of MgB$_2$, especially along $\Gamma$ to $A$. A measure of this similarity is provided by comparing the spectral function, $A(k, E_F)$, of MgB$_2$ with Li$_x$BC, Na$_x$BC and C$_x$ alloys along $\Gamma$ to $A$. Such a comparison is shown in Fig. 4, where we have plotted $A(k, E_F)$ along $\Gamma$ to $A$ for Li$_x$BC, Na$_x$BC and C$_x$ alloys with $x = 0.3$ and 0.5, as well as for MgB$_2$.

We find that $A(k, E_F)$ for Li$_{0.5}$BC is closest to that of MgB$_2$, indicating similarities in the Fermi surfaces of the two compounds along $\Gamma$ to $A$. In C$_x$ the spectral functions for $x = 0.3$ and 0.5 are $7-8$ times larger than the corresponding values in MgB$_2$, while in Na$_{0.5}$BC it is $40-45$ times larger. Based on the comparison of the various aspects of the electronic structure of Li$_x$BC, Na$_x$BC and C$_x$ alloys with MgB$_2$, we find Li$_x$BC to be the most promising candidate for showing MgB$_2$-like SC followed by C$_x$. Such a conclusion is borne out by our explicit calculation of $T_c$ as a function of hole concentration in Li$_x$BC, Na$_x$BC and C$_x$ alloys.

The calculated $T_c$ as a function of hole concentration in Li$_x$BC, Na$_x$BC and C$_x$ alloys is shown in Fig. 5, where we also show the variation in $T_c$ in MgB$_2$. Clearly, hole-doped Li$_x$BC, expected to have a $T_c$ of around 105 K with 50% hole concentration, offers the best hope for improving the $T_c$ of MgB$_2$-type superconductors. The EP coupling is much stronger in Li$_x$BC ($\lambda \sim 1.7$ for $x = 0.5$) than in MgB$_2$ or any other alloys that we have considered. Our results for Li$_x$BC are consistent with the results of Ref. 1. Our calculation also shows that Na$_x$BC, if it can be synthesized, will also have a $T_c$ comparable to that of Li$_x$BC albeit at a higher hole concentration. The change in $T_c$ of MgB$_2$ with increasing hole concentration is not large. Surprisingly, C$_x$ is also found to show SC at elevated temperature.

The work presented here can be further improved by optimizing the lattice constants $a$ and possibly $c$ [7], within the CPA, as a function of hole concentration. However, the results presented in this paper are very robust and, in our opinion, a slight change in lattice constants due to optimization will not change the main conclusions of the present work.

In conclusion, we have presented the results of a fully-relaxed, full-potential electronic structure calculations

---

**Figures:**

**Fig. 3.** The $p_x(y)$ component of B (solid line) and C (dashed line) partial DOS around $E_F$ for (a) Li$_{0.5}$BC, (b) Na$_{0.5}$BC, and (c) C$_{0.5}$, calculated using the KKR-ASA CPA method. For comparison the $p_x(y)$ component of B partial DOS in MgB$_2$ (dotted line) is also shown. The vertical dashed line indicates $E_F$.

**Fig. 4.** The calculated spectral function along $\Gamma$ to $A$ direction, evaluated at $E_F$, for $x = 0.3$ (solid line) and $x = 0.5$ (dashed line) in (a) Li$_x$BC, (b) Na$_x$BC, and (c) C$_x$ alloys. For comparison, the spectral function for MgB$_2$ (dotted line) is also shown. In (b) the spectral function for Na$_{0.5}$BC is out of range of the plot.
FIG. 5. The calculated variation in $T_c$ as a function of hole concentration for $Li_x BC$ (filled square), $Na_x BC$ (filled triangle), $C_x$ (star), and $Mg_x B_2$ (filled circle).

for $LiBC$ and $NaBC$ in $P6_3/mmc$ crystal structure and $C$ in graphite structure. Using CPA, we have discussed the effects of hole-doping in $Li_x BC$, $Na_x BC$ and $C_x$ alloys in terms of (i) total DOS as well as $Bp$ contribution to it and, (ii) the spectral function along $\Gamma$ to $A$, and shown that the electronic structure of the hole-doped alloys is similar to that of $MgB_2$. Our calculated $T_c$ clearly shows $Li_x BC$ and $C_x$ to be superconducting in the range $0.2 \leq x \leq 0.8$, and $Na_x BC$ to be superconducting in the range $0.2 \leq x \leq 0.65$, with $Li_{0.3} BC$ showing a possible $T_c$ of 105 K.

[1] J. Nagamatsu et al., Nature, 410, 63 (2001).
[2] S. L. Bud’ko et al., Phys. Rev. Lett. 86, 1877 (2001); D. G. Hinks et al., Nature 411, 457 (2001); T. Takahashi et al., Phys. Rev. Lett. 86, 4915 (2001); T. Yildirim et al., Phys. Rev. Lett. 86, 5771 (2001).
[3] Cristina Buzea and Tsutomu Yamashita, cond-mat/0108263, and references therein.
[4] J. Kortus et al., Phys. Rev. Lett. 86, 4656 (2001); M. An and W. E. Pickett, Phys. Rev. Lett. 86, 4366 (2001); K.-P. Bohnen et al., Phys. Rev. Lett. 86, 5771 (2001); N. I. Medvedeva et al., Phys. Rev. B 64, 020502 (2001); G. Satta et al., Phys. Rev. B 64, 104507 (2001); K. D. Belaschenko et al., Phys. Rev. B 64, 092503 (2001).
[5] Y. Kong et al., Phys. Rev. B 64, 020501 (2001).
[6] Prabhakar P. Singh, Phys. Rev. Lett. 87, 087004 (2001).
[7] A. Liu et al., Phys. Rev. Lett. 87, 87005 (2001).
[8] H. J. Choi et al., cond-mat/0111183 and cond-mat/0111183 (2001).
[9] H. Rosner et al., cond-mat/0111192, and references therein.
[10] See URL http://www.pcpm.ucl.ac.be/abinit.
[11] Prabhakar P. Singh and A. Gonis, Phys. Rev. B 49, 1642 (1994); Prabhakar P. Singh et al., Phys. Rev. Lett. 71, 1605 (1993).
[12] J. S. Faulkner, Prog. Mat. Sci 27, 1 (1982); and references therein.
[13] G. D. Gaspari and B. L. Gyorffy, Phys. Rev. Lett. 28, 801 (1972).
[14] P. B. Allen and R. C. Dynes, Phys. Rev. B 12, 905 (1975).
[15] Prabhakar P. Singh, submitted to Phys. Rev. Lett.,
[16] J. P. Perdew and Y. Wang, Phys. Rev. B 45, 13244 (1992); J. Perdew et al., Phys. Rev. Lett. 77, 3865 (1996).
[17] L. Vitos et al., Phys. Rev. Lett. 87, 156401 (2001).