

Quasiparticle properties of the possible superconductor materials LiBC and NaBC

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Abstract. – The quasiparticle band structures within the GW approximation of the possible superconductors LiBC and NaBC are presented. The GW correction to the LDA is shown to be strongly dependent on the degree of orbital localization, and the overall correction cannot be reproduced by a rigid band shift as in conventional semiconductors. Precise values of the interband transitions for high-symmetry points in the Brillouin zone are given. The imaginary part of the self-energy which is related to the lifetime of quasiparticles, is presented in order to be compared with future experiments. Moreover, the ground-state properties of LiBC and NaBC are studied and it is shown that the bonding is partly covalent.

Since the recent discovery of the unexpected superconducting behavior in MgB₂ [1], there has been an increasing effort in the scientific community to obtain new materials with similar properties. Although the mechanism responsible for the superconductivity in this material is not yet fully understood, making the search for similar materials difficult, a new way of achieving superconductivity in similar materials has been recently proposed [2]. It consists mainly in performing hole-doping on LiBC, a material similar to MgB₂, to make it a high-temperature (T_c) superconductor. A theoretical critical temperature as large as 100 K has been calculated by the same group [2]. Later, it has been reported [3] that other materials, such as NaBC or graphite, having electronic and crystallographic properties similar to those of LiBC, could also be promising candidates for high- T_c superconductivity. Nonetheless, no experimental evidence for superconductivity in such materials has been reported yet [4, 5]. This failure could be probably due to the lithium desintercalation process that produces less ordered materials. Therefore, even if it appears that the situation about superconductivity is far from being experimentally achievable, the initial theoretical prediction has been confirmed by an independent calculation [6] with a critical temperature of 65 K.

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TABLE I – Calculated a and c lattice parameters (in atomic units) compared with other theoretical [3,7] (the pseudopotential approximation) and experimental [8] results.

	a (a. u.)	c (a. u.)
LiBC PAW LDA ^(a)	5.16	13.23
LiBC PAW GGA ^(a)	5.22	13.38
LiBC PP LDA ^(b)	5.16	12.99
LiBC PP GGA ^(c)	5.16	13.24
LiBC Expt. ^(d)	5.202	13.342
NaBC PAW LDA ^(a)	5.21	15.26
NaBC PAW GGA ^(a)	5.29	15.60
NaBC PP ^(c)	5.25	15.62

^(a) Present work. ^(b) Reference [7]. ^(c) Reference [3]. ^(d) Reference [8].

On the other hand, the study of ternary compounds composed of only light elements is interesting by itself, and is part of a more general effort towards the understanding of low-atomic-number, Z , materials [9]. For example, vibrational properties of stoichiometric LiBC have been studied both experimentally [10] and theoretically [11]. On the other hand, one of the most important quantities characterizing an insulating or a semiconducting material, namely its band gap, has been studied very little to date for LiBC and NaBC. Values as different as 1.0 eV [2], 1.81 eV [12], and 4.3 eV [13] have been reported in the literature, whereas a complete understanding of any material cannot be achieved without a correct description of its excited states. The purpose of this work is precisely to go one step further in our knowledge of this growing field by studying the quasiparticle properties of LiBC and NaBC. In particular, precise values of the interband transitions will be given and we will show that the different degrees of localization of the orbitals can affect drastically the self-energy corrections to the LDA results.

Our letter is organized as follows. In the first part, we investigate the structural properties of LiBC and NaBC materials by means of the all-electron Projector-Augmented-Wave method (PAW) [14]. In the second part, we devote our attention to the determination of the excited states using our recently implemented GW approximation [15], and to the analysis of the self-energy correction as a function of the orbital localization.

Electronic ground state. – According to ref. [8], LiBC crystallizes in a hexagonal structure, having the $P6_3/mmc$ space group symmetry and consists of hexagonal graphite-like sheets but with an AB stacking, *i.e.*, each boron atom being superposed on a carbon atom and vice versa. To study the electronic ground state of the LiBC and NaBC materials within the density functional theory (DFT) [16], we have used the PAW method, which allows us to perform molecular-dynamic simulation while keeping an all-electron description of the wave functions [14]. To study the effect of the exchange-correlation potential on the ground-state properties, we have used either the local-density approximation (LDA) [17], or the generalized gradient approximation (GGA) [18]. The resulting lattice parameters are presented in table I and compared to other available values.

For LiBC, the LDA underestimates the experimental values, which is not surprising because of the well-known over-binding problem of this approximation. The situation improves when using the GGA, leading even to slightly overestimated values. In the case of NaBC, to our knowledge the only published result is a theoretical calculation in the GGA approximation of ref. [3]. The overall agreement between our all-electron calculation and the pseudopotential ones is quite good⁽¹⁾. The lattice parameters of NaBC are predicted to be larger than those of

⁽¹⁾To insure convergence of the LDA total energy, a mesh of 423 \mathbf{k} -points in the full Brillouin zone and an energy cut-off of 50 Ry for the plane-wave basis set have been used in our calculations.

TABLE II – Charge (in number of valence electrons) for each type of atom obtained from Bader's theory.

	Li	Na	B	C
LiBC	0.15		1.39	6.47
NaBC		0.28	1.44	6.28

LiBC due to the atomic-size effect, *i.e.*, the Na ion being bigger than the Li one. It has been suggested recently [10] that LiBC could crystallize in a lower-symmetry structure, namely the $P\bar{3}m1$, involving a puckering of B-C rings. It is interesting to mention that the results presented in table I are obtained by performing a molecular dynamics to relax the atomic positions and a Parrinello-Rahman simulation to optimize the unit cell; and in all cases, we have neither observed a distortion of the unit cell nor a displacement of atoms out of the $P6_3/mmc$ symmetry. Therefore, we join the conclusion (although obtained using different means) of ref. [19] to exclude the $P\bar{3}m1$ symmetry as the ground state of LiBC and NaBC materials. Further experimental work about the growth process of LiBC crystal is probably needed for the understanding of the Raman spectra presented in ref. [10].

The degree of covalency or ionicity of each bond is a key quantity for the understanding of the bonding properties of materials such as LiBC and NaBC. In order to determine the type of bonding in these materials, we have then performed a Bader's analysis [20,21] of their electronic charges. In this approach, all gradient paths terminating at an atom define a basin belonging to this atom. Then, the charge, as presented in table II, is obtained by integrating over the whole basin, represented in fig. 1 for each atomic species. The integrated charges using Bader's analysis are in qualitative agreement with Born effective charges of LiBC reported in ref. [11]. In particular, it can be seen that the transfer of the valence electrons from the alkali metal ion to the BC layer is far from being complete, *i.e.*, a significant part remains around the positive ion. As a consequence, the bonding between X and BC is partly covalent. The degree of covalency can probably explain why it is so difficult to synthesize $Li_{1-x}BC$ and $Na_{1-x}BC$ materials [4]. As for the energy band gap of these materials, since the DFT cannot

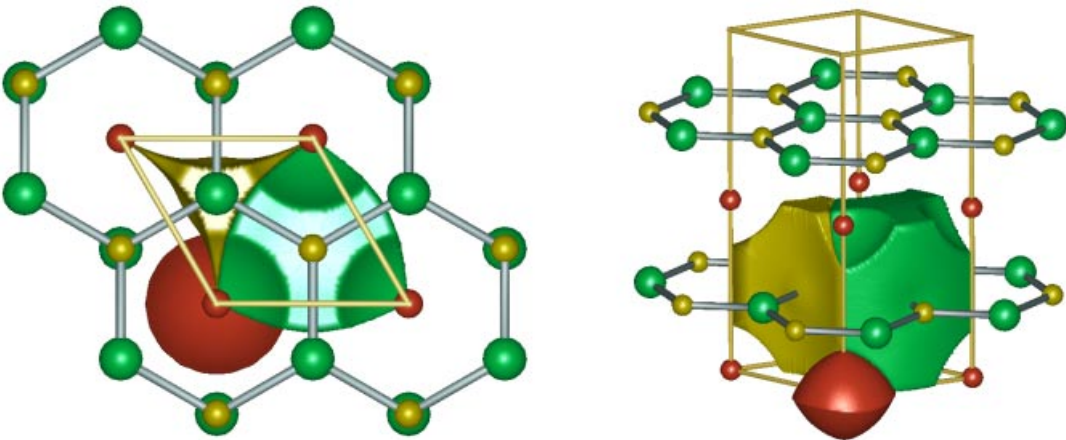


Fig. 1 – Presentation of some atomic-charge density basins for the top (left) and side (right) views of the structure of LiBC. For the color version (on-line only): Li, B, and C basins are represented, respectively, by red, green, and yellow colors. For this black and white version: The Li atom is the lowest, then comes the carbon bore ring (the carbon atom is the biggest).

deal with excited-state properties, we will address this problem in the next section using the GW approximation.

Excited-states properties. – We studied the excited-state properties within the framework of the GW approximation to the self-energy [22], which is able to overcome the limitations of the DFT concerning excited states. Within this formalism, the Kohn-Sham equations are replaced by quasiparticle (QP) equations (involving QP energies $E_n(\mathbf{k})$ and QP wave functions $\psi_{\mathbf{k}n}(\mathbf{r})$) written as

$$(T + V_{\text{ext}} + V_{\text{h}})\psi_{\mathbf{k}n}(\mathbf{r}) + \int d^3r' \Sigma(\mathbf{r}, \mathbf{r}', E_n(\mathbf{k}))\psi_{\mathbf{k}n}(\mathbf{r}') = E_n(\mathbf{k})\psi_{\mathbf{k}n}(\mathbf{r}), \quad (1)$$

where T , V_{ext} , V_{h} , and Σ are, respectively, the kinetic energy operator, the external potential due to the ion cores, the average electrostatic (Hartree) potential, and the electron self-energy operator. In the GW approximation, Σ is written as the product of the one-electron Green's function G and the screened Coulomb interaction W [22]:

$$\Sigma(\mathbf{r}, \mathbf{r}', \omega) = \frac{i}{2\pi} \int d\omega' G(\mathbf{r}, \mathbf{r}', \omega + \omega') e^{i\delta\omega'} W(\mathbf{r}, \mathbf{r}', \omega'), \quad (2)$$

where δ is a positive infinitesimal. The quasiparticle energies are then computed using a first-order expansion of the self-energy:

$$\text{Re}E_n(\mathbf{k}) = \epsilon_n(\mathbf{k}) + Z_{n\mathbf{k}} \times [\langle \Psi_{\mathbf{k}n} | \text{Re}\Sigma(\mathbf{r}, \mathbf{r}', \epsilon_n(\mathbf{k})) | \Psi_{\mathbf{k}n} \rangle - \langle \Psi_{\mathbf{k}n} | V_{xc}^{\text{LDA}}(r) | \Psi_{\mathbf{k}n} \rangle], \quad (3)$$

where the renormalization factor $Z_{n\mathbf{k}}$ has the following expression:

$$Z_{n\mathbf{k}} = \left[1 - \langle \Psi_{\mathbf{k}n} | \frac{\partial}{\partial \omega} \text{Re}\Sigma(\mathbf{r}, \mathbf{r}', \omega = \epsilon_n(\mathbf{k})) | \Psi_{\mathbf{k}n} \rangle \right]^{-1}. \quad (4)$$

In our case, the screened Coulomb interaction W is fully calculated in the random-phase approximation (RPA): no plasmon-pole model is needed. More details about our implementation are given elsewhere [15, 23].

Table III shows the quasiparticle energies for LiBC and NaBC for some high-symmetry points of the Brillouin zone. We have reported the transitions from the top valence band to the first two conduction bands. As usual, the use of the GW approximation leads to an important enhancement of the values of the different interband transitions. In particular, the minimum band gaps (underlined in table III) are increased in a significant way⁽²⁾: for LiBC, a value of 1.59 eV is obtained instead of a value of 0.84 eV within the LDA; for NaBC, the correction is even more impressive, since we end up with a value of 1.82 eV by using the GW approximation instead of only 0.78 eV⁽³⁾. An important fact is that in the case of NaBC, the transition corresponding to the minimum band gap in LDA (identified as $\Gamma_v \rightarrow \Gamma_c$ or $A_v \rightarrow \Gamma_c$) becomes within the GW : $\Gamma_v \rightarrow H_c$ (or $A_v \rightarrow H_c$). In other words, the point of the Brillouin zone where the minimum of the conduction band is lying depends on the formalism used. This is extremely important from the practical point of view since NaBC turns from a direct-band-gap material to an indirect-band-gap material. In fact, this is not surprising and points once more to the inability of the DFT to deal correctly with excited-state properties.

⁽²⁾To converge the GW quasiparticle energies we have used a \mathbf{k} -points grid of $5 \times 5 \times 3$ in the full Brillouin zone and a size of the reciprocal-space screened interaction matrix W of 487×487 (see ref. [15] for a complete description of the numerical procedure).

⁽³⁾In a recent experiment, Karimov *et al.* [24] have investigated the electronic properties of LiBC by resonant inelastic soft X-ray scattering (RIXS). However, they were unable to obtain a precise value for the gap due to smearing effect. Also, their band mapping using RIXS (occupied states only) and a LDA band structure calculation are in good agreement, but the lack of precise values prevent us from doing a comparison between experiment, LDA, and GW.

TABLE III – Quasiparticle energies interband transitions at the high symmetry points Γ , M , K , A , L , and H for LiBC and NaBC. Values corresponding to the minimum gap are underlined.

	LiBC		NaBC	
	LDA	GW	LDA	GW
$\Gamma_{8v} \rightarrow \Gamma_{1c}$	3.45	4.30	0.78	1.88
$\Gamma_{8v} \rightarrow \Gamma_{2c}$	8.54	9.80	5.48	6.60
$M_{8v} \rightarrow M_{1c}$	1.92	2.49	2.20	3.02
$M_{8v} \rightarrow M_{2c}$	3.39	3.96	3.72	4.54
$K_{8v} \rightarrow K_{1c}$	3.34	3.63	1.77	2.41
$K_{8v} \rightarrow K_{2c}$	8.34	8.81	1.90	2.56
$A_{8v} \rightarrow A_{1c}$	6.03	6.85	2.67	3.79
$A_{8v} \rightarrow A_{2c}$	8.81	10.06	2.90	4.04
$L_{8v} \rightarrow L_{1c}$	3.94	4.44	3.20	4.02
$L_{8v} \rightarrow L_{2c}$	7.92	9.57	3.34	4.16
$H_{8v} \rightarrow H_{1c}$	1.34	1.78	1.23	1.83
$H_{8v} \rightarrow H_{2c}$	9.56	10.24	1.40	2.07
Minimum gap	<u>0.84</u>	<u>1.59</u>	<u>0.78</u>	<u>1.88</u>

Figure 2 presents our quasiparticle corrections (dots) to the LDA band structure. Due to computational limitations, we have only calculated the corrections for the high-symmetry points. It is clearly seen that all the values of the different transitions are increased (see table III). However, we remark that the value of the self-energy is strongly dependent on the degree of localization of each orbital. For example, if we consider the top occupied band at the Γ point (of σ character) and the top occupied band at the K point (of π character) for LiBC, the values of $\langle \Psi | \Sigma | \Psi \rangle$ are surprisingly different: $\langle \sigma | \Sigma | \sigma \rangle = -16.45$ eV, whereas $\langle \pi | \Sigma | \pi \rangle = -12.01$ eV. This kind of variation in the matrix elements of the self-energy has been already noticed by Strocov *et al.* in their work on graphite [25]. In particular, they have reported values as $\langle \sigma | \Sigma | \sigma \rangle = -17.3$ eV and $\langle \pi | \Sigma | \pi \rangle = -13.1$ eV. Those values coincide with ours in a range of approximately 1 eV. A more advisable comparison is to look at the differences $\langle \sigma | \Sigma | \sigma \rangle - \langle \pi | \Sigma | \pi \rangle$, which are, respectively, of about 4.44 eV for LiBC and 4.29 eV for graphite. This qualitative agreement is not surprising since both materials have similar

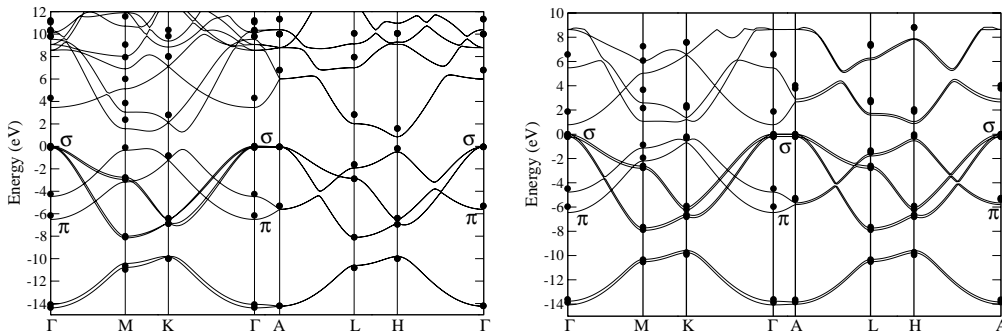


Fig. 2 – LDA band structure (full lines) and quasiparticle corrections (dots) for LiBC (left) and NaBC (right). The characters of the different bands are shown.

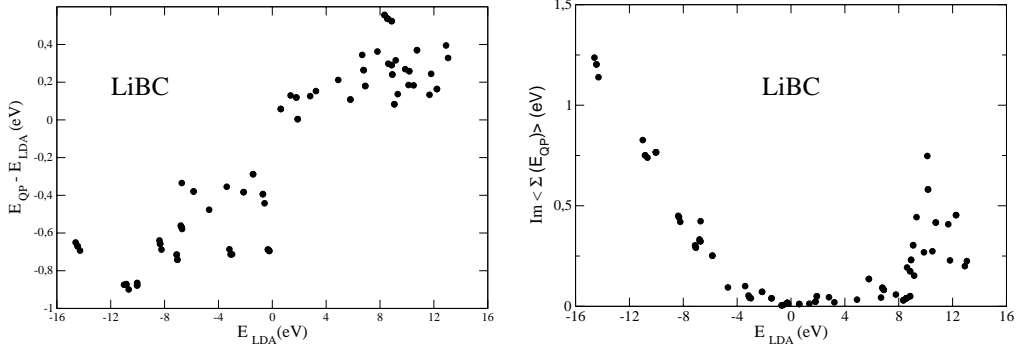


Fig. 3 – Left: quasiparticle correction $E_{QP} - E_{LDA}$ as a function of E_{LDA} for LiBC. Right: diagonal elements of the imaginary part of the self-energy as a function of E_{LDA} for LiBC. The self-energy has been calculated for the high-symmetry points Γ , M, K, A, L, and H. The Fermi level is at zero.

structural and electronic structure properties. One notices also that the strong variation of the matrix elements already appears at the DFT level: for LiBC $\langle \sigma | V_{xc} | \sigma \rangle = -15.45$ eV whereas $\langle \pi | V_{xc} | \pi \rangle = -11.56$ eV; but the inclusion of dynamical effects through the self-energy increased further the dependence of matrix elements upon the character of the electronic wave functions ($\langle \sigma | \Sigma | \sigma \rangle - \langle \pi | \Sigma | \pi \rangle = 4.44$ eV to be compared with $\langle \sigma | V_{xc} | \sigma \rangle - \langle \pi | V_{xc} | \pi \rangle = 3.89$ eV). This comment is quite general and applies also to NaBC: in this case, we obtain $\langle \sigma | \Sigma | \sigma \rangle = -16.37$ eV and $\langle \pi | \Sigma | \pi \rangle = -12.55$ eV (with a difference of 3.82 eV), whereas $\langle \sigma | V_{xc} | \sigma \rangle = -15.22$ eV together with $\langle \pi | V_{xc} | \pi \rangle = -11.89$ eV (with a difference of 3.33 eV).

This behavior can be easily illustrated by reporting the differences $E_{QP} - E_{LDA}$ and the diagonal elements of the imaginary part of the self-energy as a function of E_{LDA} , as presented in fig. 3 for LiBC. We can see clearly that the corrections are far from being the same as the ones for a more usual material like silicon (see ref. [26]): for a given value of E_{LDA} , there is a large dispersion of the values for the quasiparticle corrections, leading to corrections which can differ by a factor of almost 3. This peculiar behavior is of course related to the different kinds of orbitals in XBC compounds, and cannot be present in silicon. In this material, a dispersion of the corrections appears at high energy, but is due to the possibility of emitting plasmons. Therefore, a simple shift of the conduction bands (the so-called “scissors operator shift”) will be extremely inappropriate to obtain the correct quasiparticle band structure of LiBC and NaBC and all the related quantities, like, for example, optical properties. Also, a special feature of our GW implementation is the possibility of getting the imaginary part of the self-energy (see fig. 3), which is related to the inverse of the quasiparticle lifetime. The unusual dispersion of the quasiparticle correction also appears for the imaginary part, and this dispersion could be easily probed by time-resolved two-photon photoemission experiments.

Conclusion. – In this letter, results concerning the excited states of XBC compounds (X = Li or Na) have been presented. By calculating the quasiparticle band structures of those materials within the GW approximation, we have shown that the behavior of the correction due to self-energy effects cannot be reproduced by a simple shift of the conduction states towards higher energies, and is strongly dependent on the orbital character. We have investigated also their ground-state properties and found excellent agreement of our all-electron

calculations with other previous works. The bonding involved in those compounds has been found to be partly covalent; this can probably explain difficulties with the desintercalation process. The path is now open for further experimental studies, like photoemission and electron momentum spectroscopy, of the electronic structure of this new class of materials, and the results could be compared with the detailed data presented here.

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