Pressure effects on the electronic structure and superconducting critical temperature of Li$_2$B$_2$

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Abstract
We present the structural, electronic and superconducting properties of Li$_2$B$_2$ under pressure within the framework of the density functional theory. The structural parameters, electronic band structure, phonon frequency of the $E_{2g}$ phonon mode and superconducting critical temperature $T_c$ were calculated for pressures up to 20 GPa. We predicted that the superconducting critical temperature of Li$_2$B$_2$ is about 11 K and this decreases as pressure increases. We found that even though the lattice dynamics of the $E_{2g}$ phonon mode is similar to MgB$_2$, the reduction of the $\sigma$-band density of states at Fermi level and the raising of the $E_{2g}$ phonon frequency with pressure were determinant to decrease $\lambda$ and consequently $T_c$.

Keywords: Li$_2$B$_2$, intercalated superconductors, electron–photon coupling, critical temperature

(Some figures may appear in colour only in the online journal)

1. Introduction
High $T_c$ superconductivity in intermetallic layered structures has attracted much attention since the discovery of superconductivity in magnesium diboride (MgB$_2$) in 2001 [1]. However, MgB$_2$ remains the intermetallic material with the highest superconducting temperature (39 K) and although it is known that this property is based on the strong coupling of its covalent B sigma bands with B bond-stretching modes [2–7], it has not been possible to predict a new diboride type to enhance it. On the other hand, it is widely accepted that the superconductivity on intercalated systems such as CaC$_6$ is dominated by the interaction of free-electron-like interlayer states with soft intercalant modes. Lately, in this context, new proposals in the quest of layered intercalated superconductors have emerged. The most recent theoretical study reports that, by decorating graphene with Li atoms, a superconductor at a much higher temperature with respect to Ca-covered graphene is obtained [10]. The Li–Be layered compounds with a low-dimensional electronic structure and strong electron–phonon (e–ph) coupling are another family of Li-based compounds with possible superconducting properties under high pressure [11, 12]. More recently, there has been considerable interest in the structural stability, electronic band structure and chemical bond of Li–B compounds under high pressure [13–15].

Layered Li-based materials with a quasi-two-dimensional electronic structure and high dynamical energy scales resulting from the Li-atom motion are potential candidates for high $T_c$ superconductors. In that direction, first-principles calculations
using a data-mining approach have predicted new hypothetical intermetallic materials [16, 17] called metal-sandwich (MS) structures MS1(MB) and MS2(M2B2), which also have sp2-layers of boron as in MgB2 but separated by two metal layers M [16]. Particularly, LiB and Li2B2 proved to be marginally stable under ambient conditions and they have become favored over the known stoichiometric compounds under pressure [16, 17]. Both these compounds are remarkably interesting since the σ- and π-bands derived from their boron pₓ and pᵧ-orbitals are similar to those in MgB2 [7, 18, 19] and therefore a similar superconductor mechanism based on the electron–phonon coupling between the σ- and π-bands and the E₂g phonon mode in the boron planes was expected.

Recent calculations revealed that the electron–phonon coupling (λ) in Li2B2 was weaker than in MgB2, estimated at about 0.57 [19] in comparison to those reported for magnesium diboride ranging from 0.61 to 1.1 [2, 3, 7, 20–23]. Thus, the transition temperature of Li2B2 was reported to be around 7 K [19]. Now it is also widely accepted that in MgB2 the electron–phonon coupling takes a large contribution from σ-bands but also a small participation from π-bands [23, 24]. Therefore the seemingly unimportant π-electrons at εF could be determinant in increasing the transition temperature of Li2B2. Thus, an appropriate doping of Li2B2, in which π-electrons are increased, could result in a higher Tc than in MgB2. This hypothesis was tested by Calandra et al [18] substituting Li atoms with Mg or Al. The tests showed that it was difficult to induce a significant amount of π-states at εF with small doping because the band crossing in Li2B2 happens to be exactly at εF, around 2 eV lower than in MgB2 [7]. Furthermore, even from a thermodynamical standpoint, doping Li2B2 might be as difficult as it is for MgB2 [8].

From the McMillan equation [37] (equation (2)), Li2B2 seem to be favored compared to MgB2, because Li2B2 (0.48 states eV⁻¹) has a higher density of states of B atoms than MgB2 (0.39 states eV⁻¹) at εF and this could enhance the electron–phonon coupling constant. However, this is not enough to raise Tc. One interesting case is represented by CaBeSi [9], a material with σ- and π-bands at the Fermi level and density of states twice as high as in MgB2, but with a very low critical temperature Tc = 0.4 K. Thus, while the band structure can present strong similarities with both σ- and π-bands crossing the Fermi level, the phonon structure and the e–ph interaction could differ substantially.

In this paper, we have analyzed why the Tc of Li2B2 (7 K) has been reported to be lower than for MgB2 (39 K) and whether it is possible to enhance the e–ph coupling of Li2B2 and consequently the superconducting temperature by applying hydrostatic pressure. Since the in-plane motion of the boron atoms changes the boron orbitals’ overlap, an important electron–phonon coupling could be expected mainly for the σ-bands at εF and the E₂g phonon mode. After a careful analysis of the pressure effects on the band structure and the E₂g phonon frequency, we found that the electron–phonon coupling and Tc decreased with pressure as a result of the strong reduction of the boron-pₓ-pᵧ states contribution to the density of states at the Fermi level and the hardening of the E₂g phonon frequency as pressure was applied.

2. Computational details

We studied the Li2B2 compound (crystal structure: MS2) as a model of layered lithium borides. Li2B2 has eight atoms in the primitive unit cell and a space group P6₃/mmc (No. 194). The Wickoff positions are Li1(4f) (1/2, 1/2, 0), B1(2b) (0, 0, 1/2) and B2(2d) (1/2, 1/2, 3/2), see figure 1. The structural parameters were fully relaxed through a molecular dynamics scheme: a = b = 3.087 Å, c = 11.18 Å; α = β = 90°, γ = 120°.

The total energy calculations were performed with SIESTA (Spanish Initiative for Electronic Simulations with Thousands of Atoms) code [25, 26] based on density functional theory with exchange–correlation functionals as parametrized by Perdew, Burke, and Ernzerhof [27] for the generalized gradient approximation (GGA) [28–31]. This code is implemented with pseudopotentials to describe electron–ion interactions and numerical atomic orbitals to expand the valence wavefunctions. Pseudopotentials were generated according to the Troullier–Martins procedure [32] using the atomic configurations 1s²2s²p⁴ for Li and 1s²2s²²p⁴ for B with core radii of 2.49 and 1.24 atomic units (au) for Li and B, respectively. As the basis set for the valence wavefunctions we have employed a double-ξ basis. To calculate the integrals of the Kohn–Sham Hamiltonian, we have used a k-space sampling via the Monkhorst–Pack matrix (70 × 70 × 70) with a mesh cutoff of 280 Ryd [33]. All calculations were numerically converged when interatomic forces were less than 0.1 meV Å⁻¹.

Li2B2 phase was calculated as a function of cell volume V and c/a ratio. We performed total energy calculations for 15 volumes and seven c/a ratios in order to optimize both. Subsequently, the total energy was fitted to the Murnaghan equation of state [34] to obtain the equilibrium volume (V₀) and the P–V equation of state (EOS). Thus, from the P–V EOS the unit cell volume and c/a ratio were estimated from 0–20 GPa. The E₂g-phonon mode was calculated using the frozen-phonon model [35] that, even though it is a very simple model, is still a suitable and useful approach [10]. This approach is a direct method in which the distorted Li2B2 is treated as a crystal of a lower symmetry than the non-distorted Li2B2. Thus, total energy calculations of distorted crystals were performed to simulate the dynamics of the E₂g phonon mode.

The oscillating pattern of the E₂g mode corresponds to boron ions in opposite directions along the x- or y-axis, with Li ions stationary (figure 2). For this, we have simulated the E₂g-phonon mode as a composition of two modes: E₂g(a) and E₂g(b). Figure 2 represents the vibration pattern of these modes. To implement the displacement pattern of these modes, we defined an adimensional distortion parameter ⟨u/a⟩ related to the boron bond, where u is the magnitude of the distortion and a the in-plane lattice parameter, using the unit cell volume and c/a ratio for 0, 10 and 20 GPa previously optimized. These distortions simulated expansions and contractions of E₂g phonon mode as a function of the u parameter. Thus, to calculate the effective potential due to boron atoms oscillation we use a maximum adimensional displacement of |⟨u/a⟩| = 0.04 and steps of Δ = 0.01. Eight different displacements were calculated to simulate the vibrational dynamics of the E₂g(a).
and $E_{2g}(b)$ component modes. Thus, the energy values of these configurations were subtracted to the energy of non-distorted Li$_2$B$_2$, $\Delta E = E_0 - E_{2g}$, were $E_0$ and $E_{2g}$ represent the energy of the phonon on its equilibrium and vicinities points, respectively. The energy differences determined the restitutive potential of each oscillator and they were used to solve numerically the Schrödinger equation and obtain the characteristic frequency of each mode.

The superconducting critical temperature of Li$_2$B$_2$ under pressure was evaluated using the McMillan’s relation [37],

$$T_c = \frac{\omega}{1.2} \exp \left[ -\frac{1.04(1 + \lambda_\sigma)}{\lambda_\sigma - \mu^* (1 + 0.62 \lambda_\sigma)} \right],$$

(1)

where $\lambda_\sigma$ is the coupling constant between $\sigma$-band and the $E_{2g}$ mode, $\omega$ is the average frequency of the $E_{2g}(a)$ and $E_{2g}(b)$ component modes and $\mu^*$ is an adimensional empirical value which represents the repulsive force between Cooper pairs. To determine the coupling constant ($\lambda_\sigma$) quantitatively, we evaluated the deformation potential ($D$) for $E_{2g}(a)$ and $E_{2g}(b)$ modes under each distortion and used the isotropic limit from the Eliashberg theory [36] with the McMillan’s formula [37],

$$\lambda_\sigma = \frac{N_B(\epsilon_F)}{M} \left( \frac{\hbar^2}{M \omega^2} \right) D^2,$$

(2)

where $\omega^2$, $D$, $N_B(\epsilon_F)$ and $M$ are the average of the phonon frequency of the $E_{2g}(a)$ and $E_{2g}(b)$ modes, the deformation potential of the $\sigma$-band due to $E_{2g}$ mode, the density of states of boron atoms at Fermi level and total mass of boron atoms inside the unit cell, respectively.

3. Results and discussion

In figure 3, we show the results for the $a$ and $c$ lattice parameters, and the $V/V_0$ ratio for Li$_2$B$_2$ as a function of pressure for $0 \leq P \leq 20$ GPa. It can be seen that parameter $a$ decreases from 3.087 to 3.071 Å while $c$ parameter $c$ moves from 11.187 to 8.0 Å in the range of 20 GPa. Although both $a$ and $c$ parameters decrease, it is important to note that the slope for $c$ parameter as a function of pressure is higher than for $a$ parameter—that is, it would be easier to compress Li$_2$B$_2$ through the $z$-direction than in the plane direction. Conversely, $V/V_0$ decreases non-linearly and Li$_2$B$_2$ can be compressed about 30% when it is applied over 20 GPa.

The band structures of MgB$_2$ and Li$_2$B$_2$ are shown in figure 4. Both structures are similar to those reported before [18, 19]. Li$_2$B$_2$ presents the $\pi$- and $\sigma$-bands which are coupled with $E_{2g}$ phonon mode to induce superconductivity in MgB$_2$. However, in Li$_2$B$_2$ the sigma band is shifted up by 0.23 eV and the pi-band is shifted down by 1.31 eV, with respect to MgB$_2$. This shifting means that the $\pi-\pi^*$ crossing occurs practically at the Fermi level, resulting in a small density of states from the $\pi$-band at $\epsilon_F$. Hence, to evaluate the effects
of pressure on the electronic band structure, in figure 5 the evolution of the $\sigma$- and $\pi$-bands with pressure is shown. From that can be observed the energy position relative to $\epsilon_F$ of the $\sigma$-bands at $\Gamma$ ($E_{\Gamma}$) and $\pi$-bands at $K$ ($E_K$) as a function of pressure. These results demonstrate that both energies, $E_{\Gamma}$ and $E_K$, decrease as pressure increases. In particular, $E_{\Gamma}$ changes from 1.03 eV at 0 GPa to 0.21 eV at 20 GPa, and $E_K$ changes from 0.11 eV at 0 GPa to −0.56 eV at 20 GPa. To provide an explanation of the energy changes of $\sigma$- and $\pi$-bands in terms of the charge redistribution induced by the pressure, we estimated the charge population of the valence orbitals by using Mulliken populations [38], as shown in table 1. A charge transfer from B to Li atoms is observed. The B-p$_{xy}$ and B-p$_{z}$ orbitals lose charge, transferring it to the Li orbitals, mainly to the Li-s orbital. It should be pointed out that the values provided in the Mulliken analysis are strongly dependent on the basis set, but trends observed in the charge transfer process are reliable.

The total and partial density of states of B, B-p$_{xy}$ and B-p$_{z}$ orbitals as a function of pressure inside the unit cell are shown in figure 6. From that, it is clear that at 0 GPa the main contribution at $\epsilon_F$ is coming from the $\sigma$-band. For 0 GPa, the contributions of the B-p$_{xy}$ and B-p$_{z}$ orbitals to the density of states (DOS) at $\epsilon_F$ are 0.35 and 0.075 states eV$^{-1}$, respectively. We find that pressure induces a strong reduction of the B-p$_{xy}$ and B-p$_{z}$ orbital contributions to the DOS at $\epsilon_F$. Thus, pressure of 20 GPa induces a reduction of 50% and 37% in the B-p$_{xy}$ and B-p$_{z}$ orbitals, respectively.
and B-p_z orbital contributions, respectively, with respect to the 0 GPa pressure values. These results are summarized in table 2. From these results, we find that the behavior of the σ- and π-bands with pressure correlates with the charge transfer and the reduction of states at the Fermi level of the partial DOS corresponding to the B-p_{xy} and B-p_z orbitals. Thus, as the coupling constant \( \lambda \) is directly proportional to \( N_B(\varepsilon_F) \) and this is weighted by contributions of B-p_{xy} and B-p_z, the present result does not represent an advance in our quest to increase in comparison with MgB_2.

From equation (2), we can see that the other parameters controlling \( T_c \) and therefore \( T_c \) are the phonon frequency \( \omega \) and the deformation potential \( D \).

To further investigate the \( E_{2g} \) phonon frequency value, in figure 7 is plotted the energy as the atoms are displaced by an adimensional amount \( u/a \) according to \( E_{2g}(a) \) and \( E_{2g}(b) \) modes. Usually, phonons are harmonic for small displacements of the atoms with respect to equilibrium, but anharmonic behavior is observed for large displacements. A different source of anharmonicity takes place for atomic displacement patterns with a non symmetric atomic environment—that is, for the cases when the atom experiences a different force field for positive and negative displacements with respect to the equilibrium position. Thus, in the present case, we find that the total energy as a function of the distortions for the \( E_{2g}(a) \) and \( E_{2g}(b) \) phonon modes show an asymmetric and symmetric behavior, respectively (see figure 7). For the \( E_{2g}(a) \) mode, the distortion energy could be reasonably approximated by the anharmonic relation \( E(u/a) = A_2(u/a)^2 + A_3(u/a)^3 + A_4(u/a)^4 \), while for the \( E_{2g}(b) \) mode, it could be fitted to \( E(u/a) = A_2(u/a)^2 + A_4(u/a)^4 \). Using the calculated well potential for each pressure and numerically solving the Schrödinger equation, we obtained \( \omega(E_{2g}(a)) = 79.48 \text{ meV (641.06 cm}^{-1} \text{)} \) when Li_2B_2 is free of pressure and \( \omega(E_{2g}(a)) = 93.95 \text{ meV (757.78 cm}^{-1} \text{)} \) and \( \omega(E_{2g}(a)) = 104.39 \text{ meV (841.98 cm}^{-1} \text{)} \) for 10 and 20 GPa, respectively. Therefore, the obtained results show that the hydrostatic pressure causes an increment in \( E_{2g}(a) \) phonon frequencies, and the rise does not depend...
linearly on the increasing pressure. Similarly, we obtained \( \omega[E_{2g}(b)] = 83.04\) meV (669.78 cm\(^{-1}\)) when Li\(_2\)B\(_2\) is non-distorted and \( \omega[E_{2g}(b)] = 93.95\) meV (757.78 cm\(^{-1}\)) and \( \omega[E_{2g}(b)] = 104.78\) meV (845.13 cm\(^{-1}\)) for 10 and 20 GPa, respectively. Harmonic and anharmonic frequencies were estimated for \( E_{2g}(b) \) mode but they proved to be equal and linearly dependent of pressure. Thus, because the frequency is directly proportional to the superconducting critical temperature, these relationships could be a good way to enhance \( T_c \).

Despite that, it was important to quantify the deformation potential from the in-plane motions of the \( E_{2g} \) mode which changes the boron orbital overlap and therefore the pairing superconductor. To determine the deformation potential due to vibrations of the \( E_{2g}(a) \) and \( E_{2g}(b) \) mode phonons, we considered that only the \( \sigma \)-band is coupled to the \( E_{2g} \) phonon, even though in MgB\(_2\) it has been well established that \( \sigma \)- and \( \pi \)-bands are coupled with the \( E_{2g} \) mode. We made this approximation because of two reasons: (1) lack of \( \pi \)-states, and (2) \( \sigma \)-states are the main contribution to the electron–phonon coupling in MgB\(_2\) [39–41]. Thus, by estimating the average energy of the \( \sigma \)-band through the \( \Gamma \)-\( A \) path for each distortion, we determined the deformation potential as suggested by Khan–Allen [42], 

\[
D = \frac{1}{2}(\partial\epsilon/\partial u).
\]

As is shown in table 3, the deformation potential increased slightly as a result of an increase of electron concentration when pressure rises. However, most remarkable is that the average values of \( D \) for \( E_{2g} \) in the 0–20 GPa range are quite close to the reported value of 12.88 eV Å\(^{-1}\) for MgB\(_2\) [2] and thus this contribution would be at least comparable with magnesium diboride.

**Table 3.** Calculated values of the total density of states of boron atoms inside the unit cell at Fermi level \( N_B(\epsilon_F) \), the averaged value of the frequencies of the components of the \( E_{2g} \) phonon mode \( \omega(E_{2g}) \), the deformation potential \( D \), and the coupling constant \( \lambda \).

<table>
<thead>
<tr>
<th>( P ) (GPa)</th>
<th>( N_B(\epsilon_F) ) (states eV(^{-1}))</th>
<th>( \omega(E_{2g}) ) (meV)</th>
<th>( D ) (eV Å(^{-1}))</th>
<th>( \lambda )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.48</td>
<td>81.26</td>
<td>12.88</td>
<td>0.57</td>
</tr>
<tr>
<td>10</td>
<td>0.35</td>
<td>93.95</td>
<td>13.17</td>
<td>0.32</td>
</tr>
<tr>
<td>20</td>
<td>0.29</td>
<td>104.58</td>
<td>13.21</td>
<td>0.22</td>
</tr>
</tbody>
</table>

Finally, we evaluated the electron–phonon coupling \( \lambda \) of the \( \sigma \)-band and the \( E_{2g} \) phonon within the isotropic limit of the Eliashberg theory with the McMillan’s equation and the values of \( \omega(E_{2g}) \), \( N_B(\epsilon_F) \) and \( D \) calculated previously. These results are also shown in table 3. From these data, it is suggested that the reduced density of states of B-\( p_{xy} \) at \( \epsilon_F \) and the enhanced frequency of the \( E_{2g} \) phonon mode are the main causes for the decrease of \( \lambda \). To establish a connection between \( T_c \) and \( \lambda \), we considered the strong coupling approach from Eliashberg theory, equation (1). By adopting the conventional value of Coulomb repulsion \( \mu = 0.14 \) and two additional ones of \( \mu^* = 0 \) and \( \mu^* = 0.1 \) [43], we estimated \( T_c \) at different pressures. The results are summarized in table 4. \( T_c \) was found to decrease from 45 to 3.6 K with a null Coulomb repulsion, from 18.6 to 0.01 K with \( \mu^* = 0.1 \) and from 10.95 to 0.07 K with \( \mu^* = 0.14 \). With all choices of \( \mu^* \), the resulting \( T_c \) has a continuously reduced trend and practically vanishes at 20 GPa.

**Table 4.** Estimated values of \( T_c \) as a function of pressure for different values of Coulomb repulsion \( \mu^* = 0, 0.1 \) and 0.14.

<table>
<thead>
<tr>
<th>( P ) (GPa)</th>
<th>( \mu^* = 0 )</th>
<th>( \mu^* = 0.1 )</th>
<th>( \mu^* = 0.14 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>45</td>
<td>18.6</td>
<td>10.95</td>
</tr>
<tr>
<td>10</td>
<td>12</td>
<td>0.98</td>
<td>0.11</td>
</tr>
<tr>
<td>20</td>
<td>3.6</td>
<td>0.01</td>
<td>0.07</td>
</tr>
</tbody>
</table>

4. Conclusions

In conclusion, we have presented a first-principles investigation of the electronic structure, phonon frequency of the \( E_{2g} \) mode, the deformation potential of the \( \sigma \)-band and the electron–phonon coupling \( \lambda \) for Li\(_2\)B\(_2\) under pressure from 0–20 GPa within the framework of density functional theory. We predicted a reduction of \( \lambda \) from 0.57 at 0 GPa to 0.22 at 20 GPa. Although the lattice dynamics of the \( E_{2g} \) phonon mode proved similar to MgB\(_2\), the reduced density of states of B-\( p_{xy} \) at the Fermi level and the raising of the phonon frequency corresponding to the \( E_{2g} \) mode with pressure were determinant to decrease \( \lambda \) and consequently \( T_c \).

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