Quest for high $T_c$ in layered structures: the case of LiB

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Using electronic structure calculation we study the superconducting properties of the theoretically-devised superconductor MS1-LiB (LiB). We calculate the electron-phonon coupling ($\lambda = 0.62$) and the phonon frequency logarithmic average $(\langle \omega \rangle_{\text{log}} = 54.6 \text{ meV})$ and show that the LiB critical temperature is in the range of 10-15 K, despite the frozen-phonon deformation potential being of the same order of MgB$_2$. As a consequence, LiB captures some of the essential physics of MgB$_2$ but (i) the electron-phonon coupling due to $\sigma$ states is smaller and (ii) the precious contribution of the $\pi$ carriers to the critical temperature is lacking. We investigate the possible change in $T_c$ that can be induced by doping and pressure and find that these conditions cannot easily increase $T_c$ in LiB.

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INTRODUCTION

The quest for superconductivity in layered structures has become the focus of intense research since the discovery of superconductivity in MgB$_2$ ($T_c = 39$ K) [1]. The layered structure of MgB$_2$ generates one of its most prominent features, namely the $B 2p$ bands [2, 3, 4] which are weakly dispersing along the $k_z$ direction and have a marked two dimensional character. In MgB$_2$ the $\sigma-$bands are hole doped, but the top of these bands is only $\approx 0.5$ eV higher than the Fermi level. The $\sigma-$bands Fermi surface sheets [4], two slightly warped cylinders with axis perpendicular to the boron layers, generate a huge electron-phonon coupling along the $k_z$ direction. The carriers in the $\pi-$bands, formed by the B $2p_z$ orbitals, further enhance the average electron-phonon coupling [5].

The formation of $\sigma$ and $\pi$ states is typical of graphite-like structures composed by boron or carbon atoms. Given the success of MgB$_2$ it is natural to look for high $T_c$ superconductivity in structures having similar features. The problem is that, given the boron layers, small variations in the valence or mass of the intercalant or in the structural parameters are sufficient to considerably alter the $\sigma$ or $\pi$ bands positions or the shape of their Fermi surfaces and consequently destroy superconductivity. For one or some of these reasons AlB$_2$, ZrB$_2$, NbB$_2$, MoB$_2$, YB$_2$, TaB$_2$, TiB$_2$, HfB$_2$, VB$_2$, CrB$_2$ and CrB$_2$ are not superconducting [2, 3, 5].

The hope of finding new superconducting materials in layered structures was recently increased by the discovery of superconductivity in the graphite intercalated compounds, YbC$_6$ and CaC$_6$ [4, 10]. This is particularly promising since a huge number of intercalants are available for graphite [11]. In CaC$_6$, despite the layered structure and the existence of $\sigma$ and $\pi$ bands originated from the carbon $2p$ orbitals, the electronic structure close to the Fermi level is completely different from that of MgB$_2$. The $\pi$ bands, reminiscent of the graphite ones, and an intercalant free-electron-like band [12, 13] cross the Fermi energy. The intercalant band forms a spherical Fermi surface [14, 15]. The electron-phonon coupling of CaC$_6$ ($\lambda = 0.83$) is mainly due to coupling of the interlayer band with C vibrations perpendicular to the graphite layers and with Ca vibrations. So, even though missing the $\sigma$-bands, CaC$_6$ reaches an interesting 11.5 K $T_c$. This temperature is substantially enhanced by pressure ($T_c = 15.1$ K at $\approx 8$ GPa [16]), contrary to what happens in MgB$_2$.

As can be seen from the above examples, even if one restricts to sandwich structures formed by boron or carbon layers, the details of the electronic and phonon spectra and, subsequently, the critical temperature can change dramatically when the intercalant is included. As a consequence, a theoretical approach is absolutely necessary to identify the most probable superconductors or at least to exclude the less probable ones.

An attempt in this direction has been recently made in Ref. [17], where by using $ab$ initio methods the authors studied the possible hole-doping of LiBC, a $\approx 1$ eV gap semiconductor. The authors suggested that a $T_c$ of the order of MgB$_2$ could be reached if the insulating LiBC is substantially doped with holes to obtain Li$_{0.5}$BC. Successive experimental studies have indicated that the structural response to the introduction of holes unfavorably modifies the electronic structure of Li$_2$BC, and so far no high $T_c$ superconductivity has been found in this system [18].

Ideally designing new superconductors $ab$ initio requires three steps. The first is the determination of the
most stable structures given a set of atomic species. The second is the calculation of the electronic structure to verify that the given structure is at least metallic or can be made metallic easily. The third is the determination of the phonon dispersion and of the electron-phonon parameters.

The first point is a daunting task even if one restricts one’s search to a specific set of likely candidates. A systematic approach to tackle this problem has been recently offered in the way of data mining of ab initio calculations [20, 21, 22]. In this method one uses the information obtained from ab initio calculations of many different structures to build a database that can be then used to judge the stability of new structures. Application of this method to intermetallics has led to the identification of new layered lithium monoboride phases which have a good chance to form under proper synthesis conditions [23].

Once a stable metallic structure is given, a calculation of the phonon spectra and of the electron-phonon coupling needs to be performed to obtain $T_c$. Indeed, while some qualitative information can be extracted from electronic-structure [2], for a quantitative analysis step three is absolutely necessary.

In this work we investigate the superconducting properties of the previously determined metal sandwich (MS) lithium monoboride [23] by calculating its phonon spectrum and electron-phonon parameters. This system is metallic and, from qualitative arguments, one can infer that $T_c$ is of the same order of that of MgB$_2$ [23]. Indeed this system has an electronic structure which is a hybrid between those of MgB$_2$ and CaC$_6$, since there are hole-doped $\sigma$-bands forming cylindrical Fermi surfaces and there is an intercalant band crossing the Fermi level. Moreover the deformation potential is comparable to that of MgB$_2$ [23]. From this point of view, LiB is a much more promising material than Li$_{0.5}$BC, because even without doping it has a significant density of $\sigma$-states at the Fermi level.

Unfortunately, the full electron-phonon coupling calculations performed in this paper indicate that LiB should have a $T_c$ in a 10-15 K range. We show that LiB captures some of the important physics of MgB$_2$, namely the role of the $\sigma$-bands, but it lacks the contribution of the $\pi$ states to the electron-phonon coupling and it is only a far relative of CaC$_6$ because the interlayer band is very weakly coupled with the phonons. In an attempt to improve the situation we examine what role the hydrostatic pressure and doping can play in determining the critical temperature.

**TECHNICAL DETAILS**

In all our calculations of the layered lithium monoboride we have used the MS1 theoretical crystal structure basing our choice on the following considerations. On the one hand, it has the smallest unit cell of all MS structures, which offers computational efficiency. On the other hand, even though other stacking sequences are possible (e.g. MS2, Refs. [23, 24], MS1 is a good representative model of the layered lithium monoboride because the long-period shifts are expected to have little effect on its superconducting properties [23]. MS1-LiB has a rhombohedral unit cell with R3m space group. There are four atoms in the primitive unit cell with Wyckoff positions Li(2c)(1/2 − $z_{Li}$, 1/2 − $z_{Li}$, 1/2 − $z_{Li}$), Li(2c)(1/6 + $z_{Li}$, 1/6 + $z_{Li}$, 1/6 + $z_{Li}$), B(2c)(−$\delta$, −$\delta$, −$\delta$) and B(2c)(2/3 − $\delta$, 2/3 − $\delta$, 2/3 − $\delta$). The fully relaxed parameters are $a = b = c = 5.92 \, \text{Å}$, $\alpha = \beta = \gamma = 29.8^\circ$.

Density functional theory (DFT) calculations are performed using the Quantum Espresso code [26] within the generalized gradient approximation (GGA) [27]. We use norm-conserving pseudopotentials [28] with configuration 2$s^{1}2p^{0}$ and non-linear core correction [29] for Li, and configuration 2$s^{2}2p^{1}$ for B. The wavefunctions are expanded using a 50 Ry cutoff. The dynamical matrices and the electron-phonon coupling are calculated using density functional perturbation theory in the linear response [26]. For the electronic integration in the phonon calculation we use an $N_k = 12 \times 12 \times 12$ uniform $k$-point mesh and Hermite-Gaussian smearing from 0.05 Ry. For the evaluation of the electron-phonon coupling we use an $N_q = 40 \times 40 \times 40$ Monkhorst-Pack mesh. For the average over the phonon momentum $q$ we use an $N_q = 4 \times 4 \times 4$ $q$-point mesh. The phonon dispersion is obtained by Fourier interpolation of the dynamical matrices computed on the $N_q$ mesh.

The pressure- and doping-induced changes in the electronic properties of LiB are studied with Vienna Ab initio Simulation Package VASP [30, 31] within the GGA [27]. We use projector augmented waves (PAW) [32] pseudopotentials, in which Li semi-core states are treated as valence; the energy cutoff is set at 600 eV. For the MS1 unit cell, the 2×2×3 MS1 and 2×2×1 MS2 supercells we use 31×31×31, 18×18×6, and 18×18×10 Monkhorst-Pack k-meshes, respectively.

**BAND-STRUCTURE, DOS AND FERMI SURFACE**

The band structure of Li$_2$B$_2$ is presented in Fig. 1 (see footnote [33] for high-symmetry points notation). Similarly to what happens in MgB$_2$ [2], there are two boron $\sigma$-bands crossing the Fermi energy $\epsilon_F$. Compared to the $\sigma$-bands in MgB$_2$, these bands are even more two-dimensional (due to the larger interlayer distance) and shifted by more than 0.6 eV to higher energies at the $\Gamma$ point.
FIG. 1: (Color online) Band structure of LiB. The size of the empty (full) dots represent the amount of Li (B) character at a given \textbf{k}-point. See footnote \[33\] for high-symmetry points notation.

point. As in MgB$_2$, they generate two cylindrical Fermi surfaces (in our case with axes along the $\Gamma T$ direction, Fig. 2). The boron $\pi$ states in LiB resemble more the $\pi$ states of graphite, as they cross exactly at $\varepsilon_F$, so that LiB is lacking $\pi$ Fermi surfaces altogether. In MgB$_2$ these states cross at about 2 eV above $\varepsilon_F$, which leads to the appearance of an extended $\pi$ Fermi surface \[4\]. Another important difference between the electronic structures of the two borides is the presence of a lithium band at $\varepsilon_F$ in LiB. The position of this band resembles the intercalant band in CaC$_6$ \[12\], although in LiB it has substantial hybridization to boron states close to the T-point. The corresponding Fermi surface (a compressed sphere) is depicted in Fig. 2.

The total density of states (EDOS) and the EDOS projected over atomic orbitals is illustrated in Fig 3. The main component at $\varepsilon_F$ is given by boron $p\sigma$ states. In graphite the boron $p\pi$ EDOS at $\varepsilon_F$ is zero and increases slowly and linearly immediately after $\varepsilon_F$.

**PHONON SPECTRUM AND SUPERCONDUCTING PROPERTIES**

The phonon dispersion and the phonon density of states (PHDOS) are illustrated in Fig. 4. The phonon modes at the $\Gamma$-point are decomposed as $2A_{1g} + 2A_{2u} + 2E_g + 2E_u$. To distinguish between modes with the same symmetry but different eigenvectors we use the following notation: $A_{1g}$ $[B_z]$, $E_g$ $[B_{xy}]$, $E_u^-$ $[(\text{Li} - \text{B})_{xy}]$, $A_{1g}$ $[\text{Li}_z]$, $A_{2u}^-[\text{Li}_x]$, $E_g^+$ $[\text{Li}_{xy}]$, $A_{2g}^+[\text{Li} + \text{B}]_{xy}$, $E_u^+[(\text{Li} + \text{B})_{xy}]$, where in brackets we give the corresponding atoms and vibrations. For convenience, we label phonon branches everywhere in the Brillouin zone using the name of their representation at $\Gamma$.

Except for acoustic modes, a clear separation exists between optical Li and B vibrations. Li modes are confined in the 40-55 meV region and are not dispersive, meaning that Li-vibrations behave essentially as Einstein modes. Boron in-plane vibrations are softened along the $\Gamma T$ direction due to coupling to the $\sigma$ bands. The softening at $\Gamma$ of the $E_g$ phonon branches is approximately 20 meV,
At the zone border, substantially softer with respect to the other directions. The three acoustic modes along the ΓT direction are the phonon dispersion bands to the in-plane vibrations in LiB [23], but not as strong as in the case of MgB₂. The superconducting properties can be understood calculating the electron-phonon coupling \( \lambda_{\nu} \) for a phonon mode \( \nu \) with momentum \( \mathbf{q} \):

\[
\lambda_{\nu} = \frac{4}{\omega_{\nu} N(0) N_k} \sum_{k,n,m} |g^\nu_{kn,k+q,m}|^2 \delta(\epsilon_{kn}) \delta(\epsilon_{k+q,m})
\]

where the sum is over the Brillouin Zone. The matrix element is

\[
g^\nu_{kn,k+q,m} = \frac{(kn|\delta V/\delta u_{\nu,|k+q,m|})/\sqrt{2\omega_{\nu}}}
\]

The calculated average electron-phonon coupling is \( \lambda = \sum_{\nu} \lambda_{\nu}/N_q \approx 0.62 \) (\( N_k \) and \( N_q \) are the previously defined \( k \)-space and \( q \)-space mesh dimensions, respectively). The Eliashberg function

\[
\alpha^2 F(\omega) = \frac{1}{2N_q} \sum_{\nu} \lambda_{\nu} \omega_{\nu} \delta(\omega - \omega_{\nu})
\]

and the integral \( \lambda(\omega) = 2 \int_0^\infty d\omega' \alpha^2 F(\omega')/\omega' \) are shown in Fig. 5. As can be seen most of the contribution comes from phonon states in the 60-90 meV region and a smaller contribution comes from low energy states.

An estimate of the different contributions of the in-plane (Li\(xy\) and B\(xy\)) and out-of-plane (Li\(z\) and B\(z\)) vibrations to \( \lambda \) can be obtained from the relation

\[
\lambda = \sum_{i\alpha,j\beta} \Lambda_{i\alpha,j\beta} = \sum_{i\alpha,j\beta} \frac{1}{N_q} \sum_{\mathbf{q}} |\mathbf{G}_\mathbf{q}|_{i\alpha,j\beta} |\mathbf{C}_\mathbf{q}^{-1}|_{j\beta,i\alpha}
\]

where \( i, \alpha \) indices indicate the displacement of the \( i \)-th atom in the Cartesian direction \( \alpha \), \( |\mathbf{G}_\mathbf{q}|_{i\alpha,j\beta} = \sum_{k,n,m} 4\tilde{g}_{i\alpha,j\beta}(\epsilon_{kn}) \delta(\epsilon_{k+m}/\sqrt{2})/N(0)N_k \), and \( \tilde{g}_{i\alpha} = (kn|\delta V/\delta x_{\alpha q,m}|k+q,m)/\sqrt{2} \). The \( \mathbf{C}_\mathbf{q} \) matrix is the Fourier transform of the force constant matrix (the derivative of the forces with respect to the atomic dis-
placements). The decomposition leads to:

\[
\mathbf{A} = \begin{pmatrix}
B_{xy} & B_z & \text{Li}_{xy} & \text{Li}_z \\
0.46 & 0.00 & -0.02 & 0.00 \\
0.00 & 0.13 & 0.02 & -0.05 \\
-0.02 & 0.02 & 0.08 & -0.01 \\
0.00 & -0.05 & -0.01 & 0.07 \\
\end{pmatrix}
\]

The off-diagonal terms are small (but not negligible) compared to the total \( \mathbf{A} \). Most of the coupling is to the in-plane \( B \) vibration; contributions from the Li and the out-of-plane B vibrations are smaller. Since the \( \sigma \)-bands do not couple to the \( B \) vibrations and since there are no \( \pi \) Fermi surfaces, the coupling to \( B \) vibrations is due to the intercalant band. Note that the decomposed values of \( \mathbf{A} \) contain contributions from different modes and are summed over all the \( \mathbf{q} \)-points in the Brillouin zone. For example, \( A_{xy,B_{xy}} = 0.46 \) includes the coupling to the in-plane \( E_g, E_u \), and \( E^\pm \sigma \) branches. By examining the integrated Eliashberg function \( \lambda(\omega) \) in Fig. 3(c) and the phonon characters in Fig. 4 one can infer that the \( E_g \) branch is the most important of the three: among them it has the highest PHDOS in the 70-100 meV range, in which \( \lambda \) contains most of its total value. The soft in-plane \( E^\pm_\sigma \) branch is far less important, as the net contribution from all the soft modes having energy under 20 meV is only \( \approx 0.08 \) (Fig. 5(c)).

It is instructive to compare our result with other layered superconductors. In MgB\(_2\) the coupling of the \( \sigma \)-bands to the phonon modes is \( \lambda_{\sigma,\sigma}^{\text{MgB}_2} = 0.62 \pm 0.05 \) [4, 5], while in LiB the corresponding value is less than 0.46, as discussed above. This difference can be clarified by noting that the \( E_{2g} \) phonon linewidth \( \gamma_{q,E_{2g}} = 2\pi N(0)\omega^\sigma T^{\lambda_{\omega E_{2g}}}_q \lambda^{\pi} \) along \( \Gamma \) in MgB\(_2\) happens to be comparable in magnitude with that of the \( E_g \) mode along \( \Gamma \) in LiB. Therefore, the reduced electron-phonon coupling in LiB is mainly due to the \( E_g \) phonon frequency being smaller than that in MgB\(_2\) (\( \omega_{E_g}^{\text{MgB}_2} / \omega_{E_g}^{\text{LiB}} \approx 1.3 \) at \( \Gamma \)). This unfortunate result can be linked to the absence of the \( \pi \) carriers, which play an important role in softening of the \( E_{2g} \) mode in MgB\(_2\) [30, 57].

We find that LiB and graphite intercalated compounds have few similarities in terms of superconducting features. In particular, in CaC\(_6\) the intercalate modes are responsible of \( \approx 50\% \) of the total electron-phonon coupling, and the rest comes from vibrations of carbon modes in the direction perpendicular to the graphite layers. In CaC\(_6\) one has \( \lambda_{C_{2s}} + \lambda_{C_{3s}} = 0.33 \) and \( \lambda_{C_{4s}} = 0.33 \) [13]. In LiB the overall contribution of \( B_z, \text{Li}_{xy} \) and \( \text{Li}_z \) vibrations is less than half of that of CaC\(_6\), which means that while LiB captures some of the physics of MgB\(_2\), it does not capture the physics of graphite intercalated compounds to full extent. This is also clear from the phonon spectrum of CaC\(_6\) where the intercalent modes are at energies lower than 20 meV and one of the Ca modes undergoes a marked softening with a corresponding large electron-phonon coupling (at point \( X \) of Fig. 2 in Ref. [13]). In LiB, on the contrary, the Li modes are much higher in energies (\( \sim 50 \) meV) meV and dispersionless. The main reason for this difference comes from the mass of Li which is 5.77 times smaller than that of Ca leading to frequencies which are on average 2.4 times larger.

The critical superconducting temperature is estimated using the McMillan formula [22]:

\[
T_c = \frac{\langle \omega \rangle_{\log} \exp \left[ \frac{-1.04(1 + \lambda)}{\lambda - \mu^*(1 + 0.62\lambda)} \right]}{1.2}
\]

where \( \mu^* \) is the screened Coulomb pseudopotential and

\[
\langle \omega \rangle_{\log} = \int_0^\infty \frac{\omega^2 F(\omega) \log(\omega)/\omega \ d\omega}{\omega^2}
\]

the phonon frequencies logarithmic average. We obtain \( \langle \omega \rangle_{\log} = 54 \) meV leading to \( T_c \) of approximately 10-15 K for \( \mu^* = 0.14 - 0.1 \). This value could be further enhanced by multiband effects.

**DOPING AND PRESSURE EFFECTS**

Even though a theoretically-devised from scratch superconductor with \( T_c = 10 - 15 \) K could be considered a success of the materials prediction methodology, the stoichiometric LiB compound falls short of expectations to compete with the record-holding binary MgB\(_2\). In this section we investigate whether it is possible to favorably modify the electronic properties of LiB and achieve higher \( T_c \) by doping or applying pressure. We pay special attention to the evolution of the \( \pi \) states, since their reintroduction at \( \epsilon_F \) may soften the \( E_g \) mode and lead to a larger coupling.

As has been pointed out previously [23], the bonding \( \pi \) states are completely filled under ambient conditions. Because the band crossing in LiB at the Fermi level is accidental, it may be possible to move the crossing point with pressure and increase the \( \pi \)-bands EDOS at \( \epsilon_F \). Figure 2(a) reveals that there is indeed a rapid change in the \( \sigma \) and \( \pi \) EDOS, followed by a plateau after 5 GPa. This behavior is a reflection of two distinctly different regimes of the LiB structural changes: i) in the 0-5-GPa pressure range the Li-Li interlayer spacing quickly shrinks and the B-B bond length slightly expands so that at 5 GPa they become about 0.5 and 1.02 of their zero-pressure values, respectively; ii) for pressures above 5 GPa the Li atoms in the bilayer start experiencing the hard-core repulsion and the compound compresses more isotropically. The inset in Fig. 2(a) illustrates that by reducing the Li-Li interlayer distance one forces the charge from the intercalant band (completely emptied at about 6 GPa) into the boron \( \pi \) and \( \sigma \) states (lowered by 0.7 eV at that pressure). Once the charge redistribution is complete, no appreciable changes in the EDOS are seen for the boron
states up to at least 30 GPa. Therefore, the peculiar behavior of the nearly free electron intercalant states (also observed in other systems \cite{12,39}) is the only meaningful factor allowing modification of the LiB boron states with pressure.

These simulations demonstrate that the compression of LiB does not lead to the desired π-bands EDOS values comparable to those in MgB$_2$. Moreover, the hydrostatic pressure causes such a quick drop in the σ-bands EDOS that this will likely negate any possible enhancement in the electron-phonon coupling due to the reintroduction of the π-states at $\epsilon_F$. The phonon modes are also expected to harden under pressure, further reducing the electron-phonon coupling in LiB \cite{41}.

LiB has plenty of available bonding σ states, therefore the compound should be easy to electron-dope. A quick examination of the boron EDOS states around the Fermi level (Fig. 3 or Fig. 4 in Ref. \cite{23}) gives an idea on what possible changes in the Fermi surfaces and, eventually, in the electron-phonon coupling the doping could lead to. At small doping levels, when the rigid band approximation normally holds, the EDOS from the two dimensional σ bands should only slightly fluctuate until the states are completely filled, which happens at $\Delta_0 \approx \epsilon N(0) \Delta E \approx 0.70$ (e/eV) (1 eV) = 0.70 e/f.u. = 0.35 e/boron. The EDOS from the π bands grows slowly and even at the relatively high electron-doping of 0.35 e/boron it would amount only to about a half of what is observed in MgB$_2$. Another way to tweak the electronic structure could be to hole-dope LiB as it is done for Li$_x$BC \cite{15}. The known limitations of this approach are the buckling of the hexagonal layers and the eventual destabilization of the compound upon heavy Li depletion \cite{15}.

We first simulate the electron- (hole-) doping using a charged cell with a neutralizing positive (negative) background. Normally, in this approach one can safely relax the unit cell parameters and obtain valuable information about the bond length variation under small doping. However, in the case of the electron-doped LiB the repulsion between the negatively charged boron layers overcomes the weak binding between the lithium layers, causing the c-axis to undergo unphysical expansion even at small levels of doping. Therefore, we fix the c-axis at the zero-doping value and relax only the remaining three parameters. The set of data, shown as hollow points in Fig. 6(b), supports our earlier conclusion that the π-band EDOS cannot be easily increased. Note that the approximations used in this test, i.e. the fixed c-axis and the use of a neutralizing background, may influence the results to some extent. For example, the positive electrostatic potential from ionized dopants could bring the delocalized π-states down (in addition to the rigid band downshift) and could potentially be an important factor in increasing the π EDOS.

To address these limitations we use a more realistic model of the electron-doped LiB by substituting Li with Mg or Al. Small doping levels are obtained only for large unit cells; we use the hexagonal $2 \times 2 \times 3$-MS1 and $2 \times 2 \times 1$-MS2 supercells with 48 and 32 atoms, respectively. Replacement of one or two Li atoms in these structures results in the 1/24, 1/16, 1/12, and 1/8 concentrations of dopants per boron, and the level of doping is found in the assumption that they give up all their valence charge. In all the cases the c-axis expansion in the fully relaxed unit cells does not exceed 6%. The resulting averaged boron EDOS for the Mg and Al sets are shown in Fig. 6(b) as solid points \cite{41}. The scattered presence of dopants in the lattice should cause some dispersion of the local boron properties. A general trend observed in our supercell calculations is that a downshift of the π and σ states happens only for B layers in direct contact with the dopant. Typical values of the downshift that a single Mg (Al) atom induces in all eight atoms in a neighboring B layer are about 0.2 (0.5) eV. It is not easy to isolate the importance of different factors defining the level of B doping, i.e. the simple charge transfer, the electrostatic effect discussed above and the structural changes (expansion of the c-axis and contraction of the B-B bond). However, Fig. 6(b) demonstrates that the net effect of the substitutional doping is described reasonably well within the rigid band model.

In summary, our tests indicate that it is rather difficult to reintroduce a significant amount of π states at $\epsilon_F$ with
hydrostatic pressure or small doping, because the band crossing in LiB happens to be exactly at $\epsilon_F$, about 2 eV lower than in MgB$_2$. To have a chance of substantially increasing $T_c$, one should search for more radical ways of modifying the electronic structure of the MS metal borides.

**CONCLUSIONS AND PERSPECTIVES**

In this work we have investigated electron and phonon properties of the recently theoretically-devised superconductor LiB [23]. By studying in details the phonon properties of this hypothetical material we have found that its critical temperature is of the order of 10-15 K. Superconductivity of this hypothetical material we have found that the overall electron-phonon coupling is only $\lambda = 0.62$.

Since the discovery of MgB$_2$, no other diborides have been found with high $T_c$ (for a full list, see Ref. [12]). If we compare LiB with the known diborides, our calculated 10-15 K critical temperature is not so low, although it is far from the 39 K of MgB$_2$. Nevertheless, the study of LiB gives an important understanding. The common belief is that the main effect for the singular and unique behavior of MgB$_2$ is given by the presence of almost two-dimensional $\sigma$ bands. LiB has even more planar $\sigma$ bands and even higher $\sigma$ EDOS at $\epsilon_F$ relative to that in MgB$_2$ [23, 24]; however, their contribution to the total electron-phonon coupling turns out to be at least 25% smaller. This reduction can be attributed to the differences between the in-plane boron vibrations in the two borides, caused mainly by the lack of the $\pi$ carriers at $\epsilon_F$ in LiB. Namely, the softening of the $E_g$ mode in LiB is substantially smaller (by about a factor of two) than that of $E_{2g}$ in MgB$_2$, which makes the former mode be noticeably harder ($\omega_{E_g}^{\text{LiB}} / \omega_{E_{2g}}^{\text{MgB}_2} \approx 1.3$ at $\Gamma$). Therefore, in addition to the direct loss of the $\pi$ states contribution to $\lambda$, their absence at $\epsilon_F$ in LiB also has a strong indirect negative effect on the overall electron-phonon coupling.

We have investigated whether this somewhat unexpected obstacle, preventing LiB to be a truly high $T_c$ superconductor, could be overcome with modifications of the compound’s properties. Behavior of electronic features important for the LiB superconductivity has been examined as a function of small doping and pressure. Our results indicate that the $\pi$ EDOS increases very slowly and cannot reach the desired values, at least not before the $\sigma$ EDOS is substantially reduced. Thus, small doping and pressure are not expected to significantly improve $T_c$ in LiB. A promising direction to fix the problem would be to find a suitable LiB-based ternary alloy; this question is currently under investigation.

Theoretical development of potentially important superconducting materials is a difficult task because $T_c$ critically depends on their band structure features and vibrational properties. The challenge is even greater if one attempts to design a superconductor from scratch, since one first needs to ensure its thermodynamic stability. The case of LiB shows that it is possible to theoretically predict a compound that both i) has a good chance to form and ii) possesses interesting superconducting properties. Study of such promising candidates gives important insights into how to perform a more targeted search for novel superconducting materials.

While we were finishing writing this paper, a preprint on the related structure MS2-LiB appeared on-line [37]. The results of the paper are similar to ours except for some numerical details that can probably be related to the different unit cells and $k,q$-point samplings used [43]. However, our conclusions concerning the possibility of increasing the $T_c$ in LiB by doping are rather different, as explained in the previous Section.

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For example, the long-period shifts have little effect on the synthesized lithium monoboride could be a mixture of the two crystal structure phases [23].

The special points are: $\Gamma = (0, 0, 0), T = (1/2, 1/2, 1/2), U = (1/2 + \eta, \tau, \tau), X = (1/2, 0, 0), U' = (1/2 - \eta, -\tau, -\tau), L = (1/4, -1/4, -1/4), S = (1/2, -1/2, 0)$. Given the rhombohedral angle $\alpha$, the parameters $\eta$ and $\tau$ are expressed as $\eta = \left[1 - 2/(3\tan^2(\alpha/2) - 1)\right]/12$ and $\tau = \left[1 + 1/(3\tan^2(\alpha/2) - 1)\right]/12$.

We do not observe any significant softening of the in-plane boron phonon mode resulting from the 2% expansion of the boron-boron bond under small (below 5 GPa) pressures. The frequencies of the soft sliding modes have been shown to nearly double at 2 GPa [24].

We place the dopants in the supercell as uniformly as possible. Due to the high sensitivity of the projected EDOS to k-sampling we use a 0.2 eV smearing in the MS1 and TBA supercell calculations [23].

In compounds such as MgB$_2$, $\lambda_{qu}$ varies substantially all over the Brillouin zone. Thus a better q-point sampling than that possible in state-of-the-art ab-initio simulations is needed to obtain estimates of $\lambda$ comparable with that achieved for simple superconductors such as Nb. For this reason, in systems like MgB$_2$, the errors in parameters such as $\lambda$ or $\omega_{log}$ is probably larger than expected.