Role of Boron $p$-Electrons and Holes in Superconducting $MgB_2$, and other Diborides: A Fully-relaxed, Full-Potential Electronic Structure Study

Prabhakar P. Singh
Department of Physics, Indian Institute of Technology, Powai, Mumbai -400076, India

(January 9, 2022)

We present the results of fully-relaxed, full-potential electronic structure calculations for the new superconductor $MgB_2$, and $BeB_2$, $NaB_2$ and $AlB_2$, using density-functional-based methods. Our results, described in terms of (i) density of states (DOS), (ii) band-structure, and (iii) the DOS and the charge density around the Fermi energy $E_F$, clearly show the importance of $B$ $p$-band for superconductivity. In particular, we show that around $E_F$, the charge density in $MgB_2$, $BeB_2$ and $NaB_2$ is planar and is associated with the $B$ plane. For $BeB_2$ and $NaB_2$, our results indicate qualitative similarities but significant quantitative differences in their electronic structure due to different lattice constants $a$ and $c$.

The intricate interplay of interactions between electrons, holes and phonons is quite evident in the recently discovered superconductor Magnesium Boride, $MgB_2$. The superconducting temperature of around $\approx 39K$ in $MgB_2$ is almost at the extreme end of $T_c$’s predicted by the BCS theory for conventional superconductors. The ongoing experimental investigations suggest it to be a BCS type superconductor with confirmed isotope effects $^2$ and other related effects $^3$. However, more experiments are needed to completely characterize the nature of interaction responsible for superconductivity (SC) in $MgB_2$. Theoretical studies of $MgB_2$, since the announcement of SC by Akimitsu, have concentrated on (i) the nature of interactions responsible for SC using model Hamiltonians $^2$ and (ii) the electronic structure $^2$ and the linear response $^2$ of normal state $MgB_2$ using $ab$ initio methods but with the experimentally obtained lattice constants $a$ and $c$.

In order to understand SC in $MgB_2$, be it due to heavily doped holes $^4$, hole-doped covalent bonds $^4$, or simply due to electron-phonon interaction $^4$, it is essential to have an accurate electronic structure description of the normal state $MgB_2$. It is also becoming clear that the boron layer and the two-dimensional $\sigma$ band due to $p_{x,y}$ orbitals in that layer hold the key to SC in $MgB_2$ (we present evidence of that) $^4$. Thus an understanding of how the $\sigma$ band and the $p_{x,y}$ orbitals respond to changes in the chemical environment, lattice constants etc. could be quite useful in understanding SC in $MgB_2$ and in synthesizing new materials with $MgB_2$-like SC. Fortunately, these changes around $B$ layer can be mimicked without destroying its two-dimensional character which is essential for SC. For example, the effects of removing one electron and adding one electron around the $B$ layer can be studied by considering $NaB_2$ and $AlB_2$, respectively. Similarly, a study of $BeB_2$ (and $NaB_2$) will provide the effects of changing the lattice parameters $c$ and to a lesser extent $a$. Thus an accurate and reliable systematic study of the electronic structure of $MgB_2$, $BeB_2$, $NaB_2$ and $AlB_2$, coupled with the experimental facts of SC in $MgB_2$ and no SC in $AlB_2$, can provide substantive clues about the nature of interaction responsible for SC as well as help in synthesizing new superconducting materials with $T_c$’s comparable to that of $MgB_2$.

As the nature of bonding in boron layer depends critically on lattice constants $a$ and $c$, and since for SC one needs the electronic structure within a small energy interval of $\pm \hbar \omega_D$ ($\omega_D \equiv $ Debye frequency) around the Fermi energy, which gets affected the most due to change in lattice constants, it is of utmost importance to theoretically optimize the lattice constants $a$ and $c$. Some of the earlier studies of $MgB_2$, which are based on the experimental lattice constants, have provided a good overall description of the electronic structure $^2$ and some others have used the Fermi surface $^2$ to discuss SC in $MgB_2$. Previous study $^6$ of $BeB_2$ was carried out with assumed values for the lattice constants $a$ and $c$. A recent calculation $^6$ of $BeB_2$ gives optimized values for $a$ and $c$ but we find these values to be not fully converged. In our opinion, there is a clear need to include (a) structural relaxation of the lattice, (b) a detailed description of electronic structure in a small interval around Fermi energy, and (c) a comparison with other related compounds which have either the potential of becoming an $MgB_2$-like superconductor or help in understanding SC in $MgB_2$, in a density-functional-based electronic structure calculations of $MgB_2$. The present work is a step in that direction.

In the following, we present the results of fully-relaxed, full-potential electronic structure calculations for $MgB_2$, $BeB_2$, $NaB_2$ and $AlB_2$ in $P6/mmm$ crystal structure, using density-functional-based methods. We analyze our results in terms of (i) density of states (DOS), (ii) band-structure along symmetry directions, and (iii) the DOS and the electronic charge density in a small energy window around the Fermi energy, $E_F$, in these systems.
For our calculations, we have used ABINIT code \[^13\] , based on pseudopotentials and plane waves, to optimize the lattice constants \(a\) and \(c\) of \(MgB_2\), \(BeB_2\), \(NaB_2\) and \(AlB_2\). In order to study the band-structure along symmetry directions and site- and symmetry-decomposed densities of states, we have calculated, self-consistently, the electronic structure of these compounds using our own full-potential program as well as LMTO calculations, carried to charge self-consistent full-potential LMTO calculations.

Based on our calculations, described below, we find that in \(MgB_2\) (i) \(B\)-band is crucial for SC due to its proximity to \(E_F\). In particular, it is evident that within a small energy window around \(E_F\), the charge density is two-dimensional and it is associated with the \(B\) plane, (ii) structural relaxation leads to significant changes around \(E_F\) in the densities of states and charge density. For the hypothetical compounds \(BeB_2\) and \(NaB_2\), our results indicate qualitative similarities but significant quantitative differences in electronic structure due to very different lattice constants \(a\) and \(c\) of these compounds. A comparison of band-structure of \(BeB_2\), \(NaB_2\), \(MgB_2\) and \(AlB_2\) along symmetry directions reveals that the \(\Gamma_5\) point moves down, starting from above \(E_F\) in \(NaB_2\) to well below \(E_F\) in \(AlB_2\). If SC is due to holes then one would expect \(BeB_2\) and \(NaB_2\), if they can be synthesized, to become superconducting but not \(AlB_2\).

Before describing our results in detail, we provide some of the computational details of our calculations. The structural relaxation was carried out by the molecular dynamics program ABINIT with Broyden-Fletcher-Goldfarb-Shanno minimization technique \[^13\] using Troullier-Martins pseudopotentials \[^10\] , 512 Monkhorst-Pack \[^7\] \(k\)-points and Teter parameterization \[^13\] for the exchange-correlation. The kinetic energy cutoff for the plane waves was 110 Ry. The charge self-consistent full-potential LMTO calculations were carried out using \(2k\)-panels with the generalized gradient approximation for exchange-correlation as given by Perdew et al. \[^15\] and 484 \(k\)-points in the irreducible wedge of the Brillouin zone. The basis set used consisted of \(s\), \(p\), \(d\) and \(f\) orbitals at the \(Mg\) site and \(s\), \(p\) and \(d\) orbitals at the \(B\) site. The potential and the wavefunctions were expanded up to \(l_{\text{max}} = 6\). The input to the tight-binding LMTO calculations, carried to charge self-consistency, were similar to that of the full-potential calculations except for using spherically symmetric potentials and the space-filling atomic spheres.

In Table I we compare the calculated lattice constants \(a\) and \(c\) for \(MgB_2\), \(BeB_2\), \(NaB_2\) and \(AlB_2\) with the experimentally observed values \[^19\][20\], indicated in the parentheses. The calculated lattice constants for \(MgB_2\) and \(AlB_2\) are smaller than their respective experimental values by roughly 1%. It compares well with the differences mentioned in \[^8\] for the lattice constants of \(MgB_2\). For \(BeB_2\) and \(NaB_2\) the values obtained for \(c/a\) are 0.98 and 1.43, respectively. Although, one expected the change in \(c/a\) ratio to be small in \(BeB_2\) and large in \(NaB_2\) as compared to \(MgB_2\), however, the \(c/a\) value for \(NaB_2\) is larger than expected. Because of the large difference in the \(c/a\) ratio of \(BeB_2\) and \(NaB_2\) they can be used to explore the importance of inter-layer coupling for SC in these systems. A recent calculation \[^8\] of \(BeB_2\) gives a somewhat smaller value for \(a\) and \(c\). We have used the lattice constants as given in Ref. \[^8\] to optimize the lattice constants of \(BeB_2\). The results are in agreement with the values given in Table I. In Table I, we also show the plasma frequencies and the total density of states per spin, \(n(E_F)\), at \(E_F\) for these compounds. The plasma frequencies along \(x\) \((y\) ) direction are very similar for all four diborides but along the \(z\) direction it correlates with the \(c/a\) ratio of the compound. A smaller \(c/a\) ratio leads to enhanced coupling in the \(z\) direction.

We show in Fig. 1 the total density of states for \(BeB_2\), \(NaB_2\), \(MgB_2\) and \(AlB_2\) calculated using the ABINIT program at the optimized lattice constants of these compounds as given in Table I. The gross features of the DOS of the four compounds are similar if one takes into account the differences in the total number of valence electron. The bottom of the band is the deepest for \(AlB_2\) which has a total of nine valence electrons and shallowest for \(NaB_2\) with only seven valence electrons. However, the iso-electronic structures \(BeB_2\) and \(MgB_2\) show substantial differences in their DOS near the bottom of the band. This is due to the fact that the smaller \(c/a\) ratio leads to enhanced repulsion which pushes the \(s\) and \(p\) electrons at the \(Mg\) site downward and, at the same time, diminishes the DOS for \(B\) \(s\) and \(p\) electrons in the middle of the band. In the case of \(AlB_2\) we find that the \(B\) \(p\)-band is completely inside \(E_F\).

An important factor in determining the superconducting temperature in conventional superconductors is the DOS within an interval of \(\pm \hbar \omega_D\) at \(E_F\). In order to analyze our results in detail we have plotted in Fig. 2 the symmetry-decomposed DOS at the \(B\) site within a small energy interval around \(E_F\). From the DOS for \(AlB_2\), it is evident that it will not be superconducting, not at least in the same sense as that of \(MgB_2\), because the bands with \(x\) and \(y\) symmetry are completely filled. According to our calculations as shown in Fig. 2, \(NaB_2\) is likely to show SC with enhanced \(T_c\).

To see how the differences in the lattice constants and the number of valence electrons affect the band-structure, in Fig. 3 we have plotted the band-structure along the symmetry directions for \(BeB_2\), \(NaB_2\), \(MgB_2\) and \(AlB_2\).
We find that these differences lead to significant changes in the band-structures of $BeB_2$, $NaB_2$, $MgB_2$, and $AlB_2$. A measure of these changes is evident in the movement of $\Gamma_5$ point with respect to $E_F$ as one goes from $BeB_2$ to $AlB_2$. Due to different number of valence electrons, the $\Gamma_5$ point is well above $E_F$ in $NaB_2$ but well below $E_F$ in $AlB_2$. The differences between the band-structures of $BeB_2$ and $MgB_2$ arise due to differences in the lattice constants. Our calculations show that $\Gamma_5$ point is inside $E_F$ by about 5 $mRy$ in $BeB_2$, while it is slightly above $E_F$ in $MgB_2$. It is interesting to note that the location of $\Gamma_5$ point, around which the Fermi surface in $MgB_2$ is hole-like, has been correlated with SC in $MgB_2$ and other diborides [4]. Our $l$-character analysis shows substantial $p_x$ and $p_z$ characters along $\Gamma-A$ direction near $E_F$ in all the diborides.

To complete our analysis we have also calculated the electronic charge density within a 5 $mRy$ energy window around $E_F$ for $BeB_2$, $NaB_2$, $MgB_2$ and $AlB_2$ compounds using the TB LMTO method with the lattice constants as given in Table I. In these calculations the atomic sphere radii were adjusted to minimize the discontinuity in the Hartree potential across the atomic spheres which have been found to give reliable results [1,2]. To reduce the overlap errors in $NaB_2$, which has a large $c/a$ ratio, we have inserted an empty sphere. In Fig. 4, we show the charge density calculated within a 5 $mRy$ energy window around $E_F$ for these compounds. For $MgB_2$, $BeB_2$ and $NaB_2$ we find very similar charge density, which is due to $p_{x,y}$ orbitals in the $B$ plane. It should be noted that the holes in $MgB_2$ also originate from these planar orbitals in the $B$ plane. In contrast, the charge density around $E_F$ in $AlB_2$ has a three-dimensional character and it consists mostly of $Mg$ $s$- and $B$ $p$-electrons.

In conclusion, we have presented the results of our fully-relaxed, full-potential electronic structure calculations for $BeB_2$, $NaB_2$, $MgB_2$ and $AlB_2$ in P6/mmm crystal structure using density-functional-based methods. We have analyzed our results in terms of the density of states, band-structure, and the DOS and the electronic charge density around $E_F$ in these systems. For $MgB_2$, we find that the $p$-band of $B$ is crucial for SC due to its proximity to $E_F$. In particular, we have shown that within a small energy window around $E_F$, the charge density is two-dimensional and it is associated with the $p_{x,y}$ orbitals in the $B$ plane. For $BeB_2$ and $NaB_2$, our results indicate qualitative similarities but significant quantitative differences in the electronic structure due to differences in the lattice constants. For example, we find that the $\Gamma_5$ point in $BeB_2$ is just below the Fermi energy while in $NaB_2$ it is well above the Fermi energy.

TABLE I. The calculated lattice constants $a$ and $c$, the plasmon frequencies, and the density of states at the Fermi energy. The experimental lattice constants are shown in the parentheses.

| Compound | $a$ (Å) | $c$ (Å) | $\omega_p (eV)$ | $\omega_p^* (eV)$ | $n(E_F)$ |
|----------|---------|---------|----------------|------------------|----------|
| $BeB_2$  | 5.49(5.558) | 5.41(5.425) | 8.1 | 11.8 | 3.29 |
| $NaB_2$  | 5.70 | 8.15 | 7.75 | 3.40 | 6.75 |
| $MgB_2$  | 5.76 (5.834) | 6.59 (6.657) | 7.04 | 6.77 | 4.70 |
| $AlB_2$  | 5.63 (5.681) | 6.13 (6.149) | 8.11 | 10.02 | 2.66 |

[1] J. Akimitsu, Symp. on Transition Metal Oxides, Sendai, January 10, 2001; J. Nagamatsu, et al., Nature 410, 63 (2001).
[2] S. L. Bud’ko et al., Phys. Rev. Lett. 86, 1877 (2001).
[3] H. Schmidt et al., cond-mat/0102389; G. Karapetrov et al., cond-mat/0102312.
[4] J. E. Hirsch, cond-mat/0102117.
[5] J. M. An and W. E. Pickett, cond-mat/0102391.
[6] J. Kortus et al., cond-mat/0101446.
[7] K. D. Belashchenko et al., cond-mat/0102290.
[8] G. Satta et al., cond-mat/0102355.
[9] Y. Kong et al., cond-mat/0102490.
[10] R. Osborn et al., cond-mat/0103064.
[11] J. K. Burdett et al., Chem. Mater. 2, 12 (1989).
[12] A. I. Ivanovskii and N. I. Medvedeva, Russ. J. Inorg. Chem. 45, 1324 (2000).
[13] URL http://www.pcpm.ucl.ac.be/abinit.
[14] S. Y. Savrasov, Phys. Rev. B 54, 16470 (1996).
[15] The Stuttgart TB LMTO 4.7 package.
[16] N. Troullier and J. L. Martins, Phys. Rev. B 43, 1993 (1991).
[17] H. J. Monkhorst and J. D. Pack, Phys. Rev. B 13, 5188 (1976).
[18] J. P. Perdew and Y. Wang, Phys. Rev. B 45, 13244 (1992); J. Perdew et al., Phys. Rev. Lett. 77, 3865 (1996).
[19] Acta Cryst. 14, 309 (1961).
[20] A. Lipp and M. Roder, Z. Anorg. Allgem. Chem., 344, 225 (1966).
[21] D. R. Armstrong and P. G. Perkins, J. C. S. Farady II, 75, 12 (1979).
[22] D. R. Armstrong et al., J. C. S. Faraday II, 73, 952 (1977).
[23] Prabhakar P. Singh and A. Gonis, Phys. Rev. B 49, 1642 (1994).
FIG. 1. The total density of states calculated at the optimized lattice constants using the ABINIT program.

FIG. 2. The partial B density of states around Fermi energy calculated at the optimized lattice constants using the full-potential LMTO method.

FIG. 3. The band-structure along symmetry directions calculated at the optimized lattice constants using the full-potential LMTO method.

FIG. 4. The isosurfaces of charge density within a 5 mRy energy window around the Fermi energy in the primitive cell of BeB$_2$ (top left), NaB$_2$ (top right), MgB$_2$ (bottom left) and AlB$_2$ (bottom right), calculated at the optimized lattice constants using the TB LMTO method. The values of the isosurfaces (8,6,4,2,1) decrease as one moves away from the $B$ plane. The unit for charge density in the volume is $10^{-4}[e/(\text{a.u.})^3]$ and the view is off-diagonal at an angle of $30^0$. 
