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

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(Received 6 March 2001; published 6 August 2001)

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, we find significant differences in their electronic structure due to differences in the number of valence electrons and the lattice constants a and c.

DOI: 10.1103/PhysRevLett.87.087004 PACS numbers: 74.25.Jb, 74.70.Ad

The intricate interplay of interactions between electrons, holes, and phonons is quite evident in the recently discovered superconductor magnesium boride, MgB_2 [1]. The superconducting temperature of ≈39 K 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 [4,5] and (ii) the electronic structure [5–8] and the linear response [5,6,8,9] 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 dressed holes [4], due to hole-doped covalent bonds [5], or simply due to electron-phonon interaction [10], 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 σ band due to $p_{x,y}$ orbitals in that layer hold the key to SC in MgB_2 (we present evidence of that) [5–8]. Thus an understanding of how the σ 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 the 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 $\pm hw_D$ ($\omega_D \equiv$ 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 [5–8,11,12] and some others have used the Fermi surface [6] to discuss SC in MgB_2. Previous study [7] of BeB_2 was carried out with assumed values for the lattice constants a and c. A recent calculation [8] 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 either have the potential of becoming an MgB_2-like superconductor or help in understanding SC in MgB_2, in the 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 the symmetry directions and site- and symmetry-decomposed densities of states, we have calculated, self-consistently, the

0031-9007/01/87(8)/087004(4)$15.00

electronic structure of these compounds using our own full-potential program as well as LMTART package [14] with the optimized lattice constants. For studying the charge density in a small energy window around E_F we have used the Stuttgart TB LMTO (tight-binding linear muffin-tin orbital) package [15].

Based on our calculations, described below, we find that in MgB_2 (i) B p-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, and (ii) structural relaxation leads to significant changes around E_F in the densities of states and charge density. For the hypothetical compounds BeB_2 [16] and NaB_2, our results indicate qualitative similarities but significant quantitative differences in electronic structure due to differences in the number of valence electrons and the 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 Γ_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 [17], 512 Monkhorst-Pack [18] **k**-points, and Teter parametrization [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 2κ panels with the generalized gradient approximation for exchange correlation as given by Perdew *et al.* [19] 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 wave functions were expanded up to $l_{\max} = 6$. The input to the tight-binding LMTO calculations, carried to charge self-consistency, was similar to that of the full-potential calculations except for using spherically symmetric potential 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 [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 [6] 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 the 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 interlayer 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 calculate the total energy of BeB_2 using the full-potential LMTART program, and we find that the lattice constants as given in Table I of our paper correspond to lower energy by about 3 mRy. We have also run the ABINIT code with the information given (which is not complete) 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 the $x(y)$ 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 electrons. 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 isoelectronic 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 $\pm hw_D$ at E_F. In order to analyze our

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.

	a (a.u.)	c (a.u.)	ω_p^x (eV)	ω_p^z (eV)	$n(E_F)$
BeB_2	5.49	5.41	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

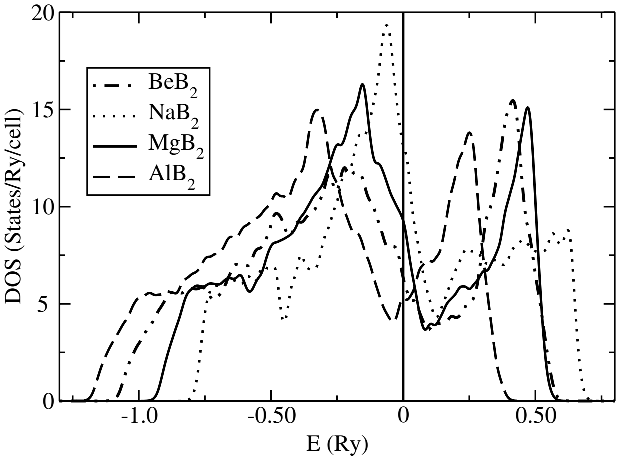

FIG. 1. The total density of states calculated at the optimized lattice constants using the ABINIT program.

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 number of valence electrons and the lattice constants 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 the Γ_5 point with respect to E_F as one goes from BeB_2 to AlB_2. Because of the different number of valence electrons, the Γ_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 the Γ_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 the Γ_5 point, around which the Fermi surface in MgB_2 is holelike [6,21,22], 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 the Γ-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 [6,23]. 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-electrons 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, the 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

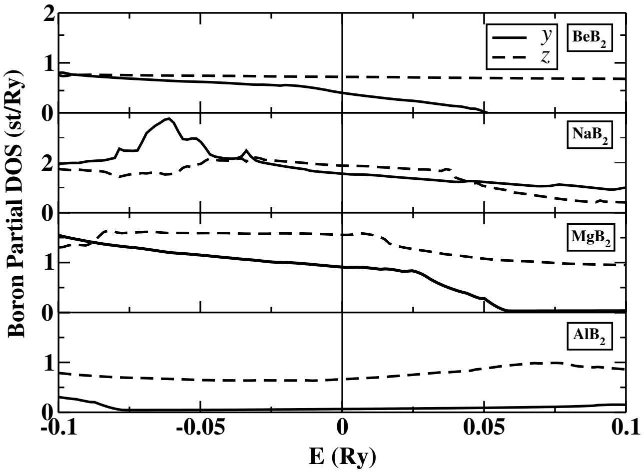

FIG. 2. The partial B density of states around Fermi energy calculated at the optimized lattice constants using the full-potential LMTO method.

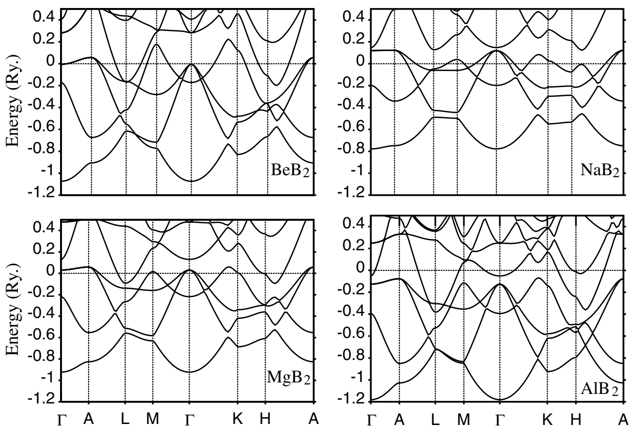

FIG. 3. The band structure along symmetry directions calculated at the optimized lattice constants using the full-potential LMTO method.

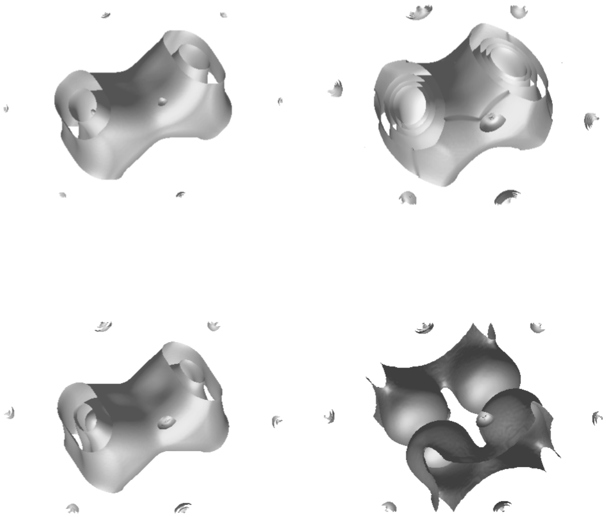

FIG. 4. The isosurfaces of charge density within a 5 mRy energy window around the Fermi energy in the primitive cell of BeB_2 (top left), NaB_2 (top right), MgB_2 (bottom left), and AlB_2 (bottom right), calculated at the optimized lattice constants using the TB LMTO method. The values of the isosurfaces $(8, 6, 4, 2, 1)$ decrease as one moves away from the B plane. The unit for charge density in the volume is $10^{-4}[e/(\mathrm{a.u.})^3]$ and the view is off-diagonal at an angle of 30°.

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 number of valence electrons and the lattice constants. For example, we find that the Γ_5 point in BeB_2 is just below the Fermi energy while in NaB_2 it is well above the Fermi energy.

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