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Electronic structure of superconducting MgB_2 and related binary and ternary borides

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First-principles full potential linear muffin-tin orbital-generalized gradient approximation electronic structure calculations of the new medium- T_C superconductor (MTSC) MgB_2 and related diborides indicate that superconductivity in these compounds is related to the existence of $p_{x,y}$ -band holes at the Γ point. Based on these calculations, we explain the absence of medium- T_C superconductivity for BeB_2 , AlB_2 , ScB_2 , and YB_2 . The simulation of a number of MgB_2 -based ternary systems using a supercell approach demonstrates that (i) the electron doping of MgB_2 (i.e., $\text{MgB}_{2-y}\text{X}_y$ with $X = \text{Be, C, N, O}$) and the creation of defects in the boron sublattice (nonstoichiometric MgB_{2-y}) are not favorable for superconductivity, and (ii) a possible way of searching for similar or higher MTSC should be via hole doping of MgB_2 (CaB_2) or isoelectronic substitution of Mg (i.e., $\text{Mg}_{1-x}\text{M}_x\text{B}_2$ with $M = \text{Be, Ca, Li, Na, Cu, Zn}$) or creating layered superstructures of the $\text{MgB}_2/\text{CaB}_2$ type.

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The discovery of superconductivity in magnesium diboride (MgB_2) (Ref. 1) has attracted a great deal of interest in this system. The transition temperature for MgB_2 ($T_C \approx 39$ K) exceeds by almost two times the record values of T_C for conventional B1- and A15-type intermetallic superconductors (SC's).² As distinct from the high-temperature SC, MgB_2 has an exclusively simple composition and crystal structure.³ The finding of a new medium- T_C SC (MTSC) raises a number of questions: (1) What is the nature of the superconductivity in MgB_2 ? (2) Is MgB_2 a unique compound of this kind or is it the first representative of a new class of MTSC's? (3) What physical and chemical properties should related MTSC's possess?

It is worth noting that among boron-containing phases MgB_2 is not a unique superconductor. A systematic search for superconductivity in a wide range of d -metal borides [and other metal-like compounds of a transition metal (TM) with light nonmetals (carbides and nitrides⁴)] has been carried out earlier.^{5,6} For instance, it was shown that the superconducting transition temperature for TM diborides (MB_2 , $M = \text{Ti, Zr, Hf, V, Ta, Cr, Mo}$) is below ~ 0.4 K. Only NbB_2 was found to be a superconductor with a T_C of about 0.6 K. A large class of superconducting (with T_C of several K) ternary (LnRuB_2 , LnRh_4B_4) and pseudoternary ($\text{Ln}_{1-x}\text{Ln}'_x$) Rh_4B_4 borides is known.⁷ In 1994, Cava *et al.*⁸ discovered superconductivity ($T_C \approx 16-23$ K) in a new class of intermetallic borocarbides (IBC's), namely layered compounds of the $\text{LnM}_2\text{B}_2\text{C}$ type. Numerous theoretical and experimental studies (see review⁹) made it possible to place IBC's into the class of conventional BCS superconductors. It is significant that bands near the Fermi level of IBC participating in electron-phonon interactions (with a high-frequency Ba_{1g} mode) are determined by interatomic σ bonds in the TMB_4 tetrahedra. For all the above-mentioned borides, the most important role in their superconductivity is played by d -electron atoms.

The electronic properties of MgB_2 are of quite a different kind. Earlier band-structure calculations of MgB_2 [by semi-empirical linear combination of atomic orbitals¹⁰ and first-principles full potential linear muffin-tin orbital¹¹ (FLMTO) methods] showed that the upper filled energy bands of MgB_2 are formed mainly due to strong B-B interactions (in honeycomb layers of boron atoms). Analogous conclusions were made recently by other authors,¹²⁻¹⁵ who pointed out that the coexistence of two-dimensional (2D) in-plane and 3D interlayer bands is a peculiar feature of MgB_2 . Based on an estimate of phonon frequencies and band-structure calculations, Kortus *et al.*¹² explain the superconductivity in MgB_2 as a result of strong electron-phonon coupling and An and Pickett¹⁵ attributed it to the behavior of $p_{x,y}$ -band holes in negatively charged boron planes. All authors¹²⁻¹⁵ emphasize the most significant role of metallic B states in the appearance of superconductivity.

To examine the possibility of superconductivity in related diborides, we studied the band structure of MgB_2 in comparison with that of CaB_2 , BeB_2 , AlB_2 , ScB_2 , and YB_2 , which are typical representatives of different groups of AlB_2 -like diborides formed by s , p , and d metals, respectively. This makes it possible to analyze effects in the following: (1) MgB_2 versus CaB_2 and BeB_2 , which are isoelectronic and the changes will be due to lattice parameters. (2) MgB_2 vs AlB_2 , for which the main differences are expected as a result of changes in the filling of bands with addition of an electron. (3) MgB_2 vs ScB_2 and YB_2 , where alongside changes in the filling of bands, the band structure and interatomic bonding will depend on the M sublattice (s or d metal). (4) AlB_2 and ScB_2 , YB_2 , which are also isoelectronic and isostructural, and changes will be due to the nature of the M sublattice (p or d metal).

In addition, using the supercell approach, we have carried out a theoretical search for possible superconductors among some MgB_2 -based ternary systems. For this purpose, we modeled the effect produced on the band structure of MgB_2

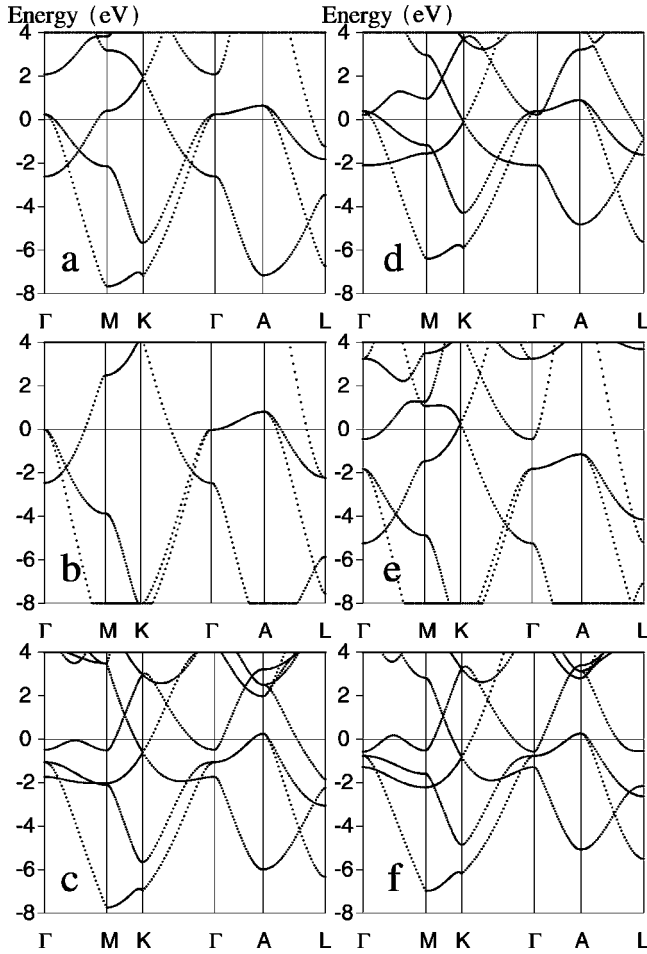


FIG. 1. Band structures of (a) MgB_2 , (b) BeB_2 , (c) ScB_2 , (d) CaB_2 , (e) AlB_2 , and (f) YB_2 .

by (1) boron sublattice doping (with Be, C, N, O), (2) magnesium sublattice doping (with Be, Ca, Li, Na, Cu, Zn), and (3) the presence of lattice vacancies in Mg and B sublattices.

The above diborides have a hexagonal crystal structure (AlB_2 -type, space group $P6/mmm$, $Z=1$)³ composed of layers of trigonal prisms of M atoms in the center of boron atoms, which form planar graphitelike networks. Their band structures were calculated by the FLMT0 method within the generalized gradient approximation for the exchange-correlation potential (FLMT0-GGA).¹⁶ Ternary and nonstoichiometric diborides were simulated with 12-atom supercells ($2 \times 2 \times 1$) and experimental lattice parameters for MB_2 ($M = \text{Be, Al, Sc, and Y}$) taken from Ref. 3. For the hypothetical phase of CaB_2 , the lattice constants ($a = 3.205 \text{ \AA}$, $c/a = 1.24$) were determined by the total energy minimization.

MgB_2 . The band structure is shown in Fig. 1. The high-energy part of the valence band (VB) of MgB_2 , made up predominantly of B $2p$ states, form two distinct sets of bands of the σ ($2p_{x,y}$) and π (p_z) types, whose k dependence differs considerably. For B $2p_{x,y}$ the most pronounced dispersion is observed along Γ -K. These bands are of the quasi-two-dimensional type, form a flat zone in the k_z direction (Γ -A), and reflect the distribution of pp_σ states in the B

TABLE I. Density of states at the Fermi level [$N(E_F)$, in states/(eV f.u.)] for MgB_2 and some related borides.

System	$N(E_F)$	System	$N(E_F)$
MgB_2	0.73	$\text{Mg}_{0.75}\text{Li}_{0.25}\text{B}_2$	0.73
CaB_2	0.92	$\text{Mg}_{0.5}\text{Li}_{0.5}\text{B}_2$	0.75
BeB_2	0.47	$\text{Mg}_{0.75}\text{Na}_{0.25}\text{B}_2$	0.73
$\text{MgB}_{1.75}\text{C}_{0.25}$	0.56	$\text{Mg}_{0.5}\text{Na}_{0.5}\text{B}_2$	0.76
$\text{MgB}_{1.75}$	0.61	$\text{Mg}_{0.75}\text{Cu}_{0.25}\text{B}_2$	0.89
$\text{Mg}_{0.75}\text{B}_2$	0.74	$\text{Mg}_{0.75}\text{Be}_{0.25}\text{B}_2$	0.62
$\text{Mg}_{0.75}\text{Ca}_{0.25}\text{B}_2$	0.69	$\text{Mg}_{0.75}\text{Zn}_{0.25}\text{B}_2$	0.51

layers. These states make a considerable contribution to $N(E_F)$, forming metallic properties of the diboride with E_F located in the region of bonding states; the conductivity is due to hole carriers.

The B $2p_z$ -like bands are responsible for weaker pp_π interactions. These 3D-like bands have maximum dispersion along (Γ -A); Mg s,p and B s states are admixed with B $2p$ bands near the bottom of the VB and in the conduction band. Thus, the peculiarities of the electronic properties of MgB_2 are associated with metallic $2p$ states of B atoms located in planar nets, which determine the DOS in the vicinity of E_F .

The valence charge density (VCD) maps (see Fig. 4 in Ref. 11) demonstrate that the interatomic bonds in the boron graphitelike layers are highly covalent, the Mg-Mg bonds have metallic character, and then there are the weak interlayer covalent Mg-B interactions. Estimates of interatomic bonds strengths (with FLMT0 calculations using empty Mg and B sublattices¹¹) also show the largest contribution to the cohesive energy from B-B interactions [B-B (68%), B-Mg (23%), and Mg-Mg (9%)]. In view of these results (see also Refs. 12–15), let us discuss the possibility of superconducting properties in related diborides.

MgB_2 versus CaB_2 . The electronic bands of these iso-electronic and isostructural compounds turned out to be similar on the whole, see Fig. 1. The differences are due to the increased lattice parameter, a , and interlayer (M -B) distances determined by M ionic radii [$r_c = 0.74$ (Mg) and 1.04 \AA (Ca)]. The main change is a downward shift of the p_z bands as compared to $p_{x,y}$ bands, so that the crossing point is located at E_F (Fig. 1) and $N(E_F)$ increases to the highest value of any material given in Table I. This may well indicate that a possibly higher T_c may be obtained if CaB_2 were stabilized. To this end, we also studied the lattice stability of the hypothetical CaB_2 by calculating the formation energy as a difference in the total energy with reference to the constituent elements in their stable modifications, viz. hcp calcium and rhombohedral boron ($\alpha\text{-B}_{12}$). It was found that the formation energy has a small, but negative value ($E_{\text{form}} = -0.12 \text{ eV/f.u.}$), which may be indicative of the possibility of real synthesis of CaB_2 . For comparison, E_{form} for MgB_2 was found to be -1.21 eV/f.u. It is known for stable diborides that c/a does not exceed ≈ 1.165 .³ For the equilibrium state of CaB_2 , we obtained $c/a = 1.24$. The most obvious way of decreasing the interlayer distance consists in the partial replacement of Ca by atoms with smaller radii. To

obtain superconductivity in such doped ternary systems, these metals should be either isoelectronic with Ca (for example, Mg, Be) or hole dopants (Li, Na, etc.)—as discussed below. They may also be prepared as layered superstructures, for example, . . . /Ca/B₂/Mg/B₂/

MgB₂ versus BeB₂. As expected, their band structures turned out to be similar, see Fig. 1. The differences are due to a downward shift of $p_{x,y}$ bands, so that they are absent above E_F at Γ . This brings about changes in the Fermi surface topology: cylinders along Γ -A are transformed into cones and this may lead to phonon hardening and suppression of T_C —as observed in recent experiments.¹⁷

MgB₂ versus AlB₂. For AlB₂ ($n_e=3.00$), the B $p_{x,y}$ bands are completely filled and AlB₂ is not a superconductor. A recent report¹⁸ on the electron-doped Mg_{1-y}Al_yB₂, demonstrates that T_C decreases smoothly and vanishes at $y=0.25$. According to our FLMTO estimates,¹¹ the interatomic bonding exhibits some changes: the contribution of Al-Al bonds to the cohesive energy increases by almost two times and the M-B bonds become covalent (see AlB₂ VCD maps in Fig. 4 of Ref. 11).

MgB₂ versus ScB₂ and YB₂. Quite a number of studies of the electronic properties of the diborides are known to date.^{19–24} We previously^{19,20} performed FLMTO calculations of all hexagonal diborides of 3d (Sc, Ti, . . . ,Fe), 4d (Y, Zr, . . . ,Ru), and 5d (La, Hf, . . . ,Os) metals and analyzed the variations in their chemical stability and some other properties (e.g., melting temperatures, enthalpies of formation). We found that the evolution of their band structures can be described within a rigid-band model (RBM). For $M=Ti, Zr, Hf$ E_F falls near the DOS minimum (pseudogap) between the fully occupied bonding bands and unoccupied antibonding bands.

In the RBM, MgB₂ and Sc, Y, La diborides all have partially unoccupied bonding bands. Comparison of their band structures shows that for ScB₂, the 2D- $2p_{x,y}$ bands are almost filled and the hole concentration is very small (near A in Fig. 1). The Sc d band along Γ -M is below E_F and the large contribution to $N(E_F)$ is due to Sc d states. The covalent M-B bonding increases considerably and the B $2p_z$ -like bands are shifted downwards at K. For both ScB₂ and YB₂, there is a small hole concentration of B $2p_{x,y}$ states at A that leads to changes of the Fermi surface and phonon properties near Γ . Thus, one can expect for these diborides only low-temperature superconductivity [for ScB₂ $T_C \sim 1.5$ K (Ref. 25)].

Modeling of new MgB₂-based ternary borides. In searching for possible superconductors among the MgB₂-based ternary systems, we simulated the effect produced on the band structure of MgB₂ by (i) doping the B sublattice with C, N, O impurities, (ii) doping the Mg sublattice with Be, Ca, Li, Na, Cu, Zn impurities, and (iii) vacancies in the Mg and B sublattices—all of which can be divided into three groups: electron dopants, hole dopants, and isoelectronic defects. The above-mentioned RBM is widely used to analyze such substitutions. Based on the density of states of MgB₂ (see Fig. 2 in Ref. 11), this model determines the following effects: hole doping should lead to partial ‘‘depopulation’’ of

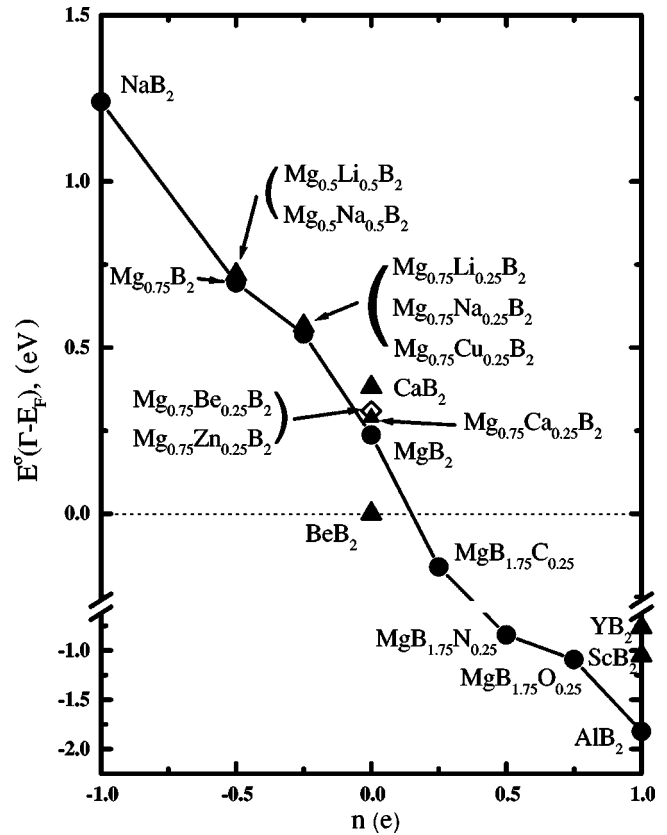


FIG. 2. The energy of the $\sigma(2p_{x,y})$ band at Γ relative to E_F [$E^\sigma(\Gamma - E_F)$] as a function of the hole- or electron-type doping (n_e —the difference of valence electron concentration relative to MgB₂).

bonding bands, a shift of E_F deep into the VB, and an increase in $N(E_F)$. A reverse effect, namely a Fermi level shift to the region of the DOS minimum (pseudogap between bonding and antibonding states), can be expected for electron doping. The role of isoelectronic dopants remains unclear within this model. One can only suppose that in this case the main effects will be associated with lattice deformations, i.e., with the changes in a and c/a .

By contrast, our FLMTO calculations for hypothetical ternary and nonstoichiometric borides demonstrate a more complicated picture (see Fig. 2 and Table I) and lead us to the following conclusions:

Boron sublattice doping. As n_e decreases (MgB₂ \rightarrow MgB_{1.75}), E_F is shifted to higher binding energies, but the value of $N(E_F)$ becomes smaller due to a partial breakdown of B-B bonds in the graphitelike B layers and changes in the energy band dispersion near E_F . For MgB_{1.75}C_{0.25}, all bonding B $p_{x,y}$ states are completely filled and E_F falls in the pseudogap, hence a decrease in $N(E_F)$. A further increase in n_e [MgB_{1.75}(N,O)_{0.25}] results in the occupation of $2p$ antibonding states. The dependence of the energy of $\sigma(2p_{x,y})$ bands at Γ relative to E_F [$E^\sigma(\Gamma - E_F)$] is shown in Fig. 2; it is seen that the superconductivity will disappear for electron doping by $0.17e$. Thus, we do not see any prospects for the enhancement of T_C in MgB₂-based ternary compounds by doping the B sublattice.

Magnesium sublattice doping. As n_e decreases in the series $\text{MgB}_2 \rightarrow \text{Mg}_{0.75}\text{Li}(\text{Na})_{0.25}\text{B}_2 \rightarrow \text{Mg}_{0.75}\text{B}_2$, $\text{Mg}_{0.5}\text{Li}(\text{Na})_{0.5}\text{B}_2$, E_F shifts to higher binding energies, but no increase in $N(E_F)$ is observed—as predicted within the RBM, see Table I. Only for 25% Cu substitution did we obtain an increase of $N(E_F)$ (cf. Table I) and there was the report²⁶—later withdrawn—that T_C increases up to 49 K with nominal 20% Cu doping of MgB_2 . Thus, we found that for Li and Na substitution, $N(E_F)$ is almost independent of the hole-dopant concentration. This fact is in agreement with the results of An and Pickett.¹⁵ The dependence $E^\sigma(\Gamma - E_F)$ as a function of n_e for both the hole and electron doping of MgB_2 is close to linear (Fig. 2). It is seen that hole doping in MgB_2 -based ternary systems retains the band-structure features of MgB_2 near the E_F —in contrast to the effect of electron doping for more than $0.17e$. Both $N(E_F)$ and $E^\sigma(\Gamma - E_F)$ in these systems are practically independent of the hole dopant, and $E^\sigma(\Gamma - E_F)$ is determined only by the hole concentration (see the results for $\text{Mg}_{0.75}\text{Li}_{0.25}\text{B}_2$ and $\text{Mg}_{0.75}\text{Na}_{0.25}\text{B}_2$ or for $\text{Mg}_{0.5}\text{Li}_{0.5}\text{B}_2$, $\text{Mg}_{0.5}\text{Na}_{0.5}\text{B}_2$, and $\text{Mg}_{0.75}\text{B}_2$ in Table I and Fig. 2). For the isoelectronic substitution $\text{MgB}_2 \rightarrow \text{Mg}_{0.75}\text{Be}(\text{Ca}, \text{Zn})_{0.25}\text{B}_2$, the value of $N(E_F)$ decreases and the $p_{x,y}$ bands move up 0.05–0.1 eV at Γ compared with MgB_2 , Fig. 2.

We believe that further searches for new MTSC should be made via hole doping of MgB_2 (or BeB_2 , CaB_2) or by

creating layer superstructures of the $\text{MgB}_2/\text{CaB}_2$ type. We are continuing these investigations taking into account the crystal lattice relaxation and calculating the substitution energies for impurities in ternary systems.

As regards higher superconducting transition temperatures, one should have a large electron-phonon coupling constant that depends on the large electronic characteristics, namely a large Hopfield parameter [the product of $N(E_F)$ and the averaged electron-ion matrix element squared] and averaged phonon frequency, $M\langle w^2 \rangle$. As no large changes in the electronic structure and $N(E_F)$ were found for hole-doped MgB_2 , one can suppose that the variation of T_C under hole doping would be determined by changes of the volume and phonon frequencies. A similar conclusion was obtained from the estimation of electron-phonon constants with applied pressure.²⁷ There we demonstrated that under pressure, the $N(E_F)$ decreases and the Hopfield constant increases; thus the main reason for the reduction of T_C under pressure according to the McMillan formula is the strong pressure dependence of phonon frequencies, which is sufficient to compensate for the electronic effects.

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