

## Electronic structure of superconducting $\text{MgB}_2$ 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)  $\text{MgB}_2$  and related diborides indicate that superconductivity in these compounds is related to the existence of  $p_{x,y}$ -band holes at the  $\Gamma$  point. Based on these calculations, we explain the absence of medium- $T_C$  superconductivity for  $\text{BeB}_2$ ,  $\text{AlB}_2$ ,  $\text{ScB}_2$ , and  $\text{YB}_2$ . The simulation of a number of  $\text{MgB}_2$ -based ternary systems using a supercell approach demonstrates that (i) the electron doping of  $\text{MgB}_2$  (i.e.,  $\text{MgB}_{2-y}X_y$  with  $X = \text{Be, C, N, O}$ ) and the creation of defects in the boron sublattice (nonstoichiometric  $\text{MgB}_{2-y}$ ) are not favorable for superconductivity, and (ii) a possible way of searching for similar or higher MTSC should be via hole doping of  $\text{MgB}_2$  ( $\text{CaB}_2$ ) or isoelectronic substitution of Mg (i.e.,  $\text{Mg}_{1-x}M_x\text{B}_2$  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 ( $\text{MgB}_2$ ) (Ref. 1) has attracted a great deal of interest in this system. The transition temperature for  $\text{MgB}_2$  ( $T_C \approx 39$  K) exceeds by almost two times the record values of  $T_C$  for conventional B1- and A15-type intermetallic superconductors (SC's).<sup>2</sup> As distinct from the high-temperature SC,  $\text{MgB}_2$  has an exclusively simple composition and crystal structure.<sup>3</sup> The finding of a new medium- $T_C$  SC (MTSC) raises a number of questions: (1) What is the nature of the superconductivity in  $\text{MgB}_2$ ? (2) Is  $\text{MgB}_2$  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  $\text{MgB}_2$  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 nitrides<sup>4</sup>)] has been carried out earlier.<sup>5,6</sup> For instance, it was shown that the superconducting transition temperature for TM diborides ( $M\text{B}_2$ ,  $M = \text{Ti, Zr, Hf, V, Ta, Cr, Mo}$ ) is below  $\sim 0.4$  K. Only  $\text{NbB}_2$  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 ( $\text{LnRuB}_2$ ,  $\text{LnRh}_4\text{B}_4$ ) and pseudoternary ( $\text{Ln}_{1-x}\text{Ln}'_x$ ) $\text{Rh}_4\text{B}_4$  borides is known.<sup>7</sup> In 1994, Cava *et al.*<sup>8</sup> 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 review<sup>9</sup>) 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  $\text{Ba}_{1g}$  mode) are determined by interatomic  $\sigma$  bonds in the  $\text{TMB}_4$  tetrahedra. For all the above-mentioned borides, the most important role in their superconductivity is played by  $d$ -electron atoms.

The electronic properties of  $\text{MgB}_2$  are of quite a different kind. Earlier band-structure calculations of  $\text{MgB}_2$  [by semi-empirical linear combination of atomic orbitals<sup>10</sup> and first-principles full potential linear muffin-tin orbital<sup>11</sup> (FLMTO) methods] showed that the upper filled energy bands of  $\text{MgB}_2$  are formed mainly due to strong B-B interactions (in honeycomb layers of boron atoms). Analogous conclusions were made recently by other authors,<sup>12-15</sup> who pointed out that the coexistence of two-dimensional (2D) in-plane and 3D interlayer bands is a peculiar feature of  $\text{MgB}_2$ . Based on an estimate of phonon frequencies and band-structure calculations, Kortus *et al.*<sup>12</sup> explain the superconductivity in  $\text{MgB}_2$  as a result of strong electron-phonon coupling and An and Pickett<sup>15</sup> attributed it to the behavior of  $p_{x,y}$ -band holes in negatively charged boron planes. All authors<sup>12-15</sup> 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  $\text{MgB}_2$  in comparison with that of  $\text{CaB}_2$ ,  $\text{BeB}_2$ ,  $\text{AlB}_2$ ,  $\text{ScB}_2$ , and  $\text{YB}_2$ , which are typical representatives of different groups of  $\text{AlB}_2$ -like diborides formed by  $s$ ,  $p$ , and  $d$  metals, respectively. This makes it possible to analyze effects in the following: (1)  $\text{MgB}_2$  versus  $\text{CaB}_2$  and  $\text{BeB}_2$ , which are isoelectronic and the changes will be due to lattice parameters. (2)  $\text{MgB}_2$  vs  $\text{AlB}_2$ , for which the main differences are expected as a result of changes in the filling of bands with addition of an electron. (3)  $\text{MgB}_2$  vs  $\text{ScB}_2$  and  $\text{YB}_2$ , 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)  $\text{AlB}_2$  and  $\text{ScB}_2$ ,  $\text{YB}_2$ , 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  $\text{MgB}_2$ -based ternary systems. For this purpose, we modeled the effect produced on the band structure of  $\text{MgB}_2$

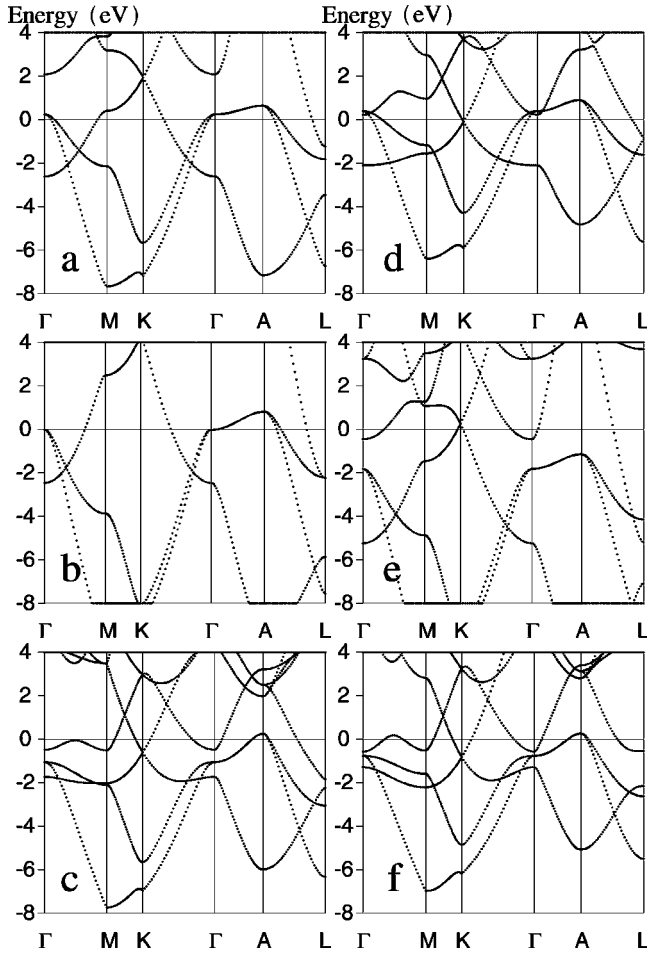


FIG. 1. Band structures of (a)  $\text{MgB}_2$ , (b)  $\text{BeB}_2$ , (c)  $\text{ScB}_2$ , (d)  $\text{CaB}_2$ , (e)  $\text{AlB}_2$ , and (f)  $\text{YB}_2$ .

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 ( $\text{AlB}_2$ -type, space group  $P6/mmm$ ,  $Z=1$ )<sup>3</sup> 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).<sup>16</sup> Ternary and nonstoichiometric diborides were simulated with 12-atom supercells ( $2 \times 2 \times 1$ ) and experimental lattice parameters for  $\text{MB}_2$  ( $M = \text{Be, Al, Sc, and Y}$ ) taken from Ref. 3. For the hypothetical phase of  $\text{CaB}_2$ , the lattice constants ( $a = 3.205 \text{ \AA}$ ,  $c/a = 1.24$ ) were determined by the total energy minimization.

$\text{MgB}_2$ . The band structure is shown in Fig. 1. The high-energy part of the valence band (VB) of  $\text{MgB}_2$ , made up predominantly of B  $2p$  states, form two distinct sets of bands of the  $\sigma$  ( $2p_{x,y}$ ) and  $\pi$  ( $p_z$ ) types, whose  $k$  dependence differs considerably. For B  $2p_{x,y}$  the most pronounced dispersion is observed along  $\Gamma$ -K. These bands are of the quasi-two-dimensional type, form a flat zone in the  $k_z$  direction ( $\Gamma$ -A), and reflect the distribution of  $pp_\sigma$  states in the B

TABLE I. Density of states at the Fermi level [ $N(E_F)$ , in states/(eV f.u.)] for  $\text{MgB}_2$  and some related borides.

System	$N(E_F)$	System	$N(E_F)$
$\text{MgB}_2$	0.73	$\text{Mg}_{0.75}\text{Li}_{0.25}\text{B}_2$	0.73
$\text{CaB}_2$	0.92	$\text{Mg}_{0.5}\text{Li}_{0.5}\text{B}_2$	0.75
$\text{BeB}_2$	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  $pp_\pi$  interactions. These 3D-like bands have maximum dispersion along ( $\Gamma$ -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  $\text{MgB}_2$  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 sublattices<sup>11</sup>) 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.

$\text{MgB}_2$  versus  $\text{CaB}_2$ . 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  $1.04 \text{ \AA}$  (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  $\text{CaB}_2$  were stabilized. To this end, we also studied the lattice stability of the hypothetical  $\text{CaB}_2$  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  $\text{CaB}_2$ . For comparison,  $E_{\text{form}}$  for  $\text{MgB}_2$  was found to be  $-1.21 \text{ eV/f.u.}$  It is known for stable diborides that  $c/a$  does not exceed  $\approx 1.165$ .<sup>3</sup> For the equilibrium state of  $\text{CaB}_2$ , 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/B<sub>2</sub>/Mg/B<sub>2</sub>/ . . . .

*MgB<sub>2</sub> versus BeB<sub>2</sub>.* 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  $\Gamma$ . This brings about changes in the Fermi surface topology: cylinders along  $\Gamma$ -A are transformed into cones and this may lead to phonon hardening and suppression of  $T_C$ —as observed in recent experiments.<sup>17</sup>

*MgB<sub>2</sub> versus AlB<sub>2</sub>.* For AlB<sub>2</sub> ( $n_e=3.00$ ), the B  $p_{x,y}$  bands are completely filled and AlB<sub>2</sub> is not a superconductor. A recent report<sup>18</sup> on the electron-doped Mg<sub>1-y</sub>Al<sub>y</sub>B<sub>2</sub>, demonstrates that  $T_C$  decreases smoothly and vanishes at  $y=0.25$ . According to our FLMTO estimates,<sup>11</sup> 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 AlB<sub>2</sub> VCD maps in Fig. 4 of Ref. 11).

*MgB<sub>2</sub> versus ScB<sub>2</sub> and YB<sub>2</sub>.* Quite a number of studies of the electronic properties of the diborides are known to date.<sup>19–24</sup> We previously<sup>19,20</sup> 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, MgB<sub>2</sub> and Sc, Y, La diborides all have partially unoccupied bonding bands. Comparison of their band structures shows that for ScB<sub>2</sub>, 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  $\Gamma$ -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 ScB<sub>2</sub> and YB<sub>2</sub>, 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  $\Gamma$ . Thus, one can expect for these diborides only low-temperature superconductivity [for ScB<sub>2</sub>  $T_C \sim 1.5$  K (Ref. 25)].

*Modeling of new MgB<sub>2</sub>-based ternary borides.* In searching for possible superconductors among the MgB<sub>2</sub>-based ternary systems, we simulated the effect produced on the band structure of MgB<sub>2</sub> 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 MgB<sub>2</sub> (see Fig. 2 in Ref. 11), this model determines the following effects: hole doping should lead to partial ‘‘depopulation’’ of

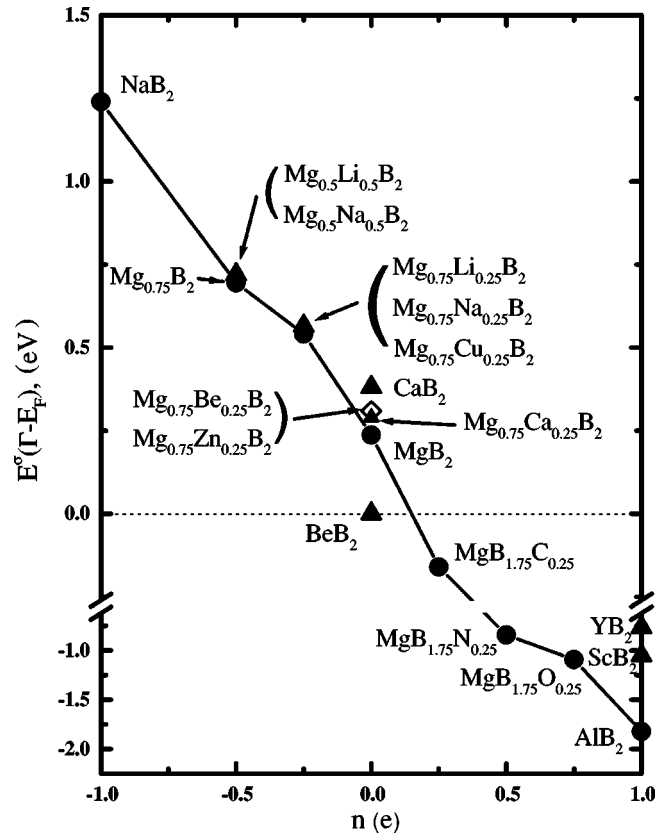


FIG. 2. The energy of the  $\sigma(2p_{x,y})$  band at  $\Gamma$  relative to  $E_F$  [ $E^\sigma(\Gamma - E_F)$ ] as a function of the hole- or electron-type doping ( $n_e$ —the difference of valence electron concentration relative to MgB<sub>2</sub>).

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 (MgB<sub>2</sub>  $\rightarrow$  MgB<sub>1.75</sub>),  $E_F$  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<sub>1.75</sub>C<sub>0.25</sub>, 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<sub>1.75</sub>(N,O)<sub>0.25</sub>] results in the occupation of  $2p$  antibonding states. The dependence of the energy of  $\sigma(2p_{x,y})$  bands at  $\Gamma$  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 MgB<sub>2</sub>-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 report<sup>26</sup>—later withdrawn—that  $T_C$  increases up to 49 K with nominal 20% Cu doping of  $\text{MgB}_2$ . 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.<sup>15</sup> The dependence  $E^\sigma(\Gamma - E_F)$  as a function of  $n_e$  for both the hole and electron doping of  $\text{MgB}_2$  is close to linear (Fig. 2). It is seen that hole doping in  $\text{MgB}_2$ -based ternary systems retains the band-structure features of  $\text{MgB}_2$  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  $\Gamma$  compared with  $\text{MgB}_2$ , Fig. 2.

We believe that further searches for new MTSC should be made via hole doping of  $\text{MgB}_2$  (or  $\text{BeB}_2$ ,  $\text{CaB}_2$ ) 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  $\text{MgB}_2$ , 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.<sup>27</sup> 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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