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## Electric field gradients in $s$ -, $p$ -, and $d$ -metal diborides and the effect of pressure on the band structure and $T_c$ in $\text{MgB}_2$

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Results of full-potential linear muffin-tin orbital generalized gradient approximation calculations of the band structure and boron electric field gradients (EFG's) for the new medium- $T_c$  superconductor  $\text{MgB}_2$  and related diborides  $MB_2$ ,  $M = \text{Be, Al, Sc, Ti, V, Cr, Mo, and Ta}$  are reported. The boron EFG variations are found to be related to specific features of their band structure and particularly to the  $M$ -B hybridization. The strong charge anisotropy at the B site in  $\text{MgB}_2$  is completely defined by the valence electrons—a property which sets  $\text{MgB}_2$  apart from other diborides. The boron EFG in  $\text{MgB}_2$  is weakly dependent on applied pressure: the B  $p$ -electron anisotropy increases with pressure, but it is partly compensated by the increase of core charge asymmetry. The concentration of holes in bonding  $\sigma$  bands is found to decrease slightly from 0.067 to 0.062 holes/B under a pressure of 10 GPa. Despite a small decrease of  $N(E_F)$ , the Hopfield parameter increases with pressure and we believe that the main reason for the reduction under pressure of the superconducting transition temperature  $T_c$  is the strong pressure dependence of phonon frequencies, which is sufficient to compensate for the electronic effects.

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Recently, Akimitsu and Nagamatsu *et al.*<sup>1</sup> reported the discovery of medium- $T_c$  superconductivity (MTSC) with  $T_c$  of about 39 K in magnesium diboride ( $\text{MgB}_2$ ) with a simple composition and crystal structure (AlB<sub>2</sub>-type, space group  $P6/mmm$ ,  $Z=1$ ). Band structure calculations showed<sup>2-7</sup> that the MTSC in  $\text{MgB}_2$  can be attributed to a strong electron-phonon coupling, a rather high density of states from two-dimensional (2D) (in-plane) metallic boron  $\sigma(p_{x,y})$  bands at  $E_F$  and the existence of  $p_{x,y}$ -band holes. By now, a number of studies have been performed with NMR,<sup>8-10</sup> which is a very powerful technique for investigating the properties of  $\text{MgB}_2$ . The measured quadrupole interaction is determined by the value of the electric field gradient (EFG), which is directly related to the charge distribution around the nucleus. Thus theoretical EFG studies are important in order to give a reliable interpretation of the experimental data based on the electronic structure.

The EFG at the boron site in  $\text{MgB}_2$  was found experimentally to be much larger than those for  $d$ -diborides (Table I). As seen from Table I, the variation in EFG for diborides covers two orders of magnitude and shows trends which cannot be explained by the crystal structure changes. For example, these EFG's in AlB<sub>2</sub> and TiB<sub>2</sub> differ by almost 3 times, but their lattice parameters  $a$  and  $c$  are approximately the same and, vice versa, equal EFG's were obtained in BeB<sub>2</sub> and  $\text{MgB}_2$ , for which the lattice parameters have the largest differences among diborides under consideration. No attempts were made previously to relate the EFG changes to the peculiarities of electronic structure.

In this paper, we present results of first-principles full-potential linear muffin-tin orbital generalized gradient approximation<sup>11</sup> (FLMTO-GGA) calculations (within the GGA for the exchange correlation potential) of the electronic

structure and EFG's at the boron site for  $\text{MgB}_2$  and other  $s$ -,  $p$ -,  $d$ -diborides. We compare the calculated EFG's with the experimental and other theoretical data and explain the EFG variation based on the anisotropy of boron  $2p$  occupancies. The pressure dependence of the EFG, which is very sensitive to the charge distribution, represents a good test for the anisotropy study. The experimental and theoretical data on the electronic and elastic behavior of  $\text{MgB}_2$  under pressure are contradictory: it was found to be nearly isotropic,<sup>12,13</sup> anisotropic,<sup>14</sup> or strong anisotropic.<sup>15,16</sup> We simulated the pressure effect on the band structure of  $\text{MgB}_2$  and estimated the changes in the EFG, boron  $p$ -occupancies, hole concen-

TABLE I. Theoretical and experimental boron EFG,  $V_{zz}$  (in  $10^{21}$  V/m<sup>2</sup>), for  $s$ -,  $p$ -, and  $d$ -diborides.

Diboride	$V_{zz}^{\text{el}}$	$V_{zz}^{\text{lat}}$	$V_{zz}$	$ V_{zz}^B ^{\text{a}}$	$ V_{zz}^B ^{\text{Expt.}}$
$\text{MgB}_2$	-1.94	0.06	-1.88		1.69 <sup>b</sup>
$\text{MgB}_2^{\text{e}}$	-2.00	0.10	-1.90		
BeB <sub>2</sub>	-2.43	0.33	-2.10		
AlB <sub>2</sub>	-1.17	0.18	-0.99		1.08 <sup>c</sup>
ScB <sub>2</sub>	-0.75	0.13	-0.60		
TiB <sub>2</sub>	-0.66	0.31	-0.35	0.38	0.37 <sup>d</sup>
VB <sub>2</sub>	-0.76	0.38	-0.38	0.39	0.43 <sup>d</sup>
CrB <sub>2</sub>	-1.01	0.42	-0.59	0.60	0.63 <sup>d</sup>
MoB <sub>2</sub>	-0.55	0.32	-0.23	0.22	0.23 <sup>d</sup>
TaB <sub>2</sub>	-0.21	0.25	0.04	<0.05	0.02 <sup>d</sup>

<sup>a</sup>Reference 28.

<sup>b</sup>Reference 8.

<sup>c</sup>Reference 29.

<sup>d</sup>Reference 30.

<sup>e</sup>Under pressure 10 GPa.

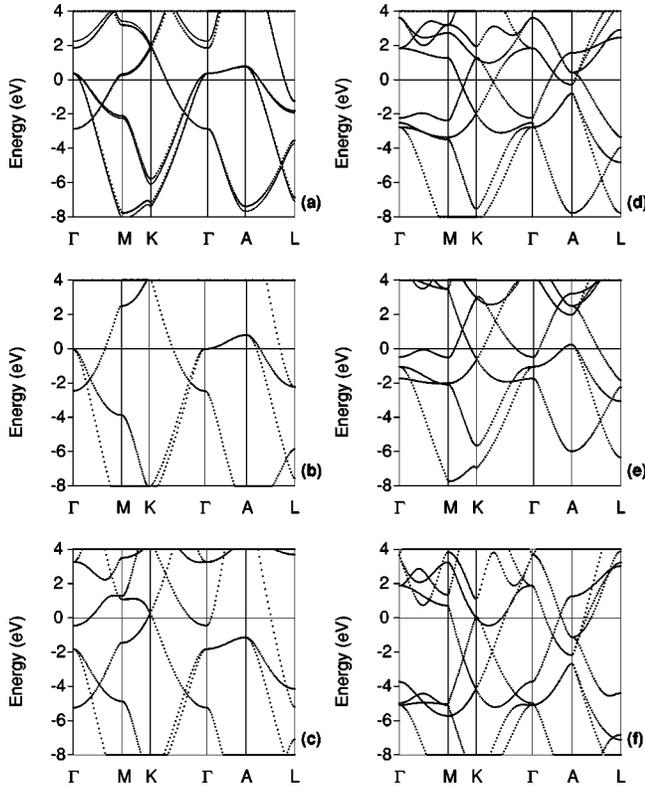


FIG. 1. Band structures of (a)  $\text{MgB}_2$  (dotted lines for zero pressure, solid lines for 10 GPa), (b)  $\text{BeB}_2$ , (c)  $\text{AlB}_2$ , (d)  $\text{TiB}_2$ , (e)  $\text{ScB}_2$ , and (f)  $\text{TaB}_2$ .

tration, and Hopfield parameter under pressure. These investigations are of interest, since the pressure dependence of the  $T_c$  is the key difference between the conventional BCS (Ref. 3) and hole<sup>17</sup> superconductivity mechanisms.

The band structures of  $\text{MgB}_2$  and some other diborides are shown in Fig. 1. There are two distinct sets of B  $2p$  bands:  $\sigma$  ( $2p_{x,y}$ ) and  $\pi$  ( $p_z$ ) types with considerably different dispersions. The B  $2p_{x,y}$  bands are quasi-2D along the  $\Gamma$ -A line in the Brillouin zone (BZ) and make a considerable contribution to the density of states at the Fermi level,  $N(E_F)$ , for  $\text{MgB}_2$ . Now it has been shown<sup>3-7</sup> that the existence of degenerate  $p_{x,y}$  states above  $E_F$  at the  $\Gamma$  point in the BZ is crucial for MTSC in diborides. The high  $T_c$  is explained by the strong coupling of these holes to the in-plane  $E_{2g}$  phonon modes.<sup>6,18</sup> The B  $2p_z$  bands are responsible for the weaker  $pp_\pi$  interactions and these 3D-like bands have maximum dispersion along  $\Gamma$ -A. The bonding and antibonding B  $p_z$  bands cross  $E_F$  at the K point, and their location and dispersion depend on the  $M$ -B hybridization. For  $\text{BeB}_2$  [Fig. 1(b)] and  $\text{AlB}_2$  [Fig. 1(c)], the  $p_{x,y}$  bands are, respectively, partly and completely filled, the Fermi surface topology changes, and medium- $T_c$  superconductivity is absent.<sup>19,20</sup> The  $p_z$  bands progressively move down in going from  $\text{BeB}_2$  to  $\text{MgB}_2$  and  $\text{AlB}_2$ , demonstrating the strengthening of  $M$ -B bonding.

The band structure and chemical bonding of all  $3d$ -,  $4d$ -, and  $5d$ -metal diborides were previously investigated in detail.<sup>21-24</sup> These studies showed that the cohesive properties of  $\text{AlB}_2$ -type diborides are explained in terms of the band

filling. The Fermi level for  $\text{TiB}_2$  ( $\text{ZrB}_2$  and  $\text{HfB}_2$ ) falls in the pseudogap where bonding states are occupied and antibonding states are empty [Fig. 1(d)]. The shift of  $E_F$  results in the partial emptying of the bonding states [ $\text{ScB}_2$ , Fig. 1(e)] or the occupation of antibonding states ( $\text{VB}_2$ ,  $\text{CrB}_2$ ,  $\text{MoB}_2$ ,  $\text{TaB}_2$ ). Both cases correspond to the lowering of the cohesive properties (melting temperature, enthalpies of formation, etc.). From first-principles estimates of  $M$ - $M$ ,  $M$ -B, and B-B bonding strengths, we found that the cohesive energy of  $d$ -diborides with filled bonding states decreases when the atomic number increases in the row due to the weakening of  $M$ -B hybridization and that the  $\text{AlB}_2$ -type diborides of the group-VII and -VIII elements are unstable.<sup>21-24</sup> Thus the main feature of the band structure of transition-metal (TM) diborides is the progressive filling of B  $p_{x,y}$ ,  $p_z$  bands and the dominant role of  $d$  states near  $E_F$ .

A systematic search for superconductivity in the  $d$ -diborides (with  $M = \text{Ti, Zr, Hf, V, Ta, Cr, Mo}$ ) showed that  $T_c$  is below  $\sim 0.4$  K.<sup>25</sup> Only  $\text{NbB}_2$  and  $\text{ScB}_2$  were found to be superconductors with a  $T_c$  of about 0.6 K (Ref. 25) and 1.5 K (Ref. 26), respectively. Recently, a relatively high critical temperature  $T_c \sim 9$  K was found in  $\text{TaB}_2$ .<sup>27</sup> As seen in Fig. 1(f), the bonding states in  $\text{TaB}_2$  are fully occupied, the Fermi level is shifted away from the pseudogap to the region of antibonding states, and Ta  $5d$  states define  $N(E_F)$  (0.9 states/eV). Among the  $3d$ -diborides, only in  $\text{ScB}_2$  are the  $2p_{x,y}$  bands not completely filled (there is a small hole concentration of these states at A), but they lie below  $E_F$  at  $\Gamma$  and the largest contribution to  $N(E_F)$  arises from Sc  $3d$  states. Based on the band structure results and calculations of the electron-phonon interaction,<sup>18</sup> one may conclude that superconductivity with medium  $T_c$  is unlikely in undoped diborides, except for  $\text{MgB}_2$ ; the absence of holes in the two-dimensional  $\sigma$  bands at  $\Gamma$  results in hardening of zone-phonon modes and weak electron-phonon coupling.

The electric field gradient tensor, defined as the second derivative of the electrostatic potential at the nucleus, was calculated directly from the FLMO charge density. The calculated principal components of the boron EFG tensor,  $V_{zz}^B$ , are shown together with other theoretical and experimental data in Table I. Note that the asymmetry parameter ( $|V_{xx}| - |V_{yy}|/|V_{zz}|$ ) is equal to 0 for the  $\text{AlB}_2$ -type structure.

The largest boron EFG's in  $\text{MgB}_2$  and  $\text{BeB}_2$  demonstrate the strongest asymmetry of the charge distribution as compared with other diborides (note that here and below we consider the absolute value of EFG's). For the  $3d$ -diborides, the EFG decreases from  $\text{ScB}_2$  to  $\text{TiB}_2$  and increases when going from  $\text{TiB}_2$  to  $\text{VB}_2$  and  $\text{CrB}_2$ . The boron EFG's for  $4d$  ( $\text{MoB}_2$ ) and  $5d$  ( $\text{TaB}_2$ ) diborides are much smaller than the EFG's for isoelectronic  $3d$ -diborides. Note that all calculated EFG's are in very good agreement with available experimental data and with full-potential linearized augmented plane-wave (FLAPW) theoretical results<sup>28</sup> (Table I).

To analyze the variation of the boron EFG's in diborides, we consider it as a sum of electron ( $V_{zz}^{\text{el}}$ ) and lattice (ion) ( $V_{zz}^{\text{lat}}$ ) contributions (Table I). For the  $s,p$ -diborides, the ion contribution is relatively small, and the boron EFG is mainly determined by the anisotropy of the valence electrons. For

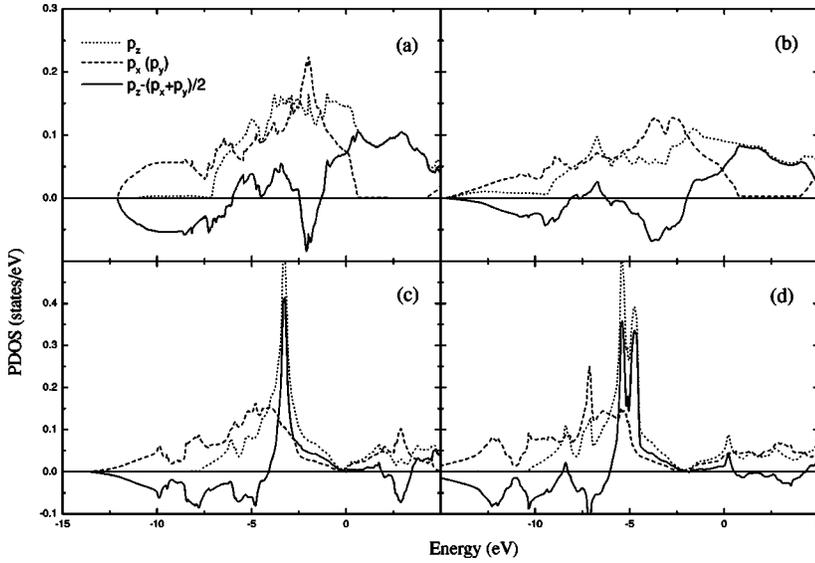


FIG. 2. Boron partial densities of  $p_{x,y}$  (dashed lines) and  $p_z$  (dotted lines) states (PDOS) and their anisotropy (solid lines) for (a)  $\text{MgB}_2$ , (b)  $\text{BeB}_2$ , (c)  $\text{TiB}_2$ , and (d)  $\text{TiB}_2$ . The Fermi level corresponds to the zero energy.

the  $d$ -diborides,  $V_{zz}^{\text{lat}}$  is larger and depends somewhat on the metal (except  $\text{ScB}_2$  where the lattice parameters are the largest). For  $\text{TaB}_2$ , the electron and ion contributions are almost equal: the EFG is positive and smallest among all diborides. The electronic contributions explain the boron EFG variation, although they overestimate the calculated and observed EFG's; clearly, the lattice contributions must be taken into account in order to obtain good agreement with experiment for  $d$ -diborides. Among the diborides, the lattice contribution is the smallest for  $\text{MgB}_2$  and the strong charge anisotropy in  $\text{MgB}_2$  is completely defined by the valence B  $p$  electrons—a property which sets  $\text{MgB}_2$  apart from other diborides.

A qualitative explanation of EFG behavior may be given based on the anisotropy of B  $2p$  partial occupancies,  $\Delta n_p = p_z - (p_x + p_y)/2$ , since  $V_{zz}^{\text{el}} \sim \langle 1/r^3 \rangle \Delta n_p$  and one may consider the boron  $p \langle 1/r^3 \rangle$  expectation value to be constant for all diborides discussed. Thus the variation of the electronic EFG's is determined by the interplay of  $p_z$  and  $p_x, p_y$  occupations. As seen from the partial density of states (PDOS) obtained by means of a Mulliken population analysis, the  $p_{x,y}$  orbitals are more occupied than are  $p_z$  orbitals (Fig. 2) and  $V_{zz}^{\text{el}}$  is negative for all diborides considered. For  $\text{MgB}_2$  and  $\text{BeB}_2$ , the high- $p_{x,y}$  peaks lying below  $-2$  eV lead to large negative  $\Delta n_p$  values and, therefore, to large boron EFG's. The small increase of  $p_z$  occupancy explains the EFG lowering for  $\text{MgB}_2$  (and  $\text{AlB}_2$ ) as compared to  $\text{BeB}_2$ . Thus the weaker  $M$ -B bonds for  $s$ - and  $p$ -diborides correspond to larger boron EFG's.

For  $d$ -diborides, the  $p_z$  PDOS is more localized due to strong covalent  $M 3d$ -B  $2p$  bonding and the high peak at 3–5 eV below  $E_F$  decreases  $\Delta n_p$  and  $V_{zz}^{\text{el}}$  compared with  $s$ - and  $p$ -diborides. Among the  $3d$ -diborides, the EFG is smallest for  $\text{TiB}_2$ , which has the strongest  $p$ - $d$  hybridization. Weaker  $p$ - $d$  hybridization (less intense  $p_z$  peak) for  $\text{ScB}_2$  and  $\text{CrB}_2$  results in a larger anisotropy  $\Delta n_p$ , and the boron EFG's are larger for these compounds than for  $\text{TiB}_2$ . Since  $4d$  and  $5d$  states are less localized than are  $3d$  states, the corresponding B  $p_z$  PDOS are broadened for  $\text{MoB}_2$  and especially for  $\text{TaB}_2$  (Fig. 2) (the strong hybridization of B  $2p$

and Ta  $5d$  states was shown also in Ref. 31), which leads to the small EFG's. While a Mulliken analysis is not an accurate approach for the calculation of orbital charges, especially for delocalized  $p$  orbitals, it still allows one to describe general trends in EFG's and to correlate them with peculiarities of the electronic structure. Thus we conclude that  $M$ -B  $p$  hybridization is the main factor controlling the boron EFG variation.

The effect of hydrostatic pressure on the EFG at the B site in  $\text{MgB}_2$  was investigated for 5 and 10 GPa with lattice parameters taken from the extrapolation formula<sup>16</sup>  $a = a_0(1 - 0.00187P)$  and  $c = c_0(1 - 0.00307P)$ . We found a very slow increase of EFG with pressure (Table I), which also demonstrates that the boron EFG's in diborides do not have a strong dependence on the interatomic distances. As the EFG is a very sensitive characteristic, no large changes are expected in the anisotropy of the B charge distribution under pressure.

As expected, the boron  $p$  bands widen under pressure [Fig. 1(a)]. One can see that the band shifts relative to  $E_F$  are different for different directions of the BZ; the main changes in the occupied  $p_{x,y}$  and  $p_z$  bands occur in the low-energy range at the  $M$ ,  $K$ , and  $A$  points. These bands move down with pressure relative to  $E_F$  along  $\Gamma$ - $M$ - $K$ - $\Gamma$  and  $A$ - $L$ , and the overall shift of the PDOS to lower energies leads to the loss of these states in the energy range from  $E_F$  to  $-2$  eV, as stated in Ref. 13. The decrease of  $p_{x,y}$  and  $p_z$  PDOS near  $E_F$  is partly compensated by its increase at lower energies, and as a result, the changes in the partial  $p$  occupations are small. We found the increase of  $p$  occupancies with pressure to be anisotropic—the larger growth of  $p_{x,y}$  occupancy compared to  $p_z$  giving an  $\Delta n_p$  increase by 0.02 of 10 GPa. An accurate calculation gives a smaller EFG than follows from  $\Delta n_p$ . As seen from Table I, the increase of B  $p$ -electron anisotropy is partly compensated by the increase of the core charge contribution, and as a result, the boron EFG in  $\text{MgB}_2$  is weakly dependent on applied pressure. Thus we conclude that the charge distribution at the B site shows more isotropic change under pressure than do the B  $p$  valence electrons due to the

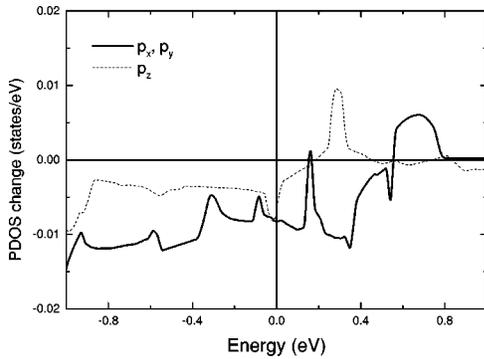


FIG. 3. The change in the boron  $p_{x,y}$  (solid lines) and  $p_z$  (dashed line) PDOS in  $\text{MgB}_2$  under a pressure of 10 GPa. The Fermi level corresponds to the zero energy.

compensating behavior of electron and core systems. NMR measurements under pressure would be important to confirm this conclusion.

The PDOS changes near  $E_F$  under a pressure of 10 GPa are shown in Fig. 3. The hole concentration in the bonding  $\sigma$  bands decreases by 0.005 (within an energy interval up to 0.8 eV). The changes in  $p_{x,y}$  PDOS are due to the behavior of these bands with pressure along  $\Gamma$ -A: the bands move down at  $\Gamma$  and up at A, resulting, respectively, in the loss of holes in the energy range up to 0.5 eV and their increase for higher energies. Although the hole  $p_z$  PDOS change is negative in

the energy interval up to 0.2 eV, its concentration is almost constant under pressure for energies up to 0.8 eV. The loss of both  $p_{x,y}$  and  $p_z$  states near  $E_F$  results in a small decrease of  $N(E_F)$  by 0.02 states/eV. Thus we showed that the carrier concentration decreases, and so the observed decrease of the resistance with pressure is likely to be connected with better coupling between the sintered grains, as suggested in Ref. 33.

Finally, we estimated the pressure dependence of the Hopfield parameter  $\eta$ , which is an electronic part of the electron-phonon coupling  $\lambda = \eta/M\langle\omega^2\rangle$ , where  $\eta = N(E_F)\langle I^2\rangle$ . The calculation of the averaged electron-ion matrix element squared  $\langle I^2\rangle$ , performed within the rigid muffin tin approximation,<sup>32</sup> gave a faster increase of  $\langle I^2\rangle$  with pressure than the  $N(E_F)$  decrease. As a result, despite a small decrease of  $N(E_F)$ ,  $(dN(E_F)/dP = -0.51\%/GPa)$ , the Hopfield parameter increases with pressure as  $d\eta/dP = +0.55\%/GPa$ . Hence the decrease of  $N(E_F)$  cannot be considered as the reason for the  $T_c$  reduction, which is known<sup>34</sup> to behave as  $dT_c/dP = -1.6\text{ K/GPa}$ . Thus, according to the McMillan formula, the main reason for the reduction of  $T_c$  under pressure is the strong pressure dependence of phonon frequencies, which is sufficient to compensate for the electronic effects.

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