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2001 J. Phys.: Condens. Matter 13 L723

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## LETTER TO THE EDITOR

# The bond ionicity of $MB_2$ ( $M = \text{Mg, Ti, V, Cr, Mn, Zr, Hf, Ta, Al and Y}$ )

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Received 25 April 2001, in final form 1 June 2001

Published 6 July 2001

Online at [stacks.iop.org/JPhysCM/13/L723](http://stacks.iop.org/JPhysCM/13/L723)

## Abstract

The bond ionicity in diborides  $MB_2$  ( $M = \text{Mg, Ti, V, Cr, Mn, Zr, Hf, Ta, Al and Y}$ ) has been studied by using the complex chemical bond theory based on a generalization of the Phillips–Van Vechten–Levine scheme. The ionicity of  $M$ – $B$  bonds decreases in the following order: Mg, Al, Mn, Y, Cr, Zr, Hf, Nb, Ta, V and Ti. The Mg– $B$  bond in  $MgB_2$  has the largest value of ionicity of 96.8% among these examined diborides. Our calculations support the recent results of band structure calculations that Mg atoms are fully ionized so that they can donate valence electrons to the system. The observed superconductivity loss in the solid solution  $Mg_{1-x}Al_xB_2$  with  $x > 0.1$  can be understood in terms of the ionicity and the number of valence electrons.

Superconductivity with a high transition temperature  $T_c \approx 39$  K has been recently discovered in magnesium diboride ( $MgB_2$ ) [1]. It has been proposed that this superconductivity results from a strong electron–phonon interaction and high phonon frequency due to the light masses of the constituent elements [2]. Measurement of the boron isotope effect was indeed observed with an isotope coefficient of  $\alpha \sim 0.25$  [3], suggesting that the superconductivity is BCS-like. The reported value of  $T_c$ , which is nearly double that of metals, seems to be either above or at the limit predicted theoretically for BCS [4]. Therefore, the electronic and crystal structure properties are expected to play a critical role in achieving superconductivity in  $MgB_2$ .

$MgB_2$  belongs to the  $AlB_2$  structural type. It crystallizes in a hexagonal cell with a space group  $P6/mmm$  (no 191). Each cell contains one Mg atom and two B atoms. The B atoms form honeycomb layers similar to the carbon layers in graphite: each boron atom is equidistant from three other boron atoms. The Mg atom layers are interleaved between them. Each Mg atom is coordinated by 12 B atoms. Electronic structure calculations [3] show that  $MgB_2$  is

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not only quite ionic between the Mg–B bond, but also has a strong covalent B–B bonding. Mg is fully ionized to donate its electrons to the system.

The  $AlB_2$  structure is a common type for some transition metals and most lanthanide diborides. Superconductivity has been searched for in these compounds [5, 6] but only  $NbB_2$  and  $(Zr,Mo)B_2$  were found to be superconductive, at 0.62 K and 11 K, respectively. By analysing the lattice strain and charge density in a series of diborides, Bianconi *et al* [7] have shown that the superconductivity in  $MgB_2$  appears nearly at a critical point in the two-variable (strain and charge density) phase diagram.

In this paper, we study the bonding properties of a series of diborides by using complex chemical bond theory [8, 9] based on a generalization of Phillips–Van Vechten–Levine (PVL) dielectric theory [10–12], which has been successfully applied to many fields such as alloy problems [13, 14], the effective lattice charge [15], bond charges [16, 17] and nonlinear optical susceptibilities [18–21]. According to PVL theory, the ionicity  $f_i$  associated with a bond that is terminated by two atoms is defined in terms of the homopolar energy gap  $E_\mu$  and the heteropolar energy gap  $C_\mu$  as

$$f_i = \frac{C_\mu^2}{E_\mu^2 + C_\mu^2}. \quad (1)$$

Accordingly, the bond covalency is given by  $f_c = 1 - f_i$ . The homopolar energy gap  $E_\mu$  may be evaluated only in terms of the bond length  $d_\mu$  as

$$E_\mu = 39.74d_\mu^{-2.48}. \quad (2)$$

The heteropolar energy gap is given as a function of the coordination number of the constituent atoms, the difference between the Coulomb potentials of the constituent atoms, as

$$C_\mu = 14.40b_\mu \exp(-k_s r_0) \left[ \left( \frac{Z_\alpha}{r_\alpha} - \frac{n}{m} \frac{Z_\beta}{r_\beta} \right) \right] \quad (3)$$

$$k_s = \left( \frac{4k_F}{\pi a_B} \right)^{1/2} \quad (4)$$

for a binary compound  $\alpha_m\beta_n$  with  $n > m$ , where  $Z_\alpha$ ,  $Z_\beta$  and  $r_\alpha$ ,  $r_\beta$  are the valence electrons and covalent radii for the atoms  $\alpha$  and  $\beta$ , respectively, the term  $\exp(-k_s r_0)$  is the Thomas–Fermi screening factor,  $a_B$  is the Bohr radius and  $k_F$  is the Fermi wavevector.  $b_\mu$  is empirically related to the average coordination numbers,  $\langle N_c \rangle$ , of the constituent atoms as

$$b_\mu = 0.089\langle N_c \rangle^2. \quad (5)$$

$\langle N_c \rangle$  is defined as

$$\langle N_c \rangle = \frac{m_i}{m_i + n_j} N_\alpha + \frac{n_j}{m_i + n_j} N_\beta \quad (6)$$

where  $N_\alpha$  and  $N_\beta$  are the coordination numbers for elements  $\alpha$  and  $\beta$ , respectively. For atoms having d electrons, the number of valence electrons  $Z_\mu$  should be replaced by an effective value  $Z_\mu^*$ , accounting for the difference in screening effects between d and sp electrons [21]. Usually this effective value  $Z_\mu^*$  is of comparable magnitude to the sum of the numbers of s, p and d valence electrons. Moreover, if atoms have unfilled d shells, further care should be taken since the transitions to these empty d levels will increase the susceptibility. In this case, the heteropolar energy gap calculated according to equation (3) should be modified by

$$(C_\mu^*)^2 = \frac{C_\mu^2 - \Gamma E_\mu^2}{1 + \Gamma}. \quad (7)$$

Here  $\Gamma$  is a coefficient accounting for the contribution of the unfilled d shell electrons, which is defined as

$$\Gamma = \frac{n_c}{n_v} \quad (8)$$

where  $n_c$  is the number of holes in the unfilled d shells and  $n_v$  is the number of total valence electrons of the constituent atoms.

Although  $MB_2$  are binary compounds, they consist of two kinds of bonds in each compound: covalent B–B bonds and metal–B bonds. It is necessary to decompose these multibond compounds into binary ones only with a single type of bonds. Based on chemical bond representations, Zhang and coworkers [8, 19, 20] succeeded in generalizing the PVL scheme for multibond systems. Using this generalized theory, any complex crystals can be decomposed into a sum of binary systems which include only one type of chemical bond. Suppose  $\alpha$  denotes cations and  $\beta$  anions, any multibond complex crystal can be written as

$$\alpha_{a1}^1 \alpha_{a2}^2 \dots \alpha_{ai}^i \dots \beta_{b1}^1 \beta_{b2}^2 \dots \beta_{bj}^j = \sum_{ij} \alpha_{m_i}^i \beta_{n_j}^j \quad (9)$$

$$m_i = N(\beta^j - \alpha^i) a_i / N_{c_{\alpha i}} \quad n_j = N(\alpha^i - \beta^j) b_j / N_{c_{\beta j}} \quad (10)$$

where  $N_{c_{\alpha}}$  and  $N_{c_{\beta}}$  are the nearest total coordination numbers of  $\alpha_i$  and  $\beta_j$  in the compounds.  $N(\beta^j - \alpha^i)$  is the nearest coordination fraction contributed by  $\alpha_i$  and  $N(\alpha^i - \beta^j)$  the nearest coordination fraction contributed by  $\beta_j$ . After decomposing the multibond compound into binary compounds with a single type of bond, the PVL scheme can be directly applied to the calculation of the chemical bond parameters.

**Table 1.** The ionicity (per cent) of M–B bonds and lattice parameters in  $MB_2$  (M = Mg, Ti, V, Cr, Mn, Zr, Hf, Nb, Ta, Al and Y).

Compound	$a$ (nm)	$c$ (nm)	$f_i$	Reference
MgB <sub>2</sub>	0.3083	0.3521	96.8	[24]
TiB <sub>2</sub>	0.3028	0.3228	22.8	[25]
VB <sub>2</sub>	0.2998	0.3057	32.3	[25]
CrB <sub>2</sub>	0.2969	0.3066	82.2	[26]
MnB <sub>2</sub>	0.3009	0.3036	91.7	[27]
ZrB <sub>2</sub>	0.3170	0.3533	81.9	[25]
HfB <sub>2</sub>	0.3142	0.3476	79.8	[28]
NbB <sub>2</sub>	0.3086	0.3306	52.1	[25]
TaB <sub>2</sub>	0.3088	0.3241	50.7	[25]
AlB <sub>2</sub>	0.3009	0.3262	91.8	[29]
YB <sub>2</sub>	0.3299	0.3836	91.0	[30]

According to the equations (9) and (10),  $MB_2$  can be decomposed as  $MB_2 = MB_{4/3} + \frac{1}{3}B_2$ . In calculation of the heteropolar energy gap  $C_{\mu}$ , Levine [12] suggested that the term

$$\left( \frac{Z_{\alpha}^*}{r_{\alpha}} - \frac{n}{m} \frac{Z_{\beta}^*}{r_{\beta}} \right)$$

in equation (3) should be replaced by

$$\left( \frac{Z_{\alpha}^*}{r_0} - \frac{n}{m} \frac{Z_{\beta}^*}{r_0} \right).$$

Here  $r_0 = d_{\mu}/2$ . On average, the replacement can slightly improve the calculated results. This modification, however, leads to the unreasonably low values of the calculated  $f_i$  for some

bonds, such as in NbB<sub>2</sub>, TiB<sub>2</sub>, and ZrB<sub>2</sub> and HfB<sub>2</sub>. Thus we still adopt equation (3) to calculate  $C_{\mu}$ . The number of effective valence electrons for the transition metals are adopted from [20]. The calculated ionicities for M–B bonds in MB<sub>2</sub> (M = Mg, Ti, V, Cr, Mn, Zr, Hf, Ta, Al and Y) along with the lattice parameters are listed in table 1. The ionicities of the all B–B bond are certainly equal to zero and not listed. From the table 1 we can see that the ionicity of M–B bonds decrease in the following order: Mg, Al, Mn, Y, Cr, Zr, Hf, Nb, Ta, V and Ti. The Mg–B bond has the highest value, 96.8%, of ionicity among all the diborides examined. This result is consistent with that of the band structure calculation [3]: the Mg atoms are fully ionized to donate their valences to the B–B layers. For the 3d transition metal diborides, the ionicities of M–B bond increase with the atomic number  $Z$  of metals from  $f_i = 22.8\%$  for Ti to  $f_i = 91.8\%$  for Mn. Similar trends are observed in group IVB and VB metal diborides with the atomic number except for Hf and Ta, which have nearly identical  $f_i$  values with Zr and Nb, respectively. The small values of  $f_i$  such as for Ti–B and V–B bonds means that metals are bonded to B in a more covalent manner. The electrons forming the covalent bonds tend to be localized in the region between the two atoms joined by the bond. Although they have four or five valence electrons, these electrons will spend more time inside the bonds than outside the bonds. The free carrier densities in these compounds are not expected to be high. In contrast, we note that the Al–B and Y–B bonds have high values of ionicities. Like Mg atoms, Al and Y can be thought to fully ionize in order to donate their valence electrons to the B layers. The free carrier density is expected to be higher than that in MgB<sub>2</sub> since they have three valence electrons each. In fact, YB<sub>2</sub> indeed exhibits a metallic conductivity between 5 K to room temperature with a resistivity as low as  $\sim 0.05$  m $\Omega$  cm [22]. A recent study [23] on the Mg<sub>1-x</sub>Al<sub>x</sub>B<sub>2</sub> solid solution series indicates that the substitution of Al for Mg causes a decrease in the superconducting transition temperature and leads to the loss of superconductivity after  $x > 0.1$ . These results agree well with our calculated ionicities for YB<sub>2</sub> and AlB<sub>2</sub>. It is predicted that the substitution of Mn for Mg in MgB<sub>2</sub> will decrease the  $T_c$  in a more rapid manner since the free carrier density in MnB<sub>2</sub> is expected to be higher than that of AlB<sub>2</sub>. The free carrier density in MgB<sub>2</sub> seems to be near optimum, resulting from the large ionicity value between Mg–B bond and the proper number of the valence electrons of Mg.

This work is financially supported by the State Key Project on Fundamental Research in China and the National Natural Science Foundation of China.

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