

ELECTRON TRANSFER AND BONDING IN THE INTERMETALLIC COMPOUNDS OF RARE EARTHS WITH THE AlB_2 -TYPE OR A CLOSELY RELATED STRUCTURE

III: THE THERMOCHEMISTRY AND STABILITY OF DIBORIDES OF p-, d- AND f-BLOCK ELEMENTS

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Summary

The electronic structure of the metal atom is decisive in determining the stability and the occurrence of a metal diboride. The observed heats of formation of metal diborides can be explained on the basis of energy contributions from electron populations in various energy levels.

1. Introduction

Previously [1, 2] we have applied Pauling's bond distance-bond order relation [3] in an investigation of the nature of the bonding in rare earth compounds with the AlB_2 structure. When correlated with thermochemical data [2, 4 - 8] information from bond orders reveals electron populations in various states.

According to studies [9] of the magnetic and electrical properties of sub-borides and monoborides each boron atom transfers 1.7 - 1.8 electrons to the metal. Our bonding model [2, 4] is based on the assumed use of the d_{xz} and d_{yz} orbitals of the metal as acceptor orbitals and predicts a maximum transfer of two electrons for each boron atom. Because of mixing or hybridization of the metal d_{xz} and d_{yz} orbitals with s and p orbitals, a maximum d-orbital character δ of $\frac{2}{6}$ is predicted. The equivalency of the hybrid orbitals [3, 10, 11] allows the prediction of a maximum electron population of $\frac{4}{6} \times 4 = 2.6667$ in the s and p orbitals. Since p elements (magnesium and aluminium) are known to form stable diborides the minimum number of transfer electrons per boron atom is 1.333. The average of the two extreme values agrees well with the results of Cadeville [9]. We can define the heat of formation of a metal diboride as the sum of the functions E_{sp} and E_d , where E_{sp} is the contribution of s and p states populated by 2.6667 electrons and E_d is the contribution of the d states. If the s and p states make one band, then the energy contribution by this band will be constant.

The contribution E_d of the d states will vary depending on the electron population. We have given previously [4] the equations for the heats of formation ΔH_f of transition metal diborides.

$$-\Delta H_f = 17.6 + 2.015\Delta\epsilon \quad (1)$$

for d^1 and d^2 systems and

$$-\Delta H_f = 9 + 4.5\Delta\epsilon \quad (2)$$

when the metal atom has more than two electrons in the d orbitals and ΔH_f is expressed in kilocalories per mole. The contributions of s and p states are respectively 17.6 and 9 kcal mol⁻¹ in eqns. (1) and (2), while $\Delta\epsilon$ gives the electron population in the metal d states ($E_d = 2.015\Delta\epsilon$ or $E_d = 4.5\Delta\epsilon$).

Since boron, which has a normal valence of three, forms three bonds with three boron neighbours in hexagonal nets in the AlB_2 structure and the minimum transfer of electrons to the metal is 1.333, it is expected that 1.6667 electrons will remain on the boron for three B—B bonds. If therefore n_{B-B} is the bond order of a B—B bond and $3n_{B-B}$ is less than 1.6667, $\Delta\epsilon = 2(1.6667 - 3n_{B-B})$ transfer electrons will populate bonding d states and will increase the heat of formation by $2.015\Delta\epsilon$ or will populate states of higher energy (when there are no more metallic states of lower energy) thereby decreasing the value of ΔH_f by $2.015\Delta\epsilon$ (eqn. (1)). Assuming the value 1.6667 to be the maximum number of electrons in the bonding states of boron, if $3n_{B-B}$ exceeds 1.6667 the excess electrons will be accommodated in the antibonding states. This situation is realizable in the borides of transition elements with a large number of d electrons (d^5 manganese onwards). The heat of formation is then reduced by an amount $4.5\Delta\epsilon = 9(3n_{B-B} - 1.6667)$ (eqn. (2)).

In a previous treatment [4] we have derived $\Delta\epsilon$ in a different way. If $n_{O_1}, n_{O_2}, n_{O_3}, \dots$ are the bond orders when the atoms are considered in their normal Pauling's valences [3], if electron transfer changes those bond orders to n_1, n_2, n_3, \dots and if there are z_1, z_2, z_3, \dots bonds of each type, then

$$\Delta\epsilon = z_1(n_{O_1} - n_1) + z_2(n_{O_2} - n_2) + z_3(n_{O_3} - n_3) + \dots \quad (3)$$

The bond orders are determined according to Pauling's logarithmic equation [3]:

$$d_n = d_1 - 0.6 \log n \quad (4)$$

where d_n is the observed interatomic distance, d_1 is the sum of the single-bond radii and n is the bond order.

2. The variation of the bond order n_{B-B} with valence of boron

The disadvantage of using eqn. (3) to determine $\Delta\epsilon$ lies in the fact that the single-bond radii used in eqn. (4) to derive n may not strictly be constant in all bonding situations. In metals the single-bond radii can vary depending

on the modification, since one modification can be denser than another. Thus, in binary alloys with one common element, more accurate data can be obtained by operating with the single-bond radius of a common element and deriving the single-bond radii of the other elements indirectly from the interatomic distances. The bond orders n_{B-B} and valences of boron are plotted in Fig. 1. The data are taken from previous work [4]. Two straight lines are obtained; one is applicable to diborides where the metal has one or two d electrons and the other is applicable where the metal has more than two electrons in the d orbitals. We can use Fig. 1 to derive the single-bond radii and valences which are consistent with the observed distances.

If we choose the valence V'_B of boron the corresponding n_{B-B} will permit derivation of the single-bond radius $r_B(1)$ of boron using the observed B—B distance according to eqn. (4). The valence of the metal will increase from V_M to $V'_M = 2(3 - V'_B) + V_M$. Since each boron forms six bonds with the metal, the bond order n_{M-B} is $\frac{1}{6}(V'_B - 3n_{B-B})$. The metal forms eight M—M bonds and hence $n_{M-M} = \frac{1}{8}\{V'_M - 2(V'_B - 3n_{B-B})\}$. The choice of V'_B is acceptable if the single-bond radius $r_M(1)$ of the metal obtained from n_{M-B} , the single-bond radius $r_B(1)$ of boron and the experimental M—B distance according to eqn. (4) are also consistent with the observed M—M distance and with the calculated value of n_{M-M} .

3. The heats of formation of AlB_2 and UB_2

In previous work [2, 4] we have not included the compounds of p-block and 5f-block metallic elements. We can therefore test the results of the refinement of our theoretical working procedure on diborides of these types of elements. Although experimental heats of formation of diborides of

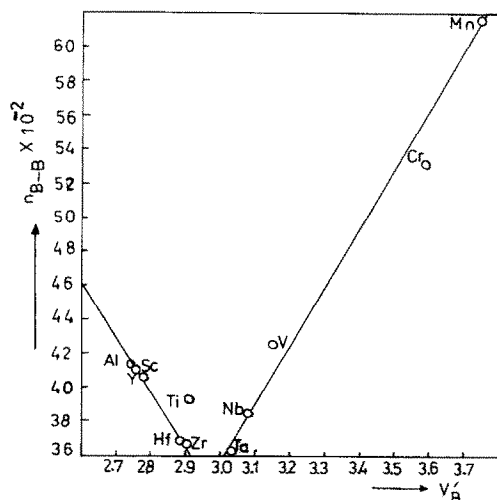


Fig. 1. The valences V'_B and the bond orders n_{B-B} of boron in metal diborides.

p-block and f-block elements are not readily available, we have obtained data for AlB_2 and UB_2 . A heat of formation of 16 kcal mol^{-1} has been reported by Damalski and Armstrong [12] for AlB_2 ; the lattice constants $a = 3.009 \text{ \AA}$ and $c = 3.262 \text{ \AA}$ have been reported by Spear [13]. The radius r_B of boron assuming B-B contacts is $a/2\sqrt{3} = 0.86862 \text{ \AA}$ and the shortest M-B distance $d_{\text{M-B}}$ is $(a^2/3 + c^2/4)^{1/2} = 2.38289 \text{ \AA}$. The M-M distance assuming M-M contacts is $c/2 = 1.631 \text{ \AA}$. The valence V'_B of boron of 2.747 gives $n_{\text{B-B}} = 0.414$ (Fig. 1) and the single-bond radius $r_B(1)$ is 0.753723 \AA according to eqn. (4). A bond order $n_{\text{M-B}}$ of 0.25083 is obtained leading to a single-bond radius $r_M(1)$ for aluminium of 1.2688 \AA . The valence V'_M of aluminium is 3.506 and $n_{\text{M-M}} = 0.062$ leading to $c/2 = 1.631 \text{ \AA}$. Since aluminium has no d orbitals in the valence shell we have $-\Delta\epsilon = 2(3n_{\text{B-B}} - 1.6667) = 0.849$ giving $-\Delta H_f = 15.9 \text{ kcal mol}^{-1}$ according to eqn. (1).

The diboride of uranium is interesting because it offers an opportunity for testing the influence of f bonding. Uranium has the electronic configuration $5f^3 6d 7s^2$. Although the d orbital lies energetically 7020 cm^{-1} (approximately 20 kcal) lower than the f orbital [14], it has empty f orbitals and f bonding cannot be ignored. Indeed f bonding occurs in lanthanum metal where the energy difference between the d and f states is approximately twice as large as that in uranium. We will assume therefore participation of f orbitals in the bonding. The effect will reduce the electron concentration in the s and p states. The lattice constants of UB_2 are $a = 3.1314 \text{ \AA}$, $c = 3.9857 \text{ \AA}$, $r_B = 0.903957 \text{ \AA}$ and $d_{\text{M-B}} = 2.690726 \text{ \AA}$. The valences are $V'_B = 2.782$ and $V'_M = 3.436$, and the single-bond radii are $r_B(1) = 0.785225 \text{ \AA}$ and $r_M(1) = 1.55714 \text{ \AA}$. The bond orders are $n_{\text{B-B}} = 0.402$, $n_{\text{M-B}} = 0.262667$ and $n_{\text{M-M}} = 0.0355$. We obtain from $n_{\text{B-B}} = 0.402$, $-\Delta\epsilon = 0.921$. If we consider these electrons to be non-bonding, the electron concentration in the s,p band is reduced to $2.6667 - 0.921 = 1.746$. Hence the heat of formation of UB_2 is $(1.746/2.6667) \times 17.6 \text{ kcal mol}^{-1} = 11.5 \text{ kcal mol}^{-1}$. An experimental value of 12 kcal mol^{-1} has been reported [15].

4. Discussion and conclusions

The tendency to f bonding among diborides of lanthanides and actinides will be largest in compounds of the light 4f and 5f elements which possess empty f orbitals [16]. Therefore increasing difficulties can be expected in attempts to prepare diborides of the light rare earths. This explains the unsuccessful attempts [15, 17, 18] to prepare the diborides of the light rare earths. Structural data, valences, bond orders and single-bond radii for some rare earth diborides are summarized in Table 1.

If for samarium diboride the same procedure is employed as that used for UB_2 , a heat of formation $-\Delta H_f$ of $11.6 \text{ kcal mol}^{-1}$ is obtained. Again if we ignore f bonding in the diborides of rare earth elements which have no empty f orbitals, heats of formation $-\Delta H_f$ of 19.5 and $19.4 \text{ kcal mol}^{-1}$ are predicted for GdB_2 and LuB_2 respectively.

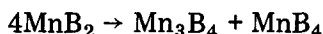
TABLE 1
Interatomic distances, single-bond radii and bond orders of some diborides MB₂

Element <i>M</i>	Lattice constants of MB ₂		Valences		Single-bond radii		Bond orders		Interatomic distances <i>M-B</i> (Å)
	<i>a</i> (Å)	<i>c</i> (Å)	<i>V</i> ' _M	<i>V</i> ' _B	<i>r</i> _M (1) (Å)	<i>r</i> _B (1) (Å)	<i>n</i> _{B-B}	<i>n</i> _{M-B}	
Sm	3.310	4.019	3.446	2.777	1.5854	0.83746	0.4041	0.26078	0.03958 2.773
Gd	3.315	3.936	3.418	2.791	1.5075	0.83744	0.3996	0.26537	0.02920 2.6906
Lu	3.246	3.704	3.474	2.763	1.4600	0.82024	0.4080	0.2565	0.04950 2.6348
U	3.1314	3.9857	3.436	2.782	1.5571	0.7852	0.4020	0.2627	0.0355 2.6907
Al	3.009	3.262	3.506	2.747	1.2688	0.7537	0.414	0.2508	0.0620 2.3829

Data are given for the diborides of the f elements samarium, gadolinium, lutetium and uranium, and of the s,p element aluminium.

Increased *f* bonding in diborides of light rare earths would cause considerable weakening of the B—B bonds, *i.e.* $1.6667 - 3n_{\text{B-B}}$ would be large. At the same time the large transfer of electrons to the metal would not necessarily give strong M—B bonds since a number $\Delta\epsilon$ of electrons would be non-bonding. Detailed treatments of *f* bonding in rare earths have been given elsewhere [16, 19].

In the diborides of the transition metals increasing the number of *d* electrons destabilizes the compound since $\Delta\epsilon$ transfer electrons have to be accommodated in the antibonding states. For example the tendency of MnB_2 to decompose:



has been reported [20] and no stable diborides are known for the case when the transition metal has more than five electrons in the valence shell.

Thermochemical data of the metal diborides, including revised heats of formation of the transition metal diborides, are summarized in Table 2.

TABLE 2

Heats of formation of metal diborides including predicted values for some rare earth metal diborides

MB_2	Bond order ^a $n_{\text{B-B}}$	$-\Delta H_f$ (kcal mol ⁻¹)		
		Experimental values ^b	Calculated values ^c	Calculated values ^d
ScB ₂	0.4103	—	19.3	20
YB ₂	0.4063	—	19.4	20
TiB ₂	0.3929	22.0	19.6	17
ZrB ₂	0.3673	—	19.9	—
HfB ₂	0.3684	26	19.6	20
VB ₂	0.4261	—	12.5	—
NbB ₂	0.3849	14	13.6	15
TaB ₂	0.3627	14	14.2	14
CrB ₂	0.5322	9	9.6	8
MnB ₂	0.6172	6	7.3	10
AlB ₂	0.4140	16	15.9	—
SmB ₂	0.4041	—	11.6	—
GdB ₂	0.3966	—	19.5	—
LuB ₂	0.4080	—	19.4	—
UB ₂	0.4020	12	11.6	15

^aThe bond orders for compounds of *d*-block transition elements which were used to reproduce Fig. 1 are taken from ref. 4.

^bExperimental data taken from refs. 12 and 21.

^cValues calculated in this work.

^dValues calculated using the method of Miedema [21].

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