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## A Study on Relation Between Band Gap and Orbital Electronegativities of *sp*-Bonded Compounds

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An empirical relation between band gap and orbital electronegativities, which are based on Zunger's orbital radii, is determined by a simplified bond orbital model. Bonding parameter for each A-B bond among 35 elements can be constructed using the empirical relation. The bonding parameter can predict compound formation between *sp*-bonding atoms with about 90 % accuracy. The error of the judgement using the bonding parameter is within about 20 kJ/g-atom of heat of formation for most of the unpredictable compounds.

**Keywords:** Band gap, Orbital electronegativity, Compound formation, Orbital model.

### INTRODUCTION

Various atomic parameters for predicting compound formation and crystal structure of the compound have been reported using quantum-mechanical calculations and empirical approaches [1-5]. Pauling's electronegativity is one of the famous parameters to estimate ionicity (or covalency) of compounds [6]. However, the parameter has been constructed on the basis of compound formation. On the other hand, dielectric electronegativity based on band gap concept is more useful to predict coordination number and several basic crystal structures [7]. Further, we inevitably encounter the empirical rule of Miedema and Gerkema [8] when we have some interest in compound formation between metals or metal and semiconductive material.

There are other current approaches on compound, particularly on classification of crystal structure, from 1970's. The current works by Simon and Bloch succeeded in classification of various fundamental crystal structures using quantum defect radii [9]. Zunger improved the quantum defect radii and constructed orbital radii for 70 elements using first principle pseudo-potential method [10]. On the other hand, Pettifor redefined the electronegativity for all elements and succeeded to classify crystal structure for vast number of compounds [11].

Taking into consideration these current studies on various compounds, we try to propose a simple and versatile parameter (we call it bonding parameter between two atoms) to predict compound formation from technological stand-point. In this paper, we focus our attention on *sp*-bonded compounds including both highly ionic and metallic ones. Firstly, we seek an empirical relation between observed band gap and bonding

parameter and the bonding parameter is constructed using the redefined orbital electronegativities derived from Zunger's orbital radii and simplified model based on bond orbital model by Harrison and Ciraci [12,13]. Subsequently, we examine the possibility of the formation of *sp*-bonded  $A_nB_m$  binary compound using the bonding parameter.

### EXPERIMENTAL

**Construction method of bonding parameter:** Several investigators have indicated the relation between band gap and electronegativity [14]. It has also been reported in semiconductor that bond energy is related with band gap [15]. Therefore, it is readily expected that there exists some correlation between band gap and electronegativity. Firstly, we examine the relation between Pauling's electronegativity and the observed band gap [16]. When we take  $(\Delta X/n_{av})^{1/2}$  as the parameter (where  $\Delta X$  and  $n_{av}$  are the electronegativity difference and average principal quantum number, respectively), we can obtain good linearity for band gap data. However, it should be noted that there are some exceptional compounds such as GaN and post-transition metal halides. Based on the relation between Pauling's electronegativity and the observed band gap, we attempt to construct a more precise parameter using the simplified bond orbital model in the next step.

According to bond orbital model, band gap is basically formed by bonding and antibonding levels of  $sp^3$  hybrid orbitals. In simple cases, we can calculate band gap energy analytically [13]. For example, the band gap for the point at the center of the Brillouin zone,  $k = 0$ , is analytically expressed as follows:

$$E_g(\Gamma) = -\{(\epsilon_p^c - \epsilon_s^c) + (\epsilon_p^a - \epsilon_s^a)\}/2 + \{(\epsilon_s^c - \epsilon_s^a)^2/4 + (4E_{ss})^2\}^{1/2} + \{(\epsilon_p^c - \epsilon_p^a)^2/4 + (4E_{xx})^2\}^{1/2} \quad (1)$$

where,  $\epsilon_p^c$ ,  $\epsilon_p^a$ ,  $\epsilon_s^c$  and  $\epsilon_s^a$  are the electronic energies of  $s$ - and  $p$ -electrons of cationic and anionic atoms, respectively and  $E_{ss} = V_{ss\sigma}$ ,  $E_{xx} = V_{pp\sigma}/3 + 2V_{pp\pi}/3$ . Further,  $V_{ss\sigma}$ ,  $V_{pp\sigma}$  and  $V_{pp\pi}$  are the off-diagonal matrix elements for  $ss\sigma$ ,  $pp\sigma$  and  $pp\pi$  bondings, respectively [17]. The first term of  $E_g(\Gamma)$  corresponds to band reduction due to  $s$ - $p$  hybridization. Although band gap depends on the wave vector, in most compounds with simple crystal structures, the value of band gap shows minimum in  $X$  and/or  $\Gamma$  points. In this paper, for simplicity, it is assumed that second and third terms in the eqn. 1 can be expressed by the function of electronegativity and principal quantum number.

Subsequently, we redefine orbital electronegativities of  $s$ -,  $p$ - and  $d$ -electrons for each element as  $(Z/r_i)^{1/2}$  [where  $r_i$  ( $i$ :  $s$ ,  $p$  or  $d$ ) and  $Z$  are Zunger's orbital radii and valence, respectively]. On account of limited space, we list up the orbital electronegativities of only second and third elements as shown in Table-1. Based on the relation between Pauling's electronegativity and the observed band gap, we assume the following linear relation between orbital electronegativities and the observed band gap in  $sp$ -bonded compounds:

$$E_g = \kappa(H_{sp}-S) + \lambda \quad (2)$$

where,  $\kappa$  and  $\lambda$  are constants and we call  $H_{sp}$  and  $S$  as  $sp$  hybrid function and band reduction term, respectively.  $H_{sp}$  can be defined as

$$H_{sp} = (\alpha_s/n_{av})^{1/2} + (\alpha_p/n_{av})^{1/2} \quad (3)$$

in the analogous way to the relation between Pauling's electronegativity and the observed band gap, where,  $\alpha_s = |(Z/r_s)_A|^{1/2} - (Z/r_s)_B|^{1/2}$  and  $\alpha_p = |(Z/r_p)_A|^{1/2} - (Z/r_p)_B|^{1/2}$ . Subsequently, we consider that  $S$  can be given by the energy difference between outermost  $s$ - and  $p$ -electrons in the same atom. In some cases, we also assume that  $S$  is influenced by the existence of  $d$ -electron in inner shell because of  $s$ - $d$  interaction. Conclusively,  $S$  is expressed as following:

$$S(sp) = \{(S_{sp}^A + S_{sp}^B)/n_{av}\}^{1/2} \quad (4)$$

$$\text{or} \quad S(sd) = \{(S_{sd}^A + S_{sd}^B)/n_{av}\}^{1/2} \quad (4')$$

where,  $S_{sp}^i = |(Z/r_s)^{1/2} - (Z/r_p)^{1/2}|$  and  $S_{sd}^i = |(Z/r_s)^{1/2} - (Z/r_d)^{1/2}|$  ( $i$ : A or B).  $S(sd)$  form is used when influenced by  $d$ -electron (in B atom in this case). Finally, we call  $(H_{sp}-S)$  as bonding parameter ( $\psi(sp)$ ) because stabilization of A-B bonding is determined by  $\psi(sp)$ . As shown in the next section, we can obtain a linear correlation between  $\psi(sp)$  and the observed band gap empirically.

## RESULTS AND DISCUSSION

First of all, the correlation between the observed band gap and  $\psi(sp)$  for 64 compounds is shown in Fig. 1 [16]. Several compounds such as BP, BN, BaO and some alkali-arsenides or -antimonides (shown by solid circles) somewhat deviate from linear correlation. However, high linearity in Fig. 1 supports that band gap of compound can be estimated by the bonding parameter constructed on orbital electronegativities.

Using eqns. 3, 4 or 4', we can easily calculate all bonding parameters of A-B bond among 35  $sp$ -elements and then band gap can be estimated by substituting a calculated bonding

TABLE-1  
ORBITAL ELECTRONEGATIVITIES OF  
SECOND AND THIRD  $sp$ -ELEMENTS

	$(Z/r_s)^{1/2}$	$(Z/r_p)^{1/2}$	$(Z/r_d)^{1/2}$
Na	0.95	0.80	—
Mg	1.49	1.33	—
Al	1.98	1.82	—
Si	2.43	2.32	—
P	2.89	2.80	—
S	3.33	3.27	—
Cl	3.74	3.70	—
K	0.81	0.68	1.64
Ca	1.23	1.09	2.43
Ga	1.99	1.79	4.20
Ge	2.34	2.18	5.00
As	2.73	2.59	5.68
Se	3.12	2.99	6.33
Br	3.47	3.36	7.00

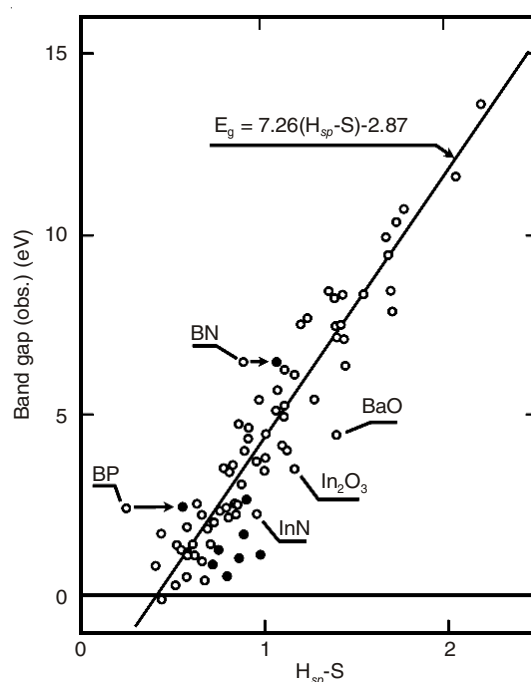


Fig. 1. Correlation between  $(H_{sp}-S)$  [or  $\psi(sp)$ ] and the observed band gap

parameter into the empirical equation in Fig. 1. Using the value of band gap, we can judge whether or not A-B bonding, that is,  $A_nB_m$  compounds is formed. The critical point for the compound formation corresponds to  $E_g = 0$ . When we use the value of  $\psi$  instead of  $E_g$ , the critical value corresponds to about 0.40.

Thus, stabilities of all A-B bonds (595 combinations) among 35  $sp$ -elements can be judged by the bonding parameter. These results are shown in Table-2. We can obtain the information on compound formation of 502 combinations among 595 A-B combinations [18]. The number of misjudging combination is 69 among 502 A-B combinations and we obtain the agreement of about 86 % to experimental data. There are 53 A-B combinations in which bonding parameter predicts no formation of compound but the formation of compound is experimentally certified. Among these combinations, heat of formation has been unknown in more than half of these compounds. Further, most of the compounds for remnant combinations show heats of formation less than 20 kJ/g-atom except boron

TABLE-2  
TYPICAL RESULTS ON COMPOUND FORMATION BETWEEN *sp*-ELEMENTS PREDICTED  
BY BONDING PARAMETER AND COMPARISON WITH EXPERIMENTAL DATA

	Li	Be	B	C	N	O	F	Na	Mg	Al	Si	P	S	Cl
K	No	KBe <sub>2</sub>	No data	C <sub>4</sub> K <sup>•</sup>	K <sub>3</sub> N <sup>#</sup>	K <sub>2</sub> O <sup>#</sup>	KF	Na <sub>2</sub> K	No	No	KSi <sup>#</sup>	K <sub>3</sub> P	K <sub>2</sub> S	KCl
Ca	CaLi <sub>2</sub>	Be <sub>13</sub> Ca	CaB <sub>6</sub>	CaO <sub>2</sub>	Ca <sub>3</sub> N <sub>2</sub>	CaO	CaF <sub>2</sub>	No	Mg <sub>2</sub> Ca	Al <sub>2</sub> Ca <sup>#</sup>	Ca <sub>2</sub> Si <sup>#</sup>	Ca <sub>3</sub> P <sub>2</sub>	CaS	CaCl <sub>2</sub>
Ga	Ga <sub>2</sub> Li <sup>#</sup>	No	GaB <sub>12</sub> ?	No data	GaN	Ga <sub>2</sub> O <sub>3</sub>	GaF <sub>3</sub>	NaGa <sub>3</sub> <sup>#</sup>	MgGa <sup>#</sup>	No	No	GaP	GaS <sub>3</sub> <sup>#</sup>	GaCl <sub>3</sub>
Ge	Li <sub>4</sub> Ge <sup>#</sup>	No	No	No	Ge <sub>3</sub> N <sub>4</sub>	GeO <sub>2</sub> <sup>#</sup>	GeF <sub>2</sub> <sup>#</sup>	NaGe <sup>#</sup>	Mg <sub>2</sub> Ge	No	No	GeP	GeS <sub>2</sub> <sup>#</sup>	GeCl <sub>2</sub> <sup>#</sup>
As	Li <sub>3</sub> As	Yes?	BASe <sup>#</sup>	AsC <sub>3</sub>	AsN	As <sub>2</sub> O <sub>3</sub> <sup>#</sup>	AsF <sub>3</sub>	Na <sub>3</sub> As	MgAs <sub>2</sub>	AlAs	SiAs <sup>#</sup>	AsP	As <sub>2</sub> S <sub>3</sub> <sup>#</sup>	AsCl <sub>3</sub> <sup>#</sup>
Se	LiSe	BeSe	B <sub>2</sub> Se <sub>3</sub>	CSe <sub>2</sub>	(SeN) <sub>x</sub>	SeO <sub>2</sub> <sup>#</sup>	SeF <sub>4</sub> <sup>#</sup>	Na <sub>2</sub> Se <sup>#</sup>	MgSe	Al <sub>2</sub> Se <sub>3</sub>	SiSe <sub>2</sub> <sup>#</sup>	P <sub>2</sub> Se <sub>3</sub> <sup>#</sup>	γ	SeCl <sub>4</sub> <sup>#</sup>
Br	LiBr	BeBr <sub>2</sub>	BBr <sub>3</sub>	CBR <sub>4</sub>	No data	Br <sub>2</sub> O	BrF <sub>3</sub> <sup>#</sup>	NaBr	MgBr <sub>2</sub>	AlBr <sub>3</sub>	SiBr <sub>4</sub> <sup>#</sup>	PBr <sub>6</sub> <sup>#</sup>	S <sub>2</sub> Br <sub>2</sub>	BrCl
Rb	No	No	No data	C <sub>6</sub> Rb <sup>#</sup>	RbN <sup>#</sup>	Rb <sub>2</sub> O	RbF	No	No	No	RbSi <sup>#</sup>	No data	Rb <sub>2</sub> S	RbCl
Se	Li <sub>2</sub> Sr <sub>3</sub>	Be <sub>12</sub> Sr	SrB <sub>6</sub>	SrC <sub>2</sub>	Sr <sub>3</sub> N <sub>2</sub> <sup>#</sup>	SrO	SrF <sub>2</sub>	No	Mg <sub>2</sub> Sr <sup>#</sup>	Al <sub>2</sub> Sr <sup>#</sup>	SrSi <sub>2</sub> <sup>#</sup>	No data	SrS	SrCl <sub>2</sub>
In	InLi	No	No	No data	InN	In <sub>2</sub> O <sub>3</sub>	InF <sub>3</sub>	InNa <sup>#</sup>	β <sup>#</sup>	No	No	InP	In <sub>2</sub> S <sub>3</sub> <sup>#</sup>	InCl <sub>2</sub> <sup>#</sup>
Sn	Li <sub>2</sub> Sn	No	No	?	Sn <sub>3</sub> N <sub>4</sub>	SnO <sub>2</sub> <sup>#</sup>	SnF <sub>2</sub> <sup>#</sup>	Na <sub>4</sub> Sn <sup>#</sup>	Mg <sub>2</sub> Sn	No	No	Sn <sub>4</sub> P <sub>3</sub> <sup>#</sup>	SnS <sub>2</sub> <sup>#</sup>	SnCl <sub>2</sub> <sup>#</sup>
Sb	Li <sub>3</sub> Sb	Be <sub>3</sub> Sb <sub>2</sub>	No	No	SbN	Sb <sub>2</sub> O <sub>3</sub>	SbF <sub>3</sub> <sup>#</sup>	Na <sub>3</sub> Sb <sup>#</sup>	MgSb <sub>2</sub>	AlSb	No	No	Sb <sub>3</sub> S <sub>3</sub> <sup>#</sup>	SbCl <sub>3</sub> <sup>#</sup>
Te	Li <sub>2</sub> Te	BeTe	No data	No data	Te <sub>3</sub> N <sub>4</sub>	TeO <sub>2</sub> <sup>#</sup>	TeF <sub>4</sub> <sup>#</sup>	Na <sub>2</sub> Te <sup>#</sup>	MgTe	Al <sub>2</sub> Te <sub>3</sub>	Si <sub>2</sub> Te <sub>3</sub>	?	No	TeCl <sub>2</sub> <sup>#</sup>
I	LiI	BeI <sub>2</sub>	BI <sub>3</sub>	No data	NI <sub>3</sub>	I <sub>2</sub> O <sub>5</sub> <sup>#</sup>	No data	NaI	MgI <sub>2</sub>	AlI <sub>3</sub>	SiI <sub>4</sub>	PI <sub>3</sub> <sup>#</sup>	No data	ICl <sup>#</sup>

: no formation of compound (predicted)

No : no formation of compound (experimental)

# : there exist another compound with different composition

? : these compounds are not in solid state in STP

and thallium compounds. Therefore, it is expected that the accuracy of judging compound formation by the bonding parameter is about 20 kJ/g-atom at most. If the error of 20 kJ/g-atom is permitted, we can obtain the agreement of about 90 %.

In the present study, bond orbital model is roughly applied to compound formation between *sp*-bonded-atoms, so that the substantial exactness of this model may decrease by the simplified formalism. Further, it is somewhat questionable to apply bonding parameter (or approximation of *sp*<sup>3</sup> hybridization) to the compound formation between atoms with only *s*-electrons. Taking into consideration such ambiguities, it is concluded that the bonding parameter constructed on orbital electronegativities and simplified bond orbital model shows good agreement with experimental results.

## Conclusion

Relation between orbital electronegativities and the observed band gap is empirically determined by simplified bond orbital model. Based on the relation, bonding parameters for 595 A-B combinations between 35 *sp*-elements can be constructed for predicting compound formation. Further, using the bonding parameter, the formation of binary compound between *sp*-elements can be judged with an accuracy of about 86 %. Most of the unpredictable compounds show small heats of formation less than 20 kJ/g-atom except several compounds. If the error of about 20 kJ/g-atom is permitted, the agreement to experimental results reaches to about 90 %. In the present paper, formalism between band gap and orbital electronegativities has been performed empirically, so that it is expected that the formula given in this paper may not always satisfy the optimum condition for the relation between band gap and orbital electronegativities. Further, there must be some

questionable points in the simplification of bond orbital model. If we can obtain a more elaborate relation between band gap and orbital electronegativities and some additional parameter, a more precise formula will be obtained for predicting compound formation.

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