Bond character and structural classification of inorganic carbon compounds based on the band parameters

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Abstract

Bond character and structural classification of typical inorganic compounds between carbon and other elements (M) were examined by using the two band parameters (hybrid function (H) and gap reduction parameter (S)), which were constructed by the pseudopotential radii of Zunger through modelling based on the bond orbital model. Respective bond character between carbon and other elements can be estimated by the ionicity (F_i) defined by the formula $F_i = H^2/(H^2+4S^2)$. Knowledge of the two band parameters enables us to construct a structural map for typical inorganic carbon compounds and it can be seen from the structural map that the crystalline forms of typical carbon compounds change from intercalation structures related to graphite, through CaC_2 type structures with an acetyl ion and stoichiometric carbide, to interstitially-ordered carbides, with decreasing ionicity of the M–C bond. The structural map also suggests that inorganic carbon compounds are not formed, except for compounds with an intercalation structure related to graphite, in the domain satisfying the condition of $(f_{inv}H)^2+(2f_{inv}S)^2 \leq (1.6)^2$, where f_{inv} is the compositional factor. Further, it was clarified that the possibility of formation of endohedral fullerene is scarcely influenced by d and/or f electrons and that the possibility is controlled only by the ionicity of the sp-bonds between carbon and the other element. © 1997 Elsevier Science S.A.

Keywords: Bond character; Band parameters; Carbon compound; Structural classification; Fullerene; Ionicity

1. Introduction

Up to the present time, it has been reported that there exist many functional and engineering carbon compounds. For example, carbon nitride has potential as a harder material than diamond [1,2]. Fullerene is also one of the most interesting materials among various carbon compounds [3,4]. Further, some transition metal carbides, such as TiC and HfC have been available for various materials with specific functions such as hard coating [5], thermoelectric and optoelectric usages [6]. In the present study, an attempt has been made to interpret bond character and structural classification of carbon compounds by use of two band parameters [7,8], based on modelling of the localized electron theory [9]. A structural map for carbon compounds was also constructed by selecting these two band parameters as the structural coordinates. Lastly, it was determined whether any element could be introduced into the fullerene cage from the standpoint of the ionicity based on two band parameters.

2. Two band parameters

The two band parameters used in this study are constructed by use of the pseudopotential radii (values exactly at the crossing points of the pseudopotentials) of Zunger [10], based on the concept of the bond orbital model. These parameters basically correspond to the ionic and covalent band gaps proposed by Phillips [11]. The details of the two band parameters are described elsewhere [7,8]. The band parameters are called the hybrid function (H) and gap reduction parameter (S), which are defined by the valence and the pseudopotential radius for each valence electron. For sp-bonded compounds, these parameters are given by the following equations;

$$H = (\alpha_s/n_{av})^{1/2} + (\alpha_p/n_{av})^{1/2}, \tag{1}$$

$$S_{sp} = ([S_{sp}(A) + S_{sp}(B)]/n_{av})^{1/2}, \tag{2}$$

where $\alpha_s = |(Z/r_s)_A^{1/2} - (Z/r_s)_B^{1/2}|$ and $\alpha_p = |(Z/r_p)_A^{1/2} - (Z/r_p)_B^{1/2}|$, and r_s, r_p and Z are Zunger's pseudopotential radii and valence for each constituent atoms, respectively. Further, n_{av} is the average principal quantum number for A

and B atoms and $S_{sp}(M) = |(Z/r_s)_M^{1/2} - (Z/r_p)_M^{1/2}|$ (M; A or B).

When a contribution of d electrons to sp bonding is required for an M–C bond, the effect is approximated by expressing the gap reduction parameter as follows;

$$S_{spd} = ([S_{sp}(A) + S_{sd}(B)]/n_{av})^{1/2}. \tag{3}$$

In Eq. (3), $S_{sd}(B)$ is defined for the case when the B atom provides some contribution of d electrons. In addition to the two band parameters, another parameter which is called the compositional factor (f_{inv}) is required for the construction of the structural map. The compositional factor is defined by the formula; $f_{inv} = 4N_A N_B x_A x_B / (N_A x_B + N_B x_A)^2$, where N_A and N_B are the numbers of valence electrons of A and B atoms, and x_A and x_B are the molar contents of A and B atoms, respectively. Details of the compositional factor are described elsewhere [7]. Ionicity, which is an important parameter in the description of the character of the chemical bond, can also expressed by the two band parameters using the following equation [7,12];

$$F_i = (f_{inv}H)^2 / [(f_{inv}H)^2 + 4(f_{inv}S)^2]$$
$$= H^2 / [H^2 + 4S^2] \tag{4}$$

Therefore, the bond character and structural classification of carbon compounds are examined by H and S without considering the compositional factor.

3. Structural map for inorganic carbon compounds

Numerical values of H and S for sp bonding can be easily determined because the pseudopotential radii for s and p electrons of 70 elements are given by Zunger [10]. Because of the pseudopotential radii of lanthanide elements, except for La, the numerical values of H and S for lanthanide compounds are calculated by the pseudopotential radii of s, p and d electrons for lanthanide elements, which were determined by linear interpolation using these pseudopotential radii of La and Hf [13]. Further, we need the numerical ratio of d or f electron contributions to sp bonding in order to calculate the numerical values of H and S for transition metal– and lanthanide–carbon compounds. In the present study, the contribution of d and/or f electrons is approximated by the sd hybridization effect (including the f electron effect in the case of lanthanide compounds) and the numerical ratios of sd hybridization, which were determined from the relation between the pseudopotential radius and the interatomic distance [13], are used as the contribution of d or f electrons to sp bonding. Furthermore, for simplicity, the contribution of d or f electrons was considered only for the gap reduction parameter. The gap reduction parameters (S_{av}) including sd hybridization effect are estimated by the following equation;

$$S_{av} = S_{sd}R_{sd}/2 + S_{sp}(1 - R_{sd}/2) \tag{5}$$

where R_{sd} is the ratio of the sd hybridization determined by the relation between interatomic distance and pseudopotential radius in the elemental substances [13]. In the equation, the factor of 1/2 is taken into account for merely estimating the gap reduction parameter of the M–C bond by the average S value (S_{av}) of the AB type carbon compound.

When H_{sp} and S_{av} are chosen as the structural coordinates, we obtain a structural map for various inorganic carbon compounds, as shown in Fig. 1. Because carbon compounds of alkaline-earth and lanthanide elements show the CaC_2-type structure [14], the compounds with the CaC_2-type structure are also plotted in this map, although the CaC_2-type compounds are not purely inorganic on account of the existence of an acetylene-type bond. In this map, inorganic carbon compounds can be distinguished by finding out whether a carbon-rich, stoichiometeric or metal-rich compound is formed for the respective elements, except for actinide and inert elements. The assignments of the compound formation of respective elements are given in Tables 1 and 2. Data on the compound formation of carbon with other elements are quoted from Refs. [15] and [16]. It was found that various stable carbon compounds are placed in the domains outside the circular arc boundary with its center at the origin and with a radius of about 1.6 (that is, $(f_{inv}H_{sp})^2 + (2f_{inv}S_{av})^2 = (1.6)^2$). On
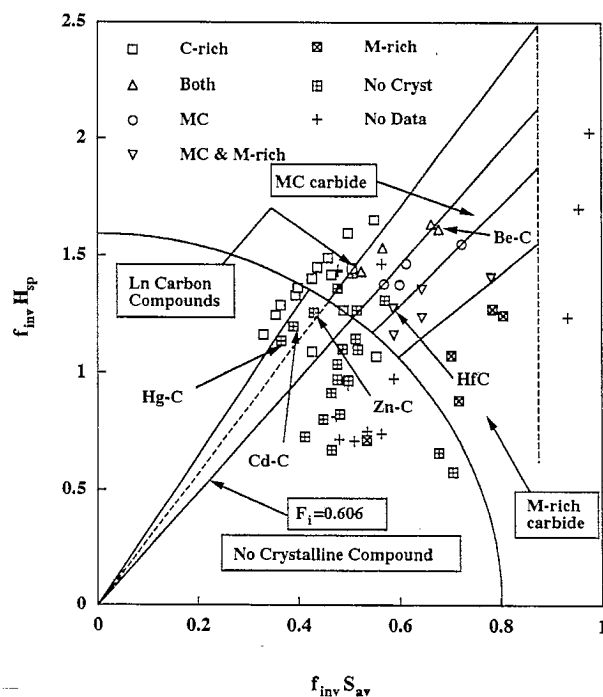

Fig. 1. Structural map of typical inorganic compounds of carbon with other elements by taking the band parameters (H_{sp} and S_{av}) as the structural coordinates, combined with the compositional factor (f_{inv}). The details of the band parameters and composition factor are explained in the text.

Table 1
Inorganic compounds of carbon with various sp-bonded and transition-metal elements and the classification of these compound types

Element	Compounds	Type	Element	Compounds	Type
Li	LiC, LiC_n ($n = 6, 12$ etc)	C-rich	Sc	Sc_2C, $Sc_{15}C_{19}$, Sc_4C_3	Both
Be	Be_2C, $BeC_2(m)$	Both		$Sc_{13}C_{10}$	
B	B_4C	M-rich	Ti	TiC	MC
C	–	–	V	VC, V_6C_5, V_2C, V_8C_7	MC and M-rich
N	No data	No		V_4C_{3-x}	
O	No data	No	Cr	$Cr_{23}C_6$, Cr_3C_2, Cr_7C_3	M-rich
F	No data	No	Mn	Mn_3C, Mn_7C_3, Mn_5C_2,	M-rich
Na	NaC, NaC_{24}, NaC_{64}	C-rich		$Mn_{23}C_6$	
Mg	Mg_2C_3, MgC_2	C-rich	Fe	Fe_4C, Fe_3C, Fe_5C_2, Fe_2C,	M-rich
Al	Al_4C_3	M-rich		Fe_7C_3	
Si	SiC	MC	Co	$Co_2(m)$, $Co_3C(m)$	No comp
P	No data	No	Ni	$Ni_3C(m)$	No comp
S	No data	No	Cu	$Cu_2C_2(m)$, $CuC_2(m)$	No comp
Cl	No data	No	Zn	No compound	No comp
K	KC_n ($n = 4, 8, 16$ etc)	C-rich	Y	YC_2, Y_2C, $Y_2C_3(m)$	Both
Ca	CaC_2	C-rich	Zr	ZrC	MC
Ga	No data	No	Nb	Nb_2C, Nb_6C_5, NbC	MC and M-rich
Ge	No compound	No comp	Mo	MoC_{1-x}, Mo_2C	MC and M-rich
As	AsC_3	C-rich	Tc	No compound	No comp
Se	Se_2C	M-rich	Ru	No compound	No comp
Br	No data	No	Rh	No compound	No comp
Rb	RbC_n ($n = 8, 16$ etc)	C-rich	Pd	No compound	No comp
Sr	SrC_2	C-rich	Ag	$Ag_2C_2(m)$	No comp
In	No compound	No comp	Cd	No compound	No comp
Sn	No compound	No comp	La	LaC_2, La_2C_3	C-rich
Sb	No compound	No comp	Hf	HfC	MC
Te	No data	No	Ta	TaC, Ta_2C	MC and M-rich
I	No data	No	W	WC, W_2C	MC and M-rich
Cs	CsC_n	C-rich	Re	$Re_2C(m)$	No comp
Ba	BaC_n	C-rich	Os	No compound	No comp
Tl	No compound	No comp	Ir	No compound	No comp
Pb	PbC_2	C-rich	Pt	No compound	No comp
Bi	No compound	No comp	Au	$Au_2C_2(m)$	No comp
Po	No compound	No comp	Hg	No compound	No comp
At	No data	No			

Remarks: C-rich, M-rich and MC mean carbon-rich, metal-rich and stoichiometric carbon compounds, respectively. No comp means no formation of inorganic carbon compound and the case of forming metastable compound is also included in this notation.

Table 2
Inorganic compounds of carbon with lanthanide elements and the classification of these compound types

Element	Compounds	Type
La	LaC_2, La_2C_3	C-rich
Ce	CeC_2, Ce_2C_3	C-rich
Pr	PrC_2, Pr_2C_3	C-rich
Nd	NdC_2, Nd_2C_3	C-rich
Pm	No data	No
Sm	SmC_2, Sm_2C_3, Sm_3C	Both
Eu	EuC_6, EuC_2, Eu_2C_3, Eu_3C	Both
Gd	GdC_2, Gd_2C_3, Gd_2C, Gd_3C	Both
Tb	No data	No
Dy	DyC_2, Dy_2C_3, Dy_2C, Dy_3C	Both
Ho	HoC_2, Ho_2C_3, Ho_2C, Ho_3C	Both
Er	ErC_2, $Er_2C_3(m)$, $Er_{15}C_{19}$, Er_3C	Both
Tm	No data	No
Yb	YbC_6, YbC_2, Yb_2C_3, $Yb_{15}C_{19}$, Yb_4C_5, Yb_2C	Both
Lu	LuC_2, Lu_2C_3, $Lu_{15}C_{19}$, Lu_3C	Both

the other hand, no stable inorganic compound of carbon is placed in the domain within the circular arc boundary, except for some carbon compounds of the alkali elements, arsenic and selenium. Further, it is indicated that the crystalline form of a carbon compound depends on the ratio of H_{sp} to S_{av} and the form changes from carbon-rich type through stoichiometric MC type to metal-rich type according as the ratio of H_{sp} to S_{av} decreases, in other words, the ionicity of the M–C bond. For some elements such as the lanthanides, Y and Sc, there exist both carbon-rich and metal-rich compounds, and these compounds are located between the domains of carbon-rich (so-called intercalated) type and stoichiometric compounds.

We can classify lanthanide carbon compounds into two groups, that is, the metal-rich and carbon-rich compounds. As shown in Tables 1 and 2, only carbon-rich compounds are formed for La, Ce, Pr and Nd, while both carbon- and metal-rich compounds are formed for other lanthanides, except for Pm, Tb and Tm. When lanthanide carbon compounds are plotted on the structural map using H_{sp} and

S_{av}, as shown in Fig. 2 (the plots of Ce–C and Pr–C bonds are superimposed), these two groups of lanthanide carbon compounds cannot be so well separated by the straight line with constant ratio of H_{sp} to S_{av} (that is, the constant ionicity of $F_i = 0.665$) because Eu and Yb carbon compounds are placed in the domain of carbon-rich compounds. On the other hand, these two groups of lanthanide carbon compounds can be well separated on the structural map by selecting H_{sp} and S_{sp} as the structural coordinates.

Misplacements were observed for the carbon compounds of several elements as shown in Fig. 1. As indicated before, the compounds of As and Se are misplaced in the domain inside of the circular arc boundary. On the other hand, several metastable carbon compounds are found for some post (Ib and IIb group)- and late (VIIa and VIIIa group)-transition metals, such as Cu and Ni. The carbon compounds of late transition metals are well placed in the structural map, while it is difficult to estimate the placements for the carbon compounds of post-transition metals (that is, Cu, Ag and Au) because the numerical values of two band parameters for these compounds could not be easily estimated. Here, the numerical values were calculated by assuming the complete sp-charater for the bonding between the post-transition metal and carbon, and the data were plotted on the structural map of Fig. 1 as carbon-rich compounds. It will be necessary to reconsider these placements by taking into account some effect of the d electrons.
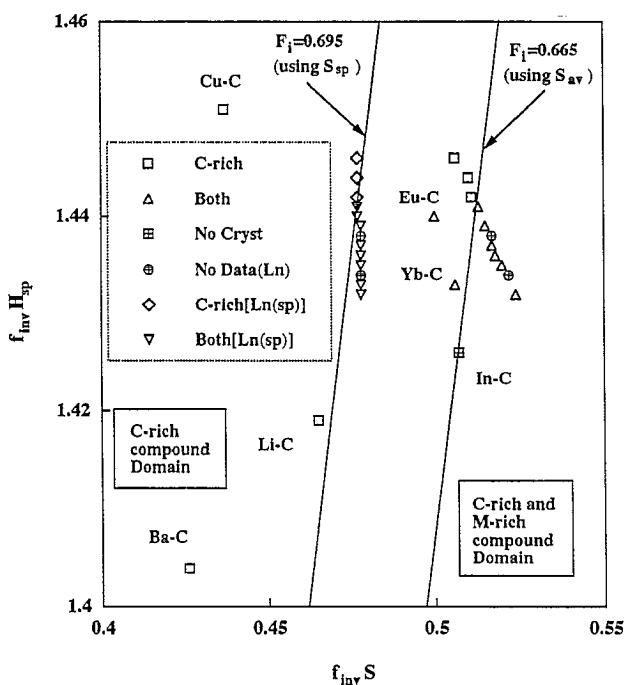

Fig. 2. Partial structural map of carbon compounds of lanthanides by using two band parameters as the structural coordinates. In the figure, two cases of taking S_{sp} and S_{av} as the abscissas are illustrated, where S_{sp} and S_{av} are the sp and average gap reduction parameter, respectively. Details of the difference are explained in the text.

4. Endohedral fullerene and the structural map

Endohedral fullerenes have been of much interest to many investigators, because it has been postulated that these fullerenes have various characteristic properties, such as superconductivity. Recently, the stability of endohedral fullerene was interpreted by use of Pauling's electronegativity values and it was indicated that endohedral fullerene $M@C_m$ can be formed in a stable state when the electronegativity of the element M is less than 1.54 [17]. As indicated in the previous paper [7,12], the band parameters are constructed from the orbital electronegativities, and the ionicity for the respective chemical bond can be estimated by the two band parameters, so that it is expected that the stability of endohedral fullerene will be understood in more detail from the standpoint of bond character.

Examining the stability data of endohedral fullerene [17] using the structural map based on H_{sp} to S_{av}, it is obvious that the structural map is not suitable for determining whether any element can be introduced into the fullerene cage or not. That is, the possibility of endohedral fullerene formation can not be understood from a knowledge of the structural stability of the inorganic carbon compound. The failure to understand the structural map is attributed to the selection of S_{av} as the abscissa, in which the contribution of d and/or f electrons is taken into consideration. When the experimental results on the endohedral fullerenes are examined using the structural map based on H_{sp} and S_{sp}, these data can be well understood by the structural map based on the sp bonding as shown in Fig. 3. Thus, the possibility of endohedral fullerene formation can be interpreted by the ratio of H_{sp} to S_{sp}, and an element with a ratio of more than 2.58 (which corresponds to 0.624 in ionicity scale) can be introduced into the fullerene cage. Disagreements between the prediction and the experimental results are found in Mg, Al and Pb.

5. Discussions

The crystal structure map based on H_{sp} and S_{av}, as shown in Fig. 1, can predict whether the C–C bond or the M–C bond is stable for inorganic carbon compounds, although the additional condition of $(f_{inv}H_{sp})^2 + (f_{inv}S_{spd})^2 \geq (1.6)^2$ is required. The structural map enables us to determine the stability of the M–C bond from its ionicity because the ionicity for the M–C bond can be determined by H/S. When the ionicity of the M–C bond exceeds about 0.60, the M–C bond becomes unstable and a graphite-like C–C bond and/or acetylene-type ion are stabilized, resulting in the occurrence of intercalation and/or CaC_2 type compounds. Both metal- and carbon-rich compounds are observed for heavy lanthanides, Sc, Y and Be, so that the carbon bond with these elements is located in the transition region with their ionicity ranging from 0.6
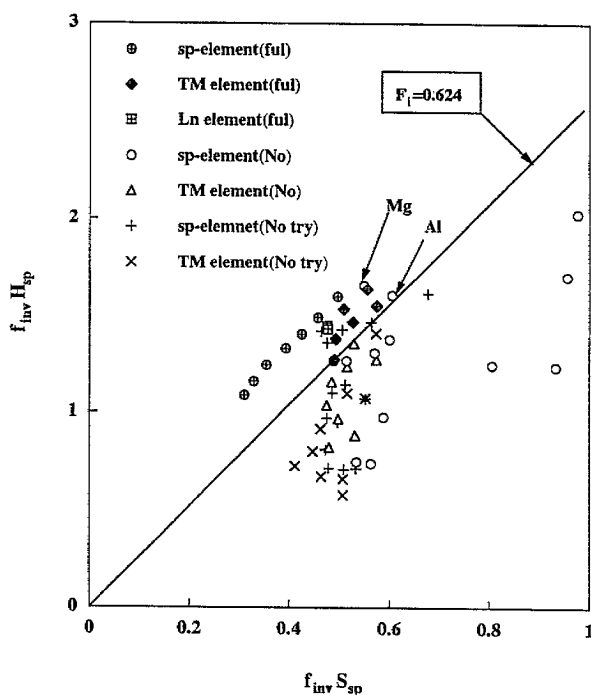
Fig. 3. Interpretation of the possibility of endohedral fullerene formation by structural mapping based on the two band parameters for the sp bonding scheme. Experimental results for the formation of endohedral fullerenes are quoted from Ref. [4].

to 0.665 (see Fig. 2), in which the bond formed between the metallic element and carbon changes from $M-C_2$ bonding to $M-C$ bonding, through the intermixed region.

Unsatisfactory separation for the compound formation of lanthanide with carbon was obtained in the structural map based on the H_{sp} and S_{av} because Eu–C and Yb–C combinations were not well placed, as shown in Fig. 2. Accordingly, the unsatisfactory separation suggests that the contributions of sd hybridization in the bonding between Ln and carbon are smaller than those expected from the elemental lanthanides. In contrast, a satisfactory separation for the compound formation of lanthanide with carbon was obtained in the expression based on sp-bonding, that is, on H_{sp} and S_{sp}. The well-separated placement indicates a small contribution of sd hybridization for the bonding between Ln and carbon. The discrepancy in behaviour of different lanthanides with respect to the formation of carbon- and/or metal-rich compound may be explained by calculating the sd hybridization. A critical value of sd hybridization has been determined by linearly decreasing it while maintaining the ratio of the sd hybridization for Sm–C bond to that for Eu–C at 1.39. The critical value obtained by this method was about 1%, thus suggesting an insignificant contribution from sd hybridization in Ln–C bonding.

When the ionicity becomes less than about 0.60 ($0.41 \leq H/S$), MC type stoichiometric compounds can be formed within the condition of $(f_{inv}H_{sp})^2 + (f_{inv}S_{spd})^2 \geq (1.6)^2$. In the domains with the ionicity less than about 0.60, the formation of p–d bonding makes a large contribution to the stabilization of the M–C bond, except for SiC. This suggests that the concept of ionicity based on the two band parameters, cannot distinguish between the p–d bond and the sp^3 hybridized bond because the formation of the Si–C bond is attributed to the sp^3 hybridization. The condition of $(f_{inv}H_{sp})^2 + (f_{inv}S_{spd})^2 \geq (1.6)^2$ is also taken into account for the formation of interstitially-ordered compounds that are placed in the domain with the ratio of H/S less than 1.81. These interstitially-ordered compounds can only be formed in the combination between the transition metal and carbon. The formation of such interstitially-ordered compounds can probably be attributed to the stabilization of non-bonded d-electrons by their occupation of the d-band below the Fermi level [18,19]. By increasing the number of outermost electrons, some of the d-electrons must occupy the p–d band with antibonding character, resulting in no formation of a chemical bond between a late TM element and carbon. The change of bonding characteristics between TM and carbon are expressed by the gradual transfer of their plots to a position with a lower H_{sp} value on the right side as the number of valence electrons of the TM element increases.

Possibility of the formation of endohedral fullerene is well explained by the structural map using S_{sp} as the abscissa rather than S_{spd}. The result suggests that the possibility of endohedral fullerene formation is determined by the sp character of the bonding between the carbon of fullerene and the element introduced into the fullerene cage. As shown in Fig. 2, elements with an ionicity higher than 0.624 can be introduced into the fullerene cage. According to Smalley et al. [17], an element with a Pauling's electronegativity value of less than 1.54 can be introduced into the fullerene cage. When the critical ionicity of the M–C bond is calculated using the Pauling's formula; $f_i = 1 - \exp[-(\chi_A - \chi_B)^2]$, where χ_A, χ_B are the Pauling's electronegativities of the A and B atoms, the critical ionicity value obtained was 0.225. The critical ionicity from the Pauling's formula is quite different from the value obtained from band parameters. This difference is attributed to the fact that Pauling's ionicity is defined for single bonds. When we use the modified formula; Nf_i/M [11], instead of f_i, where N is the valence of the cationic atom and M is the number of resonating bonds, the critical ionicity is estimated to be 0.613. Thus, the critical electronengativity for formability of endohedral fullerene shows excellent agreement with the ionicity predicted by the band parameters.

Viewing the possibility of endohedral fullerene formation from the standpoint of compound formation, the fullerene can endohedrally introduce the elements which form their carbon compounds with the intercalation structure to graphite, CaC_2 structure and only stoichiometric carbide, except for SiC. The discrepancy between Si and transition metals in their bonding to carbon may be

attributed to the fact that the band parameter description cannot distinguish between sp^3 and p–d bonding.

The disagreements for Mg and Al remain unclear, although their high p-character may be related to lack of formation of their endohedral fullerenes. The disagreement for Pb is plotted on a very close position to the boundary line with a ratio of 2.58, by which the formation of endohedral fullerene is separated. The possibility of endohedral fullerene formation is suggested for Ga, In and Tl among untried elements.

6. Summary

It was indicated that bond character between carbon and other elements and the crystalline forms of their carbon compounds are effectively described by the two band parameters (hybrid function (H) and gap reduction parameter (S)), which are constructed by the pseudopotential radii of Zunger through a modelling of the bond orbital model. From the structural map based on these band parameters, the crystalline forms change from an intercalation structure related with graphite, through a CaC$_2$-type structure with an acetyl ion and stoichiometric carbide, to an interstitially-ordered carbide, with decreasing ionicity of the M–C bond (M; other element except for C). Domains of stoichiometric and interstitially-ordered carbides were not clearly separated from each other and there exists an intermixed region between these domains. The boundaries between the other three main structures of the carbon compounds are fairly well determined by the lines with constant ionicities. Except for the formation of an intercalation structure related with graphite, no formation of inorganic carbon compounds was suggested in the domain satisfying the condition of $(f_{inv}H_{sp})^2 + (2f_{inv}S_{av})^2 \leq (1.6)^2$. The two band parameters can also describe the condition for the possibility of endohedral fullerene formation by the ionicity of sp-bonding between carbon and another element, and elements having an ionicity of more than about 0.62 can be endohedrally introduced into the fullerene cage. Further, a small contribution of d and/or f electrons

to the possibility of endohedral fullerene formation is supported by the successful description based on the sp-bonding scheme.

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