BONDING ANALYSIS IN SOLID STATE COMPOUNDS: BORON CARBON OF RARE EARTH METALS

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ABSTRACT:

The combination of boron and carbon elements with rare earth metals leads to the formation of materials having interesting physical and structural properties. In theses compounds of formula $M_xB_yC_z$, The non-metal atoms form either two-dimensional networks, or mon-dimensional zig-zag chains, or finite linear units of various length. The dimensionality of boron-carbon sublattice is related to the average valence electron count (VEC) per light atom (B or C). The bonding properties of rare earth metal boron carbide compounds are analysed by means of extend Hückel tight-binding calculations. Results indicate that these compounds can be described in first approximation as being built of anionic units interacting with not fully oxidized metallic cations.

1. INTRODUCTION

Ternary and higher order phases comprising a rare earth metal, boron, and carbon show a particularly rich and varied structural chemistry.[1] These structure types can be classified in three different families according to the dimensionality of the boron-carbon sublattice : two-dimensional (2-D) networks, or one-dimensional (1-D) zig-zag chains, or finite linear units of various length. Such compounds are attractive not only as new materials with interesting physical properties, but also simply as solid-state analogous of molecular organic and organometallic compounds containing all-carbon ligands.[2]

Finite boron-carbon units stabilized in metallic lattices are rather scarce and limited in length to three or four atoms as demonstrated in the metal and carbon-rich compounds Sc_2BC_2,[3] $Ce_5B_2C_6$,[1c] $La_5B_2C_6$.[4] We report herein on the characterisation of chains with up to 13 atoms that are contained in new cerium, lanthanum, and neodymium boride carbide materials. $La_{15}B_{14}C_{19}$,[5] $M_{10}B_9C_{12}$ (M = La, Ce, Nd),[6] and $Ce_4B_4C_5$[7]are obtained as lustrous black pellets by are melting and subsequent annealing of the elements for several days. We analyze here the bonding in the compounds listed in Table 1 containing finite boron-carbon units.

2. DESCRIPTION OF THE STRUCTURES

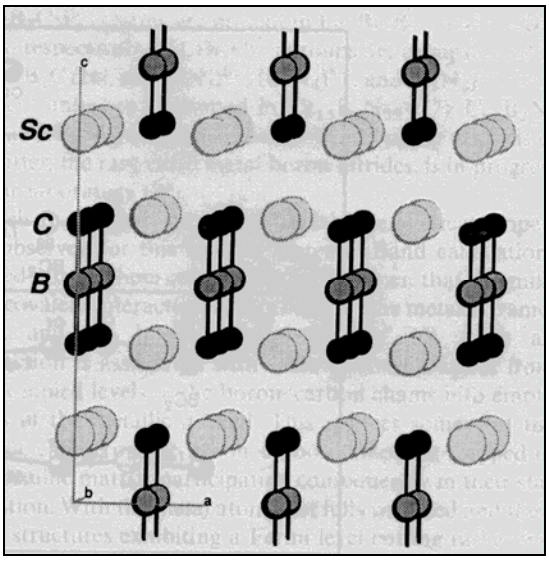
In all compounds, the metallic sublattice results from a regular or irregular stacking of two-dimensional (2-D) square nets, giving rise to a three-dimensional (3-D) frame-work with metal-metal separations comparable to that measured in metallic elements. In some cases, the 2-D square nets can be slightly corrugated. Such an arrangement leads to the formation of small channels of different sizes in which roughly linear B_xC_y units encapsulated, as exemplified by Sc_2BC_2 and $La_5B_2C_6$ which contains respectively C-B-C and C-B-C-C (see Figure 2) entities.

The finite boron-carbon units which have been stabilized in ternary rare earth metal boron carbide compounds. Two-atom C_2 and three atoms BC_2 are found in metal- and carbon-rich compounds such as Sc_2BC_2 and $Ce_5B_2C_6$, four atoms BC_3 chains are encountered in $La_5B_2C_6$ as shown in Figure 1. Longer chains are observed when the B/C ratio increases as $La_{15}B_{14}C_{19}$, which contains chains 11-membered B_4C_7 and B_5C_6 units, $Ce_{10}B_9C_{12}$, in which inserted 13-membered B_5C_8 (the longest chain observed in these compounds), and 8-membered B_4C_4 chains as listed in Table 1.

Table 1 : Rare earth metal boron carbide compounds containing finite boron-carbon units.

Type structural		c.e.v.	réseau B-C	B/C	réf.
$La_{15}B_{14}C_{19}$		4.94	$[B_4C_7][B_5C_6]$	0.74	5
$Ce_{10}B_9C_{12}$	La	5.00	$[B_5C_8][B_4C_4]$	0.75	6
$Ce_5B_4C_5$		5.22	$[B_4C_4][B_3C_3]$ $[BC_2][C]$	0.8	7
$La_{10}B_9C_6$		5.40		1.5	8
$U_5B_2C_7$		5.44		0.29	9
$Ce_5B_2C_6$	La, Ho	5.63	$[BC_2][C_2]$	0.33	1c
$La_5B_2C_6$	Pr, Ce	5.63	$[BC_3][C]$	0.33	4
$Sm_5B_2C_5$		5.67	$[BC_2]$	0.5	20
Sc_2BC_2	Gd	5.99	$[BC_2]$ $[C]$	0.4	19 3
Lu_3BC_3		6	$[BC_2][C]$	0.33	10

a)



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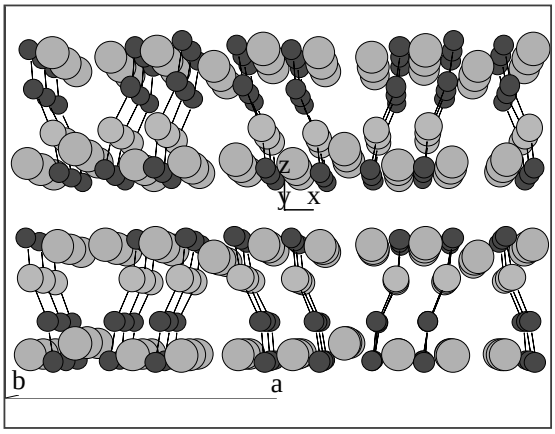


Figure 1 : Structural arrangement of Sc_2BC_2 (a) and $La_5B_2C_6$ (b).

3. BONDING ANALYSIS

Calculations in LMTO- ASA and EHTB[10] methods were carried out on the new $La_5B_2C_6$ phase. The total densities of states and their projections resemble each other in the two methods (Figure 2). The density of state is divided into two parts. The higher part is in mainly metallic, while the lower part is predominant of boron and carbon. One notes the metallic participation in the lower part and a participation of the boron carbon chains in the higher part. Among the few FMO (Frontiers Molecular orbitals) of the boron-carbon fragments which we chose, only the 3π orbital of BC_3 interacts strongly with the metallic network and is stabilized of more than 1eV by acquiring an occupation of 2.02 electrons. One notes for LMTO calculations that the *f*-AO of metal interact slightly and remain localised around –5 eV and that the major metal contribution comes from the *d*-AO as shown on the Figure. The electronic occupations after interaction of some FMO of the various chains encountered in the $M_xB_yC_z$ compounds are gathered in Table 2. contributes to a large extent to the covalent bond between the metal atoms and boron and carbon atoms constituting B_mC_n molecular chains. These notable covalence degrees illustrated by the nets charges calculated for different compounds:

$[Ce_{10}B_8C_{10}]$: $(Ce^{1,33+})_5[(BC_2)^{2,7-}(B_3C_3)^{3,7-}(B_4C_4)^{4,5-}C^{2,3+}]_{1/2}$

$[La_{15}B_{14}C_{19}]$: $(La^{1,19+})_{15}(B_4C_7)^{6,7-}(B_5C^{65,6-})_2$

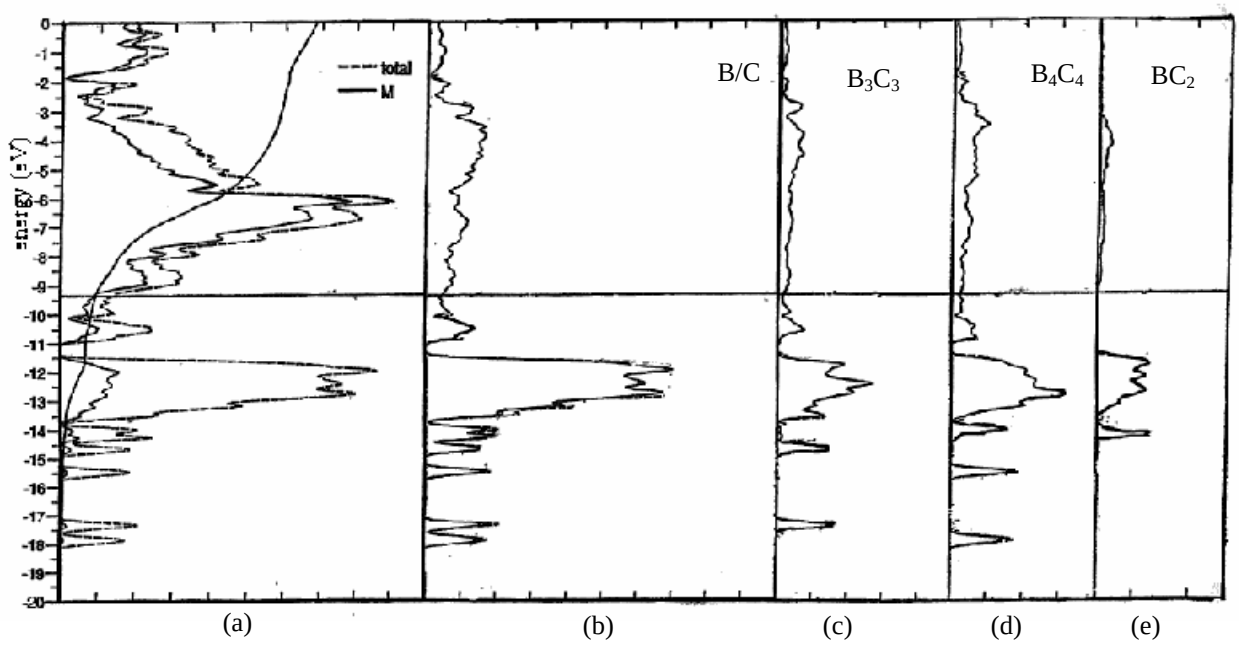
$[La_5B_2C_6]$: $(La^{1,11+})_5\,(BC^{32,77-})_2$

Table 2: FMO Occupations of B_XC_Y chains encountered in different compounds listed in Table 1.

BC2(Ce5B2C6)	2πu	1πg	2σu	1πu
dB-C(1.52,1.71)	3.08	1.67	3.28	1.60
BC3(La5B2C6)	4π	3π	5σ	2π
	0.19	2.02	1.70	3.33
B3C3	5π	4π	3π	7σ
	0.13	1.75	2.48	1.19
B4C4(Ce10B9C12)	3πg	3π**g**	2πg	2π
	0.27	1.90	3.25	3.21
B4C4(Ce5B4C5)	0.39	2.03	3.21	3.15
B5C8	5πg	5πu	4πg	4πu
	0.5	0.98	2.38	2.5
B4C7	4πg	4πu	3πg	3πu
	0.54	2.25	2.28	3.30
B5C6	4πg	4πu	3πg	3πu
	0.48	1.30	3.25	3.25

CONCLUSION

The theoretical analysis of boron carbides of rare earths $M_xB_yC_z$ M_x enabled us to highlight a significant covalence between the non-metal molecular entities and their metal host. This covalence results from an electronic donation significant of certain orbital boron-carbon towards the metal network and from a light retro-donation of the metal levels occupied in acceptors orbital of the molecular entities. This covalence which is, for a significant share, at the origin of the character more or less binding of the contacts metal-metal, via a phenomenon of coupling through connections (through-bond interaction): the states constituting the bottom of the d-band of the metal sub-network mix in a flexible way with the anion occupied states and give on those a certain binding metal-metal character. There we have examples of coordination compounds in solid state chemistry.



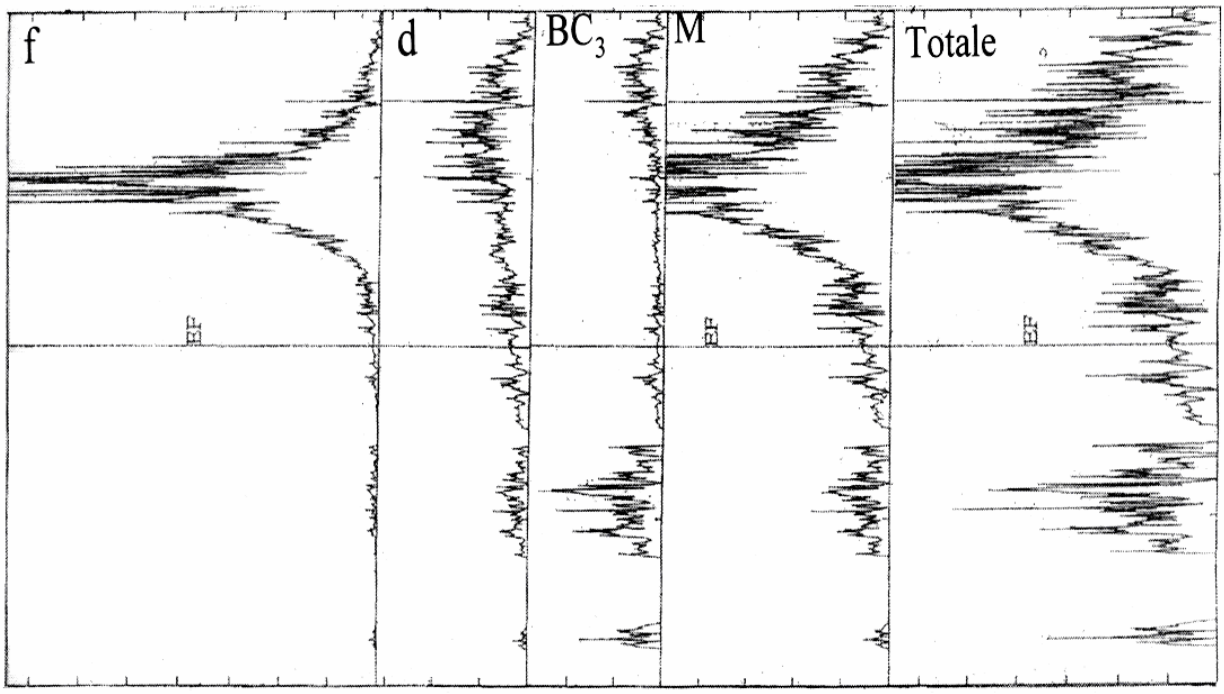


Figure 2 : Density of states and their projections for $La_5B_2C_6$obtained from EHTB (a) and LMTO (b).

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