



Rings and chains in solid-state metal borides and borocarbides. The electron count matters

Souheila Lassoued^{a,b}, Régis Gautier^b, Ahmed Boutarfaia^c, Jean-François Halet^{b,*}

^a Laboratoire de Chimie Appliquée, Université Mohamed Khider, 07000 Biskra, Algeria

^b Sciences Chimiques de Rennes, UMR 6226 CNRS-Ecole Nationale Supérieure de Chimie de Rennes-Université de Rennes 1, F-35042 Rennes cedex, France

^c Faculté des Sciences et de la Technologie et Sciences de la Matière, Université Merbah Kasdi-Ouargla, Ouargla, Algeria

ARTICLE INFO

Article history:

Received 28 September 2009

Received in revised form 24 November 2009

Accepted 26 November 2009

Available online 2 December 2009

Keywords:

Borides

Borocarbides

Solid-state compounds

Electron counting

Theoretical calculations

ABSTRACT

The bonding and structural arrangement in a few representative ring- or chain-containing solid-state metal borides and borocarbides are analyzed with respect to the electron count of the non-metal entities. Similarities (and differences) with molecular analogs are emphasized.

© 2009 Elsevier B.V. All rights reserved.

1. Introduction

The reader of JOMC might be somewhat amazed to see a solid-state chemistry paper here and his first temptation might be to quickly turn off the pages to reach the following article. This would be a pity. Indeed, there is value in considering a solid as a molecule, a big one, but just a molecule. Both molecules and solids deal with the same fundamental questions: where are the electrons, where are the bonds [1]? The few examples of solid-state compounds discussed below, borrowed from the metal boron or metal boron carbon chemistries, will serve to illustrate that there are similarities between the bonding in molecules and that in solids. We will try to use the same tools, including relationships between the electron count and geometric structure, to effectively describe and understand the stoichiometry and the bonding in some solids containing chains and rings.

2. Rings in metal borides and borocarbides

Clusters, rings, chains are not the privilege of molecular chemistry. They are also largely observed in solid-state chemistry. Rings for example are encountered in many solid-state boron-containing compounds [2]. This is the case for instance in some layered ternary borides adopting the YCrB₄ [3], ThMoB₄ [4] and Y₂ReB₆ [5]

structure-types, in which the boron atoms form two-dimensional (2D) layers which alternate with metallic sheets made of rare-earth metals (*RE*) and transition metals (*T*) or eventually main group metals [6] (see Fig. 1). All are based on different rings which merge to each other to form 2D networks of boron atoms. Indeed, these networks differ by the way the boron atoms arrange themselves. In both YCrB₄ and ThMoB₄ structure-types, the boron atoms form pentagonal and heptagonal rings. The pentagons fuse two by two and are surrounded by heptagons. Having the same stoichiometry *RETB*₄, these two arrangements are polymorphic in a way since they differ by the way the fused pentagons are positioned to each other. In some cases, these two arrangements are characterized with the same metals [7]. The *RE* atoms sit above and below the heptagons and the *T* atoms above and below the pentagons. Somewhat related also, is this structure of stoichiometry *RE*₂*TB*₆ exemplified with Y₂ReB₆ [5] where, in addition to pentagons and heptagons, there are hexagons forming the boron layers.

Solid-state chemists and physicists are interested in these compounds because some of them develop interesting physical, especially magnetic properties [8]. We have, on our side, decided to revisit the bonding of this type of compounds with the aid of theoretical quantum calculations of the extended-Hückel tight-binding (EH-TB) and periodic Density-Functional-Theory (DFT) types. Preliminary results are reported here.

Why are we interested in that? These compounds consist of layers of boron atoms, as does MgB₂, which was discovered to superconducting at 39 K a few years ago [9]. The metal/non-metal ratio

* Corresponding author. Tel.: +33 2 23236778; fax: +33 2 23236840.

E-mail address: halet@univ-rennes1.fr (J.-F. Halet).

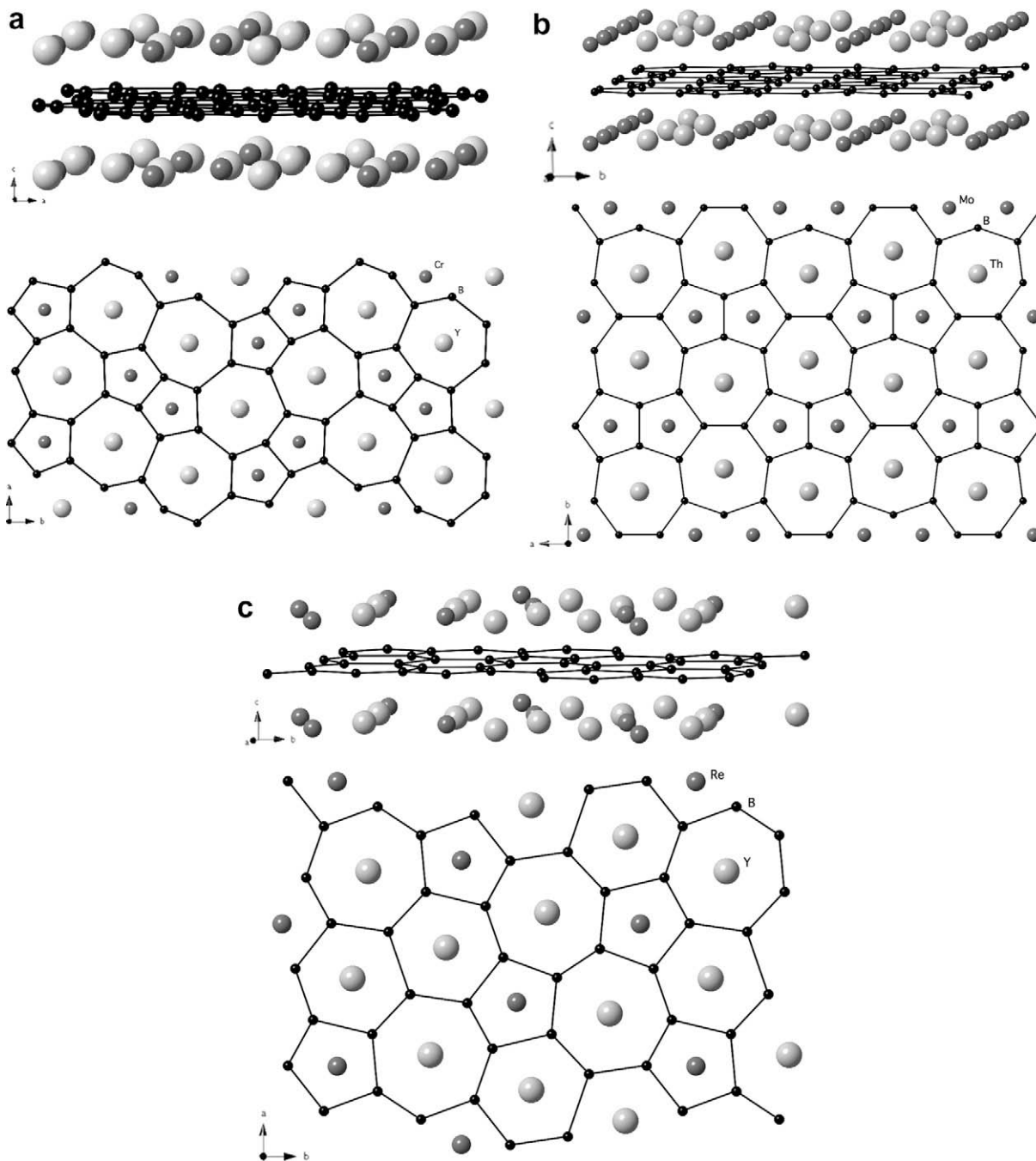


Fig. 1. Side (above) and top (below) views of the YCrB_4 (a), ThMoB_4 (b), and Y_2ReB_6 (c) structure-types. Large, medium and small spheres represent rare-earth (RE) metal, transition (T) metal and boron atoms, respectively.

is the same, i.e., 1:2, although the rings themselves differ in shape with benzene-like rings in MgB_2 (isoelectronic to graphite) and, as said previously, pentagons plus heptagons in RETB_4 . Therefore, we may ask ourselves whether there is a relationship between the electronic structure of MgB_2 and that of these RETB_4 and RE_2TB_6 compounds [10]?

It is noteworthy that the boron arrangement observed in YCrB_4 is strongly related to the 2D B_2C_2 arrangement encountered in the ternary rare-earth metal boron carbide ScB_2C_2 where pentagons and heptagons are also found [11] (see Fig. 2). Is there a relationship between these two compounds?

Two fused pentagons make a pentalene-like motif. One pentagon fused to one heptagon will lead a molecular chemist to think

of an azulene-like unit. Fusion of a pentagon, a heptagon and now a hexagon leads to a benzazulene-like motif. We may wonder whether there is some interest to compare them with organic molecules such as pentalene C_8H_6 , azulene C_{10}H_8 , or benzazulene anion $(\text{C}_{13}\text{H}_9)^-$. With metal above and below the rings, we think of multidecker-like “molecules” in solids. Organic rings can be also be complexed with organometallic fragments [12].

As molecular chemists we are used to see how the electron count governs the shape of molecules. This is also true for solids [1]. We deal with the same fundamental questions: where to find electrons and bonds? In solids, the ionic concept popularized by Zintl, Klemm and others [13], which is based on the simple idea that in compounds A_xB_y , the more electropositive A atoms relative

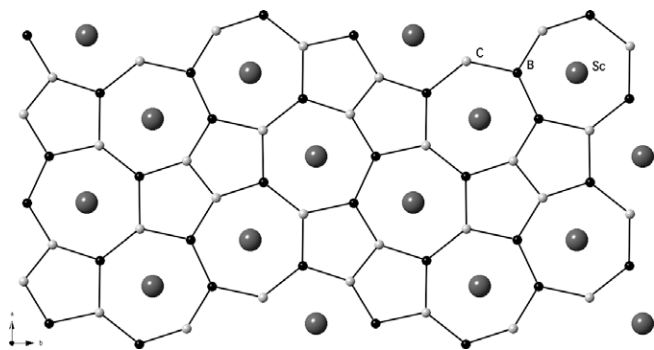


Fig. 2. Top view of the ScB_2C_2 structural arrangement.

to a main group elements B, transfer their electrons to the B atoms, which then use them to form bonds, is very useful. R. Hoffmann used to say that “This very simple idea is the most important theoretical concept (and how not very theoretical it is!) in solid state chemistry... It explains so much chemistry, and it forges a link between solid state chemistry and organic, or main group, chemistry” [1a]. But this supposes a rather large electronegativity difference between the constituting elements. This may be not the case in ternary compounds discussed here. Nevertheless, let us start with such an ionic model. We know it is a crude approximation, but often very useful to understand the electronic properties of the non-metal part in a solid [1]. In other words, what could be the formal oxidation state of the boron network in the RETB_4 and RE_2TB_6 compounds? This is the difference between solid-state and molecular compounds. The metal electrons in a binary or ternary solid-state compound can serve as a reservoir, which can be fully or partially used to supply the electron requirements of the main-group partner. Too many electrons for the main-group atoms is fine. Some can be retained by the metals. Not enough electrons for the

Table 1

Ternary compounds which crystallize in the YCrB_4 , ThMoB_4 , and Y_2ReB_6 structure-types.^a

Structure-type	Compounds			
YCrB_4	YCrB_4	GdCoB_4	DyCoB_4	ErRuB_4
	YReB_4	TbVB_4	DyReB_4	ErCoB_4
	YFeB_4	TbCrB_4	HoVB_4	TmCrB_4
	YRuB_4	TbMoB_4	HoCrB_4	TmAlB_4
	YCoB_4	TbWB_4	HoMoB_4	TmReB_4
	CeCrB_4	TbMnB_4	HoWB_4	TmFeB_4
	CeMnB_4	TbReB_4	HoMnB_4	TmRuB_4
	CeFeB_4	TbFeB_4	HoReB_4	TmOsB_4
	PrCrB_4	TbRuB_4	HoFeB_4	TmCoB_4
	NdCrB_4	TbOsB_4	HoRuB_4	$\alpha\text{-YbAlB}_4$
	SmCrB_4	TbCoB_4	HoOsB_4	LuCoB_4
	GdVB_4	DyVB_4	HoCoB_4	$\alpha\text{-LuAlB}_4$
	GdCrB_4	DyCrB_4	ErVB_4	UVB_4
	GdMoB_4	DyMoB_4	ErCrB_4	UCrB_4
	GdWB_4	DyWB_4	ErMoB_4	UMnB_4
	GdMnB_4	DyMnB_4	ErWB_4	UFeB_4
	GdReB_4	DyFeB_4	ErMnB_4	UCoB_4
	GdFeB_4	DyRuB_4	ErReB_4	
	GdRuB_4	DyOsB_4	ErFeB_4	
	ThMoB_4	ThMoB_4	ThReB_4	UWB_4
ThVB_4		ThWB_4	UReB_4	$\beta\text{-LuAlB}_4$
UMoB_4				
Y_2ReB_6	Y_2ReB_6	Ho_2ReB_6	Tm_2ReB_6	Lu_2ReB_6
	Gd_2ReB_6	Er_2ReB_6	Yb_2AlB_6	Tb_2ReB_6
	Dy_2ReB_6			

^a See Refs. [3–8].

main-group atoms generally is not. The compound then does not exist.

Let us start by the RETB_4 compounds. A look at the full list of compounds, which adopt the YCrB_4 or ThMoB_4 structure types (see Table 1), does not seem to be very helpful. If it is possible to propose an oxidation state for the rare-earth metals (often +III or eventually +IV for Ce or Th), it is less obvious for the transition metals. Indeed, these structure-types are adopted with nearly all the transition metals. A glance at the boron–boron distances experimentally measured in these compounds is neither useful. They range from 1.60 to over 2.00 Å for YCrB_4 (the X-ray structure is not very precise [3]) and from 1.80 to 1.85 Å in ThMoB_4 [4] for instance. This indicates more or less formal single B–B bonds, but we know how “flexible” can be boron–boron bonds separations [1b,2,6].

Obviously, several oxidation states might theoretically be possible for the boron network in the RETB_4 compounds. EH-TB calculations (see computational details) were first made on one boron layer with different formal negative charges (from $(\text{B}_4)^{4-}$ to $(\text{B}_4)^{7-}$). The density of states (DOS), which is in some ways the molecular orbital diagram of a solid, for one boron layer taken from YCrB_4 and ThMoB_4 is given on the top and the middle of Fig. 3,

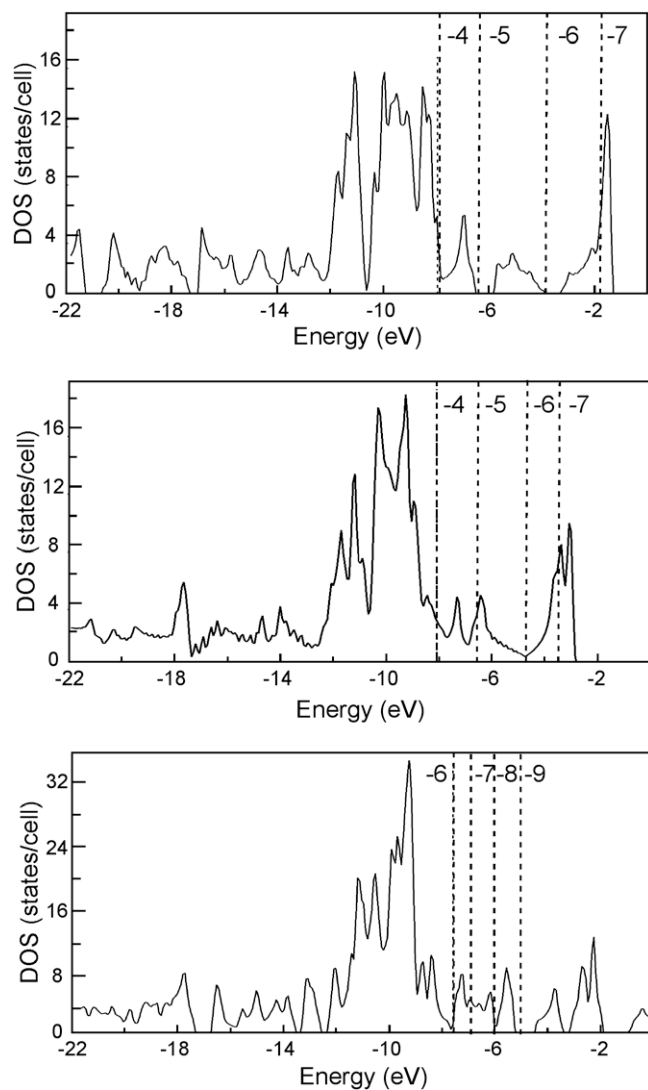


Fig. 3. Total EH-TB DOS of one boron $(\text{B}_4)^{n-}$ layer encountered in YCrB_4 (top), ThMoB_4 (middle), and one boron $(\text{B}_6)^{n-}$ layer encountered in Y_2ReB_6 (bottom). Fermi levels are indicated for $n = 4\text{--}7$ for $(\text{B}_4)^{n-}$ and $n = 6\text{--}9$ for $(\text{B}_6)^{n-}$.

respectively. The shape of the DOS seems to be sensitive to the B–B distances. For the boron layer encountered in YCrB_4 , holes in DOS at the Fermi level occurs for the charges of 5– and for 6–, whereas a hole at the Fermi level is just observed for the charge of 6– for the boron layer observed in ThMoB_4 . We think that in compounds where the connectivity between the atoms is low, a situation where there is a hole at the Fermi level (that is a HOMO–LUMO energy gap) for the main-group atom partner is generally preferred over that with a high DOS (that is an open-shell electron configuration). It is like in molecules, there are more examples with closed-shell electron configurations than with open-shell electronic configurations. This is often seen as a criterion of “stability”. Interestingly enough, in both cases, for the charges of 4–, which would render these layers isoelectronic to graphite and the graphitic-like boron layers of MgB_2 , the Fermi level cuts some DOS. This probably means that such boron arrangements made of merged pentagons and heptagons need slightly more electrons with respect to graphite-like arrangements to exist. This leads us to propose that the formal oxidation state for the boron networks in these compounds is 6– which implies the metals to adjust: 3+ or 4+ for the *RE* metal and 3+ or 2+ for the *T* metal. The reader may argue that there is also a hole at the Fermi level for 5– in the case of the boron layer taken out from YCrB_4 , and consequently, 3+ or 4+ for the *RE* metal and 2+ or + for the *T* metal should also be envisaged. This is true and calculations are in progress to better understand why this is the case for YCrB_4 but not for ThMoB_4 .

What happens for the 3D compounds? The purpose here is not to bother the reader who is not used to work with solid-state chemistry and its jargon, so only the main results are briefly reported. Covalent interactions between the metal and boron atoms in YCrB_4 and ThMoB_4 modify somewhat the DOS of the boron network (it is like in a complex where metal–ligand interactions occur), but the main conclusions remain the same. Projected DOS obtained from periodic DFT calculations of LMTO type (see computational details) indicate that there is hardly any participation of boron at the Fermi level and the conducting properties are essentially governed by the nature of the transition metal into play (see Fig. 4, top and middle). YCrB_4 is computed to be semi-conducting and ThMoB_4 should be metallic in character according to their total DOS.

An interesting question concerns the “stability” of the boron arrangement observed in the YCrB_4 structure-type with respect to that encountered in ThMoB_4 (see above). Most of them crystallise in the YCrB_4 structure-type rather than the ThMoB_4 structure-type (see Table 1). Is it for thermodynamical reasons, or electronic reasons? Interestingly, both arrangements are adopted for YbAlB_4 and LuAlB_4 [7]. We do not expect much difference in energy between the “polymorphic” forms since the local arrangement of the boron atoms is fairly similar in both arrangements. They simply differ by the way the fused pentagons are positioned to each other, in a zigzag fashion in YCrB_4 and in a linear fashion in ThMoB_4 (vide supra). Full-geometry optimizations carried out at the DFT level of theory for various *RE* and *T* metals with the two arrangements YCrB_4 and ThMoB_4 indicate that, regardless of the metals, the YCrB_4 arrangement is computed to be the most stable. We conclude that the YCrB_4 arrangement is the thermodynamically stable phase whereas the ThMoB_4 arrangement is the kinetically stable phase [7].

A similar study was performed on the RE_2TB_6 compounds. Calculations were first carried out on one boron layer taken from Y_2ReB_6 with different negative charges (from 6– (isoelectronic to graphene) to 9–) in order to try to answer the same questions concerning the oxidation state of the boron network. Because of a hole in the DOS at the Fermi level (see Fig. 3, bottom), the formal charge $(\text{RE}^{3+})_2\text{T}^{3+}(\text{B}_6)^{9-}$ is proposed. This seems to indicate again that 2D boron networks made of merged pentagons, heptagons, and hexa-

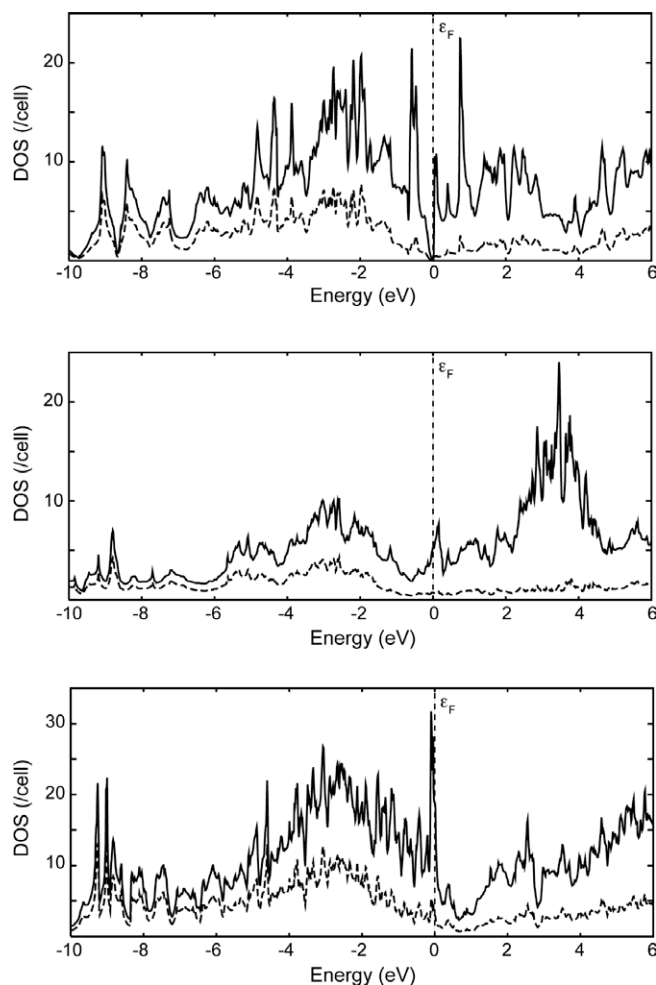


Fig. 4. Total (solid) and B projected (dotted) LMTO DOS of YCrB_4 (top), ThMoB_4 (middle), and Y_2ReB_6 (bottom).

gons are somewhat electron-rich than graphite-like networks. Similarly to YCrB_4 and ThMoB_4 covalent interactions between the metal and boron atoms in the 3D compound Y_2ReB_6 modify somewhat the DOS of the boron network. Metallic character is expected according to the total DOS (see Fig. 4, bottom).

As said earlier, YCrB_4 and the boride carbide ScB_2C_2 [11] contain the same topological non-metal layers with pentagons and heptagons (see Fig. 2). Of course replacement of half of the boron atoms by carbon atoms require less electrons from the surrounding metals explaining why there are no metals above and below the heptagons in the latter. Surprisingly enough, preliminary EH–TB calculations on B_2C_2 layer extracted from ScB_2C_2 show a hole at the Fermi level for $(\text{B}_2\text{C}_2)^{2-}$, i.e., isoelectronic to graphene. Periodic and molecular calculations are in progress to try to interpret such a result.

With two kinds of atoms, boron and carbon into play we are faced to the question of their distribution. This is termed the *coloring problem*: The same topology, here pentagons and heptagons, but different ways to order the atoms [13]. Indeed, six “simple” different ways can be envisaged for the B_2C_2 network of ScB_2C_2 [14]. This is like isomerism in molecules. Often an isomeric form may be energetically preferred over another one. Similarly in solids, one coloring may be energetically preferred over another one. We [15] and others [16] tackled this problem some years ago for other layered MB_2C_2 (*M* = rare-earth or alkaline earth metal) phases [15,16]. In these compounds, the boron–carbon layers are made

of fused rhombuses and octagons. The metals are located above and below the octagons. Two distributions inside the layers were experimentally proposed: Either B and C atoms alternate within the diamonds with B–B and C–C contacts between the diamonds, this is Coloring I, experimentally proposed with La and Y [15]. Alternatively, B and C atoms alternate within the diamonds and between the diamonds, this is Coloring II, experimentally observed for Ce, but also Ca [15]. On the basis of DFT calculations, we were able to claim that regardless of the metal, Coloring II was more stable than Coloring I. Indeed, it was shown that in these compounds the metals essentially must act as two-electron donors with respect to the boron–carbon network adopting Coloring II, the other electrons remaining in the relatively narrow d or f bands of the metals [15]. The same study will be carried out for ScB_2C_2 .

3. Chains in metal borides and borocarbides

Polyalkyne chains, in which the carbon atoms are held together by alternating C–C triple and single bonds, are quite stiff and thus of interest with respect to the design of molecular wires for nanotechnology where electronic communication must occur. One problem is that most alkynes are rather reactive because the high energy content of the triple bonds, preventing very long chains to be synthesised. It is therefore no surprise that the record for a string of carbon atoms in a polyalkyne has not changed since the beginning of the seventies with a chain of 32 atoms stabilised at both ends by silyl groups [17]. Compounds of this sort become easier to make when the chain length is decreased and introducing organometallic fragments as terminal groups. Indeed, organometallic wires with linear carbon chains from 2 to 28 have been characterized [18].

Such compounds such as $[\text{trans-}(p\text{-tol})\{\text{P}(p\text{-tol}_3)\}_2\text{Pt}]_2(\mu\text{-C}_{28})$ [19] contain, in turn, pieces of the hypothetical metastable allotropic 1-D phase of carbon called carbyne (karbin) or chaoite. Its preparation although claimed by some, remains a challenge. We know that if it were characterized, such an infinite 1-D linear carbon chain would be subject a Peierls distortion (the Jahn-Teller effect in solids) and therefore would be made up of alternating triple and single bonds, analogously to the carbon chains encountered in organometallic wires. Indeed, there is a solid-state analog of infinite carbyne with LiB, which contains infinite boron rods running in channels made by the Li atoms [20] (see Fig. 5). In the Zintl-Klemm paradigm, LiB can be formulated Li^+B^- . B^- being isoelectronic with C, the reader will not be surprised to learn that the boron chains show alternating short (ca. 1.4 Å) and long (ca. 1.7 Å) B–B separations.

Contrarily to molecular carbon wires, solid-state metal carbides with finite long chains are not well characterized. This probably can be attributed to the fact that all the C_n chains will have a formal charge of $4-$ for $n \geq 3$. Consequently, if C_2 dumb-bells are largely observed in solid-state chemistry (acetylene-like C_2^{2-} , ethylene-like C_2^{4-} , or even ethane-like C_2^{6-}), the longest chain does not exceed C_3 in Sc_3C_4 [21]. However, replacement of some carbon atoms with less-electron rich boron atoms permits B_mC_n chains with more than 10 atoms to be encountered. Indeed, a variety of examples from BC_2 up to B_5C_8 so far, coming from the area of rare-earth metal boron–carbon compounds are known (see Table 2) [22–26]. This is exemplified by LaBC, characterized a while ago during a new investigation of the La–B–C system [26]. In this compound, the metal atoms form distorted square and corrugated metallic layers. They stack in such a way that they form holes in which are encapsulated finite B_5C_5 chains (see Fig. 6). These worm-like entities buried in the solid are fairly linear and the measured B–B, B–C, and C–C separations, ca. 1.5 Å, correspond approximately to coordinated double bonds. As the reader might guess, proper location of B

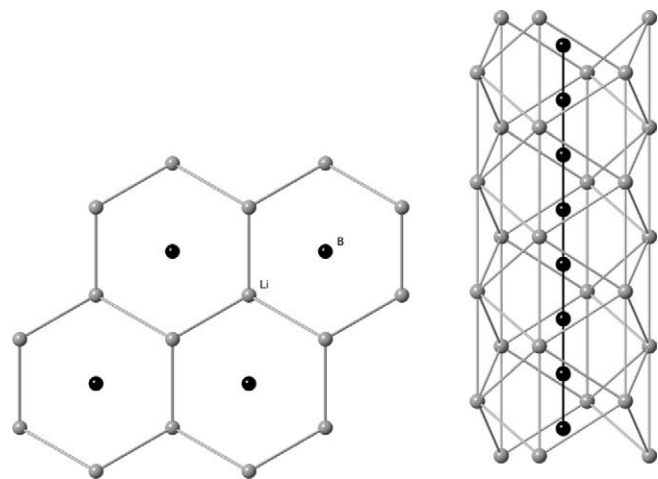


Fig. 5. Top view (left) and side view (right) of the structural arrangement of LiB. Grey and black spheres represent lithium and boron atoms, respectively.

Table 2

Examples of different finite chain-containing rare earth metal boron carbides structurally characterized.^a

Structure-type	B–C chain-type ^b
$\text{La}_{15}\text{B}_{14}\text{C}_{19}$	$[\text{B}_4\text{C}_7]^{8-}$ $[\text{B}_5\text{C}_6]^{9-}$
LaBC (Ce, Pr, Nd, Sm)	$[\text{B}_5\text{C}_5]^{9-}$
$\text{La}_{10}\text{B}_9\text{C}_{12}$ (Ce, Pr, Nd)	$[\text{B}_5\text{C}_8]^{9-}$ $[\text{B}_4\text{C}_4]^{8-}$
$\text{La}_5\text{B}_4\text{C}_5$ (Ce, Pr, Nd, Sm)	$[\text{B}_4\text{C}_4]^{9-}$ $[\text{B}_3\text{C}_3]^{7-}$ $[\text{BC}_2]^{5-}$ $[\text{C}]^{4-}$
$\text{Nd}_5\text{B}_3\text{C}_5^c$	$[\text{B}_2\text{C}_4]^{6-}$ $[\text{B}_3\text{C}_3]^{7-}$ $[\text{BC}_2]^{5-}$ $[\text{BC}_3]^{5-}$
$\text{Pr}_{25}\text{B}_{12}\text{C}_{28}$ (Nd) ^f	$[\text{B}_2\text{C}_4]^{6-}$ $[\text{B}_3\text{C}_3]^{7-}$ $[\text{BC}_2]^{5-}$ $[\text{C}]^{4-}$
$\text{La}_5\text{B}_2\text{C}_6$ (Ce, Nd, Gd, Ho)	$[\text{BC}_3]^{5-}$ $[\text{C}]^{4-}$
$\text{Pr}_{15}\text{B}_6\text{C}_{20}$ (Nd) ^d	$[\text{B}_3\text{C}_3]^{7-}$ $[\text{B}_4\text{C}_4]^{9-}$ $[\text{C}]^{4-}$
Sc_2BC_2 (Nd)	$[\text{BC}_2]^{5-}$
$\text{Gd}_5\text{B}_2\text{C}_5$ (Y, Ce–Sm, Gd–Tm)	$[\text{BC}_2]^{5-}$ $[\text{C}]^{4-}$
Lu_3BC_3 (Sc, Gd–Er)	$[\text{BC}_2]^{5-}$ $[\text{C}]^{4-}$
$\text{Sc}_3\text{B}_{0.75}\text{C}_3$	$[\text{BC}_2]^{5-}$ $[\text{C}]^{4-}$
$\text{Tb}_{15}\text{B}_4\text{C}_{14}$ (Gd–Lu) ^c	$[\text{BC}_2]^{5-}$ $[\text{C}]^{4-}$
Pr_2BC (Nd) ^e	$[\text{B}_2\text{C}_2]^{6-}$

^a See Ref. [22].

^b Formal charge assuming cumulenic forms.

^c Ref. [23].

^d Ref. [24].

^e Ref. [25].

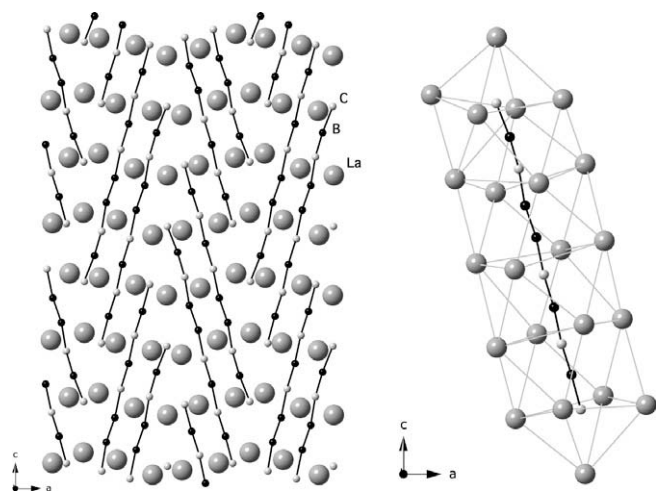
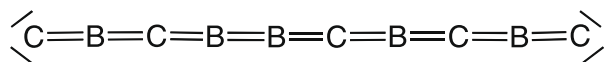


Fig. 6. Structural arrangement of LaBC (left) and metal environment of the B_5C_5 chain (right). Large grey, medium black and small grey spheres represent rare-earth (RE) metal, boron and carbon atoms, respectively.



Scheme 1.

and C atoms simply on the basis of X-ray measurements is not obvious. This is often made on the basis of the chemical environment (carbon likes to be in octahedrally surrounded), the electronegativity (carbon will prefer at the termination of the chain) as well as theoretical calculations. The latter help also to understand the bonding in these rods and the electrical properties of the compounds [22].

With formal double bonds between these atoms, these B_mC_n oligomers are analogs of cumulenic carbons chains C_n^{4-} , i.e., chains with only C–C double bonds, which are rather scarce in molecular chemistry [18]. To obey the octet rule for each atom, a charge of 9– is required for the B_5C_5 unit [26]. Two lone pairs on the terminal carbon atoms and one negative charge for each boron atom in the chain generate the Lewis formula shown in Scheme 1. Indeed theoretical calculations on an isolated $[B_5C_5]^{9-}$ “molecule” indicate a small energy gap separating the highest occupied MO from the lowest unoccupied MO, both of π type [26]. With such a formal anionic charge on the B_5C_5 unit, the La atoms need not to be fully oxidized ($LaBC \equiv [La^{1.8+}]_5[B_5C_5]^{9-}$). Metal electrons must remain in the metallic band and the compound is expected to be an electrical conductor as confirmed by DFT calculations on the 3-D LaBC compound [26]. Of course, there are some covalent interactions between the sub-lattices of the B–C chains and the La atoms, but the Zintl-Klemm idea and the electron counting provide a good estimate of the qualitative electronic structure of the compound.

B_5C_5 encountered in LaBC is not the longest boron–carbon chain observed in this kind of compound. As said earlier, the longest chain, so far, is B_5C_8 , found in $La_{10}B_9C_{12}$ (see Table 2) [22]. As B_5C_5 , B_5C_8 can be considered as a cumulenic-like oligomer with a formal charge of 9–. In principle, there is no reason to stop at this length. We think that if we can adjust the stoichiometry, the size and the electron count, a solid-state compound containing infinite –B–C–B–C– rods with a cumulenic form, that is, with double bonds between B and C atoms should be synthesized. This would constitute another inorganic model for the hypothetical metastable carbyne discussed earlier, but with equi-spaced atoms since the necessity for a Peierls distortion in the infinite carbyne C_∞ chain or $[B^-]_\infty$ chains is removed in an isoelectronic chain with alternating heteroatoms.

4. Concluding remark

The point of this paper we have given here is that, as generally observed for molecules, the electron count matters and governs the structural arrangement of main-group rings or chains contained in solid-state compounds as illustrated with a few examples borrowed to metal borides or borocarbides. Similarities (and differences) between the solids, which were chosen and some organic or organometallic molecules have emerged and their comparison can help in describing and understanding the bonding in both compounds. We hope that the reader read it all and enjoyed the topics somewhat outside the corpus of molecular organometallic chemistry.

Acknowledgment

S. Lassoued is grateful to the University of Biskra, Algeria, for providing her a travel grant. The authors acknowledge the Centre Informatique National de l'Enseignement Supérieur (CINES) for computing facilities.

Appendix A. Computational details

Extended Hückel Tight-Binding (EH-TB) calculations [27] were carried out on isolated boron or boron–carbon layers or chains extracted from X-ray crystallographic structures using the program CAESAR [28]. The exponents (ξ) and valence shell ionization potentials (H_{ii} in eV) were, respectively, as follows: 1.3, –15.2 for B 2s; 1.3, –8.5 for B 2p, and 1.625, –21.4 for C 2s; 1.625, –11.4 for C 2p. Density Functional-Theory (DFT) band structure calculations of $YCrB_4$, $ThMoB_4$, and Y_2ReB_6 were performed with the scalar relativistic tight-binding linear muffin-tin orbital method in the atomic spheres approximation including the combined correction (LMTO) [29] using the program TB-LMTO-ASA 4.7 [30]. These calculations were carried out using the experimental X-ray crystal structures. Exchange and correlation were treated in the local density approximation using the von Barth-Hedin local exchange correlation potential [31]. The k -space integration was performed using the tetrahedron method [32]. Charge self-consistency and average properties were obtained from 135, 1710, and 90 irreducible k -points for the calculations of $YCrB_4$, $ThMoB_4$, and Y_2ReB_6 , respectively. The DOS curves were shifted so that the Fermi level lies at 0 eV. Geometry optimizations of $YCrB_4$ and $ThMoB_4$ were performed with the CASTEP 4.3 code [33] with Projector Augmented-Wave potentials [34] using the PBE functional [35]. Both structure-types were considered for the two compounds. A cut-off energy of 500 eV was used for all compounds. The Brillouin zone was sampled with 30 irreducible k -points calculated using a Monkhorst-Pack scheme. Structural details are provided as Supporting information.

Appendix B. Supplementary material

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorgchem.2009.11.037.

References

- [1] (a) See for example: R. Hoffmann, *Solids and Surfaces, A Chemist's View of Bonding in Extended Structures*, VCH, New York, USA, 1988; (b) T.P. Fehlner, J.-F. Halet, J.-Y. Saillard, *Molecular Clusters. A Bridge to Solid State Chemistry*, Cambridge University Press, Cambridge, UK, 2007.
- [2] See for example: T. Mori, in: K.A. Gschneidner, Jr., J.-C. Bunzli, V. Pecharsky (Eds.), *Handbook on the Physics and Chemistry of Rare Earths, Higher borides*, North-Holland, Amsterdam, 2008, pp. 105–173.
- [3] Yu.B. Kuzma, *Sov. Phys. Crystallogr.* 15 (1970) 312.
- [4] P. Rogl, H. Nowotny, *Monatsh. Chem.* 105 (1974) 1082.
- [5] Yu.B. Kuzma, S.I. Svarichevskaya, *Kristallografiya* 17 (1972) 658.
- [6] (a) Yu.B. Kuzma, *Crystal Chemistry of Borides*, Vyscha Shkola, Lviv, 1983.; (b) Yu.B. Kuzma, N.F. Chaban, *Binary and Ternary Systems containing Boron*, Metallurgia, Moscow, 1990.; (c) E. Villars, L.D. Calvert, *Pearson's Handbook of Crystallographic Data for Intermetallic Phases*, second ed., vol. 2, ASM International, Materials Park, OH, 1991.
- [7] R.T. Makaluso, S. Nakatsukui, K. Kuga, E.L. Thomas, Y. Machida, Y. Maeno, Z. Fisk, J.Y. Chan, *Chem. Mater.* 19 (2007) 1918.
- [8] (a) T. Mori, H. Borrmann, S. Okada, K. Kudou, A. Leithe-Jasper, U. Burkhardt, Yu. Grin, *Phys. Rev. B* 76 (2007) 064404; (b) I. Veremchuk, T. Mori, Yu. Prots, W. Schnelle, A. Leithe-Jasper, M. Kohout, Yu. Grin, *J. Solid State Chem.* 181 (2008) 1983.
- [9] J. Nagamatsu, N. Nakagawa, T. Muranaka, Y. Zenitani, J. Akimitsu, *Nature* 410 (2001) 63.
- [10] N.I. Medvedeva, Yu.E. Medvedeva, A.L. Ivanovskii, *Dokl. Phys. Chem.* 383 (2002) 75.
- [11] G.S. Smith, Q. Johnson, P.C. Nordine, *Acta Crystallogr.* 19 (1965) 668.
- [12] (a) F. Edelmann, S. Töfke, U. Behrens, *J. Organomet. Chem.* 308 (1986) 27; (b) J.J. Schneider, U. Denninger, *Z. Anorg. Allg. Chem.* 630 (2004) 1908; (c) S. Balduzzi, H. Müller-Bunz, M.J. McGlinchey, *Chem. Eur. J.* 10 (2004) 5398; (d) S. Bendjaballah, S. Kahlal, K. Costuas, E. Bévilion, J.-Y. Saillard, *Chem. Eur. J.* 12 (2006) 2048; (e) J. Zhang, S. Petoud, *Chem. Eur. J.* 14 (2008) 1264.
- [13] J.K. Burdett, S. Lee, T.J. McLarnan, *J. Am. Chem. Soc.* 107 (1985) 3063.
- [14] J.K. Burdett, *J. Phys. Chem.* 87 (1983) 4368.
- [15] X. Rocquefelte, S.E. Boulfelfel, M. Ben, Yahia J. Bauer, J.-Y. Saillard, J.-F. Halet, *Angew. Chem., Int. Ed.* 44 (2005) 7542.

- [16] (a) J.K. Burdett, E. Canadell, T. Hughbanks, *J. Am. Chem. Soc.* 108 (1986) 3971;
(b) J.M. Olivia, M. Llunell, P. Alemany, E. Canadell, *J. Solid State Chem.* 176 (2003) 375.
- [17] (a) R. Eastmond, T.R. Johnson, D.R.M. Walton, *Tetrahedron* 28 (1972) 4601;
(b) S. Kim, *Angew. Chem. Int. Ed.* 48 (2009) 7740;
(c) W.A. Chalifoux, R. McDonald, M.J. Ferguson, R.R. Tykwinski, *Angew. Chem. Int. Ed.* 48 (2009) 7910.
- [18] (a) See for example: S. Szafert, J.A. Gladysz, *Chem. Rev.* 103 (2003) 4175;
(b) S. Szafert, J.A. Gladysz, *Chem. Rev.* 106 (2006) PR1.
- [19] Q. Zheng, J.C. Bohling, T.B. Peters, A.C. Frisch, F. Hampel, J.A. Gladysz, *Chem. Eur. J.* 12 (2006) 6486.
- [20] M. Wörle, R. Nesper, *Angew. Chem., Int. Ed.* 39 (2000) 2349.
- [21] (a) R. Pöttgen, W. Jeitschko, *Inorg. Chem.* 30 (1991) 427;
(b) R. Pöttgen, W. Jeitschko, *Z. Naturforsch., Teil B* 47 (1992) 358.
- [22] (a) J. Bauer, J.-F. Halet, J.-Y. Saillard, *Coord. Chem. Rev.* 178–180 (1998) 723;
(b) M. Ben Yahia, J. Roger, X. Rocquefelte, R. Gautier, J. Bauer, R. Guérin, J.-Y. Saillard, J.-F. Halet, *J. Solid State Chem.* 179 (2006).
- [23] V. Babizhetskyy, Hj. Mattausch, A. Simon, unpublished results.
- [24] V. Babizhetskyy, Hj. Mattausch, K. Hiebl, A. Simon, M. Ben Yahia, R. Gautier, J.-F. Halet, *J. Solid State Chem.* 181 (2008) 1882.
- [25] V. Babizhetskyy, Hj. Mattausch, A. Simon, *Z. Anorg. Allg. Chem.* 632 (2006) 2115.
- [26] (a) V. Babizhetskyy, Hj. Mattausch, A. Simon, R. Gautier, J. Bauer, J.-F. Halet, *Z. Anorg. Allg. Chem.* 631 (2005) 1041;
(b) V. Babizhetskyy, K. Hiebl, Hj. Mattausch, A. Simon, *Solid State Sci.* 11 (2009) 501.
- [27] (a) R. Hoffmann, *J. Chem. Phys.* 39 (1963) 1397;
(b) M.-H. Whangbo, R. Hoffmann, R.B. Woodward, *Proc. R. Soc. Lond. A* 366 (1979) 23;
(c) M.-H. Whangbo, R. Hoffmann, *J. Am. Chem. Soc.* 100 (1978) 6093.
- [28] J. Ren, W. Liang, M.-H. Whangbo, *Crystal and Electronic Structure Analysis Using CAESAR*, 1998, <<http://www.primec.com>>.
- [29] (a) O.K. Andersen, *Phys. Rev. B* 12 (1975) 3060;
(b) O.K. Andersen, *Europhys. News* 12 (1981) 4;
(c) O.K. Andersen, in: P. Phariseau, W.M. Temmerman (Eds.), *The Electronic Structure of Complex Systems*, Plenum Publishing Corporation, New York, 1984;
(d) O.K. Andersen, O. Jepsen, *Phys. Rev. Lett.* 53 (1984) 2571;
(e) H.L. Skriver, *The LMTO Method*, Springer-Verlag, Berlin, 1984;
(f) O.K. Andersen, O. Jepsen, M. Sob, in: M. Yussouf (Ed.), *Electronic Band Structure and Its Application*, Springer-Verlag, Berlin, 1986.
- [30] G. Krier, O. Jepsen, A. Burkhardt, O.K. Andersen, *The TB-LMTO-ASA program*, version 4.7, Max-Planck-Institut für Festkörperforschung, Stuttgart, Germany.
- [31] U. von Barth, L. Hedin, *J. Phys. C* 5 (1972) 1629.
- [32] P.E. Blöchl, O. Jepsen, O.K. Andersen, *Phys. Rev. B* 49 (1994) 16223.
- [33] M.D. Seagall, P.J.D. Lindan, M.J. Probert, C.J. Pickard, P.J. Hasnip, S.J. Clark, M.C. Payne, *Condens. Matter* 14 (2002) 2717.
- [34] P.E. Blöchl, *Phys. Rev. B* 50 (1994) 17953.
- [35] J.P. Perdew, S. Burke, M. Ernzerhof, *Phys. Rev. Lett.* 77 (1996) 3865.