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First-principles study of ternary metal borocarbide compounds containing finite linear BC_2 units

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Abstract

Electronic structures of the ternary metal borocarbide compounds Sc_2BC_2, Al_3BC_3 and Lu_3BC_3 containing linear BC_2 units are compared using density functional calculations. Results reveal a covalent bonding between the metallic matrix and the formally BC_2^{5-} nonmetal anions which is stronger for the aluminum compound than for the two others.

Keywords: Rare-earth metal borocarbide; Aluminum borocarbide; Electronic structure; Density functional calculations

1. Introduction

The structural chemistry of boron-containing compounds is particularly rich and varied [1–4]. It includes ternary rare-earth metal borocarbide solid state materials of formula $M_xB_yC_z$ (M = Sc, Y, Ln, An), which constitute a growing family offering a broad diversity of original topologies, most of them unique, especially with respect to the bonding within the nonmetal framework [5]. In these compounds, boron and carbon atoms generally form either two-dimensional (2D) networks, which alternate with 2D sheets of metal atoms, or one-dimensional (1D) carbon branched zigzag boron chains running into channels built by the metal atoms, or finite pseudo-molecules of various sizes trapped into holes built by the metallic matrix. The dimensionality of the nonmetal network is related to its electron richness, which can be approximately evaluated through the average valence electron count (VEC) per nonmetal atom, assuming fully oxidized (usually M^{3+}) metal atoms [5]. The lowest VEC (typically between 4.2 and 4.6) are found for the compounds containing 2D nonmetal networks. Compounds containing 1D arrangements of nonmetal atoms have larger VEC values, ranging between 5 and 5.4. The largest VEC are found for the phases containing finite nonmetal units. In these latter compounds, the C–B–C chain is one of the most encountered unit [5–8]. Sc_2BC_2 is the unique compound where only BC_2 chains are present in the structure [9]. As shown in Fig. 1, each carbon atom is surrounded by five scandium atoms and one boron atom that form an octahedron. Linear BC_2 units exhibit short internuclear B–C distances of 1.4747(1) Å. Close Sc–Sc contacts are observed along the *a* or *b* directions (3.300 Å) and in the (110) planes (3.144 Å). Few years ago, the aluminum borocarbide Al_3BC_3 has been characterized [10]. Isolated C atoms are located at the center of Al_5 trigonal bipyramids which are linked by common vertices of the basal plane to give layers of the composition Al_3C, similar to Al_4C_3 (see Fig. 1). Linear CBC units with a B–C distance of 1.441(2) Å are located between these Al_3C layers. Recently, a lutetium boride carbide with the same stoichiometry but a somewhat different crystal structure, Lu_3BC_3, was synthesized [6]. Lu_3BC_3 is also made of slabs of isolated carbon atoms in a metallic environment connected by linear CBC units (B–C= 1.446(7) Å). However, in the case of Lu_3BC_3 the linear

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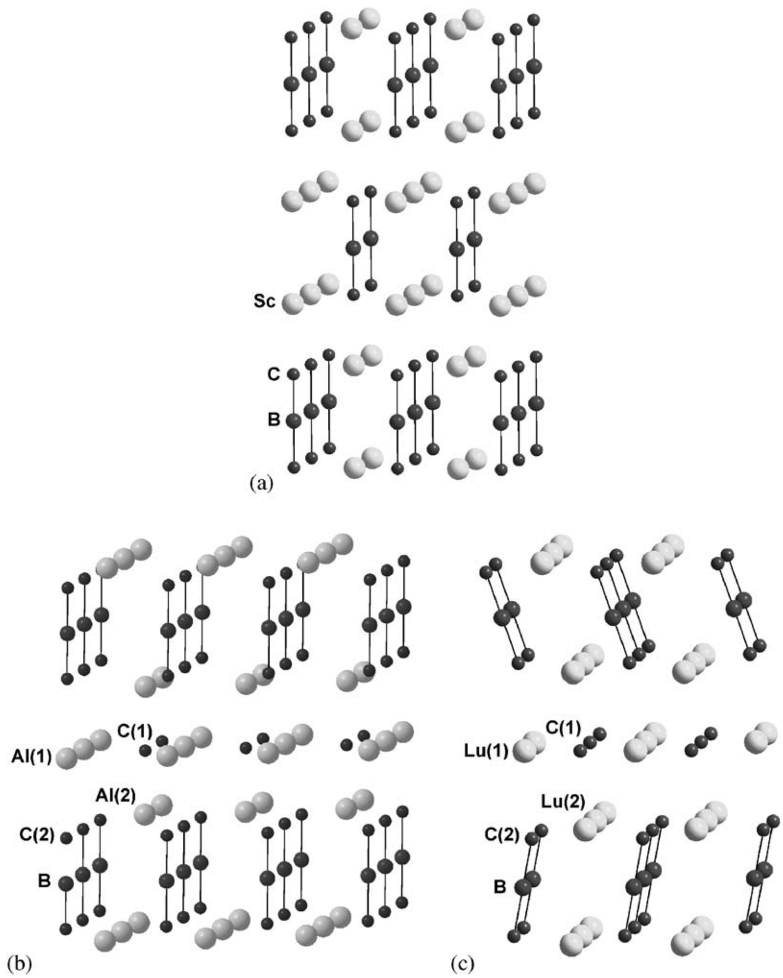

Fig. 1. The crystal structures of Sc_2BC_2 (a), Al_3BC_3 (b), and Lu_3BC_3 (c).

CBC units are located inside bicapped elongated cubes of metal atoms, whereas in Al_3BC_3 they are located in trigonal antiprisms (see Fig. 1).

Previous theoretical studies of Sc_2BC_2 and Lu_3BC_3 have shown that the bonding in these compounds can be in a first approximation described within the $(Sc^{2.5+})_2(BC_2{}^{5-})$ and $(Lu^{3+})_3(C^{4-})(BC_2{}^{5-})$ ionic formalisms, respectively [6,9a]. In this description, the formal charge of 5- attributed to the CBC units fulfills the closed-shell requirement, rendering them isoelectronic to CO_2 or $(N_3)^-$ and accounting for their linearity and for the short B–C separation. Linear isoelectronic anions such as $(C_3{}^{4-})$, (CBN^{4-}) or (NBN^{3-}) are also encountered in the solid state [11–14].

Obviously, the bonding description of Al_3BC_3 within the ionic limit is similar to that of Lu_3BC_3, i.e., $(Al^{3+})_3(C^{4-})(BC_2{}^{5-})$. However, no theoretical calculation on this phase has been carried out, so far. Moreover, it should be interesting to compare the electronic structure of Al_3BC_3 with that of Lu_3BC_3 and Sc_2BC_2, by using the same computational method. Therefore density functional (DF) calculations were conducted within the LMTO formalism on Al_3BC_3, as well as on Lu_3BC_3 and Sc_2BC_2, for the sake of comparison. It should also be noted that this paper reports the first accurate theoretical investigation of Sc_2BC_2.

2. Computational section

The self consistent ab initio band structure calculations of Sc_2BC_2, Al_3BC_3, and Lu_3BC_3 were performed with the scalar relativistic tight-binding linear muffin-tin orbital method in the atomic spheres approximation including the combined correction (LMTO) [15]. Exchange and correlation were treated in the local density approximation using the von Barth-Hedin local exchange correlation potential [16]. Within the LMTO formalism, interatomic spaces are filled with interstitial spheres. The optimal positions and radii of these additional "empty spheres" (ES) were determined by the procedure described in Ref. [17]. One non-symmetry-related ES with $r_{ES} = 0.96$ Å was introduced for the calculations on Sc_2BC_2, as well as three and six non-symmetry-related ES with $0.56\,\text{Å} \leqslant r_{(ES)} \leqslant 1.40\,\text{Å}$ and $0.56\,\text{Å} \leqslant r_{(ES)} \leqslant 1.09\,\text{Å}$ for the calculations on Al_3BC_3 and Lu_3BC_3, respectively.

The full LMTO basis set consisted of 6*s*, 6*p*, 5*d* and 4*f* functions for Lu spheres, 4*s*, 4*p*, and 3*d* functions for Sc spheres, 3*s*, 3*p*, and 3*d* functions for Al spheres, 2*s*, 2*p* and 3*d* functions for B and C spheres and *s*, *p* and *d* functions for ES. The eigenvalue problem was solved using the following minimal basis set obtained from Löwdin downfolding technique: Lu (6*s*, 5*d*, 4*f*), Sc (4*s*, 3*d*), Al (3*s*, 3*p*), B (2*s*, 2*p*), C (2*s*, 2*p*) and ES (1*s*). The *k* space integration was performed using the tetrahedron method [18]. Charge self-consistency and the average properties for Sc_2BC_2, Al_3BC_3, and Lu_3BC_3 were obtained from 349, 148, and 364 irreducible *k* points, respectively. The density of states (DOS) and crystal orbital Hamiltonian population (COHP) [19] curves have been shifted so that the Fermi level lies at 0 eV.

3. Results and discussion

Since the crystallographic structure of Sc_2BC_2 shows only BC_2 units (and no other nonmetal group), its electronic structure is presented at first. COHP indicating energetic contribution of crystal orbitals between orbitals and/or atoms were computed for several contacts in the structure [19]. The resulting curves are sketched in Fig. 2 with total and projected DOS curves. The DOS peak lying below −10 eV is mainly composed of B and C orbitals. These levels contribute strongly to the B–C bonding energy as well as the DOS peak that lies between ca. −5 and −1 eV. An integrated COHP (ICOHP) value of –0.729 Ry/cell is computed for B–C bonds. The Fermi level cuts a weak B–C antibonding DOS peak. Some weakly B–C bonding levels are located at higher energy, between ca. 2 and 5 eV, below strongly B–C antibonding levels. Similar behavior were computed for the crystal orbital overlap population using extended Hückel (EH) calculations for Sc_2BC_2 [9a]. It has been shown that B–C antibonding DOS peak around the Fermi level mainly derives from the π_u^* molecular orbital (MO) of the BC_2 fragments whereas the B–C bonding levels that lie just above show a strong character of the π_g MO of the BC_2 unit. Such results are consistent with the formal charge of 5 assigned to the BC_2 units [9a]. The main difference between the EH and DF DOS curves is the occurrence of a gap of ca. 1 eV appearing 0.5 eV below the Fermi level, in the EH one. This gap separates occupied bands which mainly derive from the BC_2 units from the metallic *d*-band, of which the very bottom is occupied (formal metal charge: +2.5). Such a gap does not exists in the DF DOS, indicating stronger covalent interaction between the metallic atoms and the BC_2 units. Consistently, an averaged ICOHP value of −0.151 Ry/cell is computed for the Sc–C bonds. A significant contribution of the Sc atoms is observed in the occupied levels. Very weak metal–metal interaction occurs as shown by the computed value of –0.027 Ry/cell for the shortest Sc–Sc distances. According to the DOS curve, electric conduction is expected.

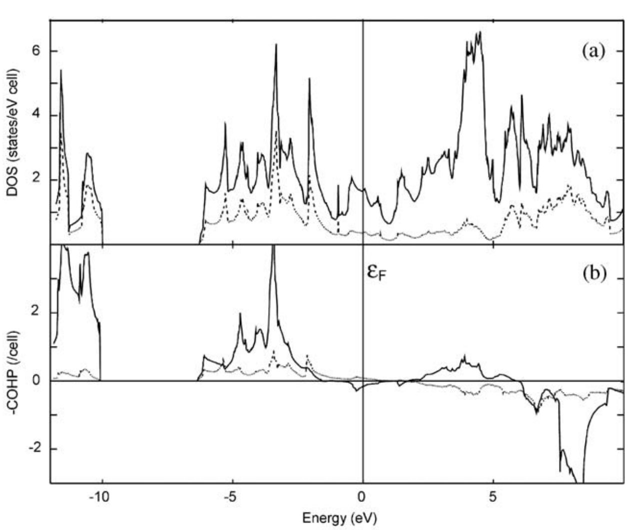

Fig. 2. LMTO calculations for Sc_2BC_2: (a) Total DOS (solid) and BC_2 contribution (dotted), (b) B–C (solid) and Sc–C (dotted) COHPs for B–C bonds equal to 1.4747 Å and Sc–C bonds ranging from 2.238 to 2.338 Å.

As said above, the Al_3BC_3 structure exhibits AlC nets which alternate with Al_2BC_2 layers. Isolated C(1) atoms are surrounded by 5 aluminum atoms that form a trigonal bipyramid, the vertices of which are Al atoms of the Al_2BC_2 nets. The computed DOS of Al_3BC_3 shown in Fig. 3 is separated into three parts. The lowest part extending over the energy range −13 to −10 eV derives predominantly from the *s* orbitals of the Al, B and C atoms whereas the highest occupied part is made up mainly from the *p* orbitals of these elements. Decomposition of the different constituting groups indicates a strong covalent interaction between the metal cations and the (BC_2^{5-}) and C^{4-} anions, as evidenced by the presence of a metallic participation into the boron–carbon occupied bands, and vice versa some participation of the BC_2 groups and C atoms in higher vacant bands. Significant ICOHP values of −0.301 Ry/cell and −0.209 Ry/cell for the Al(1)–C(1) and Al(2)–C(1), respectively, and −0.240 Ry/cell for the Al(2)–C(2) are computed. Considering that Al–C distances are of the same order as in the aluminum carbide Al_4C_3 [20] (average Al–C distances are equal to 2.02 Å), such strong interaction were foreseen as in the binary compound. This latter value is much stronger than that between metal atoms and the C atoms of the BC_2 groups in Sc_2BC_2. Compared to this latter compound, the double bonds of the BC_2 groups are computed to be

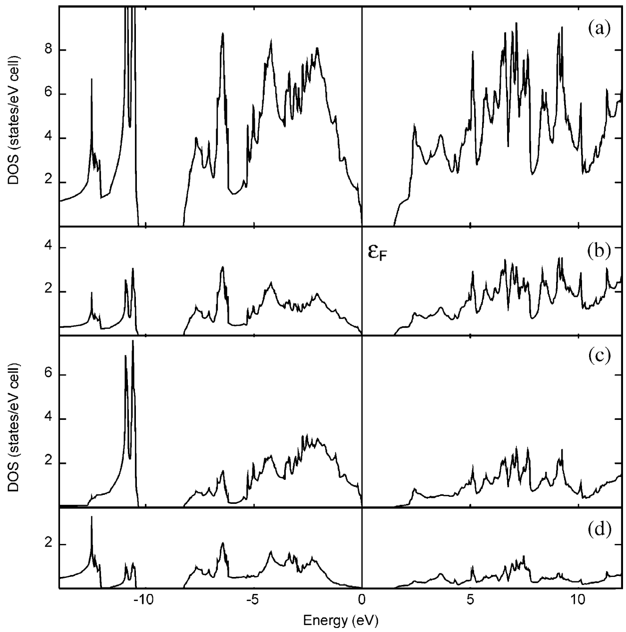

Fig. 3. LMTO calculations for Al_3BC_3: (a) Total DOS, (b) Al contribution, (c) BC_2 contribution, (d) C(1) contribution.

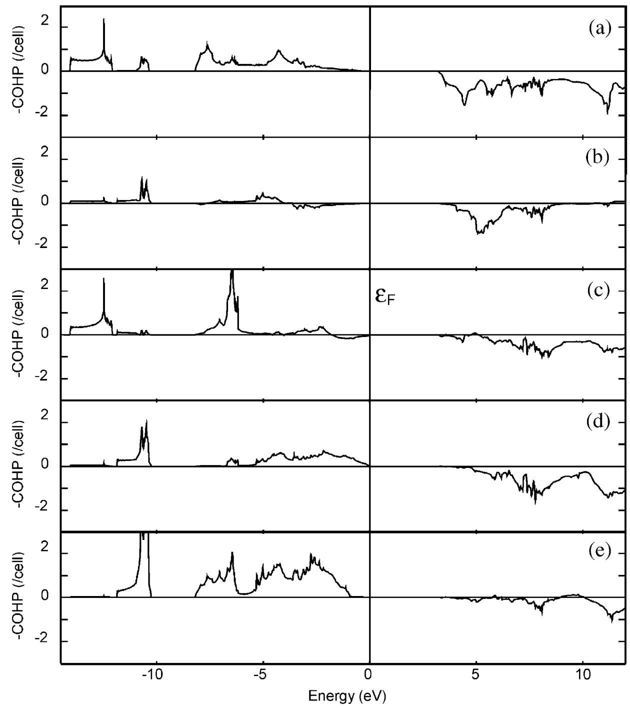

Fig. 4. LMTO COHP calculations for Al_3BC_3: (a) Al(1)–C(1) (1.967 Å), (b) Al(1)–C(2) (2.531 Å), (c) Al(2)–C(1) (2.027 Å), (d) Al(2)–C(2) (2.031 Å), (e) B–C(2) (1.441 Å).

weaker, B–C ICOHP value is equal to –0.632 Ry/cell, although the B–C bond is shorter (1.441 Å to be compared to 1.4747 Å in Sc_2BC_2). This ICOHP difference is consistent with the more covalent character of the Al–C interaction in Al_3BC_3 (averaged Al–C(2) ICOHP is equal to –0.224 Ry/cell whereas averaged Sc–C ICOHP in Sc_2BC_2 is equal to –0.165 Ry/cell). That induces a poorer electronic transfer of the Al atoms to the BC_2. Less electrons are therefore localized on the BC_2 chains and the B–C double bond is weaker. This significant ICOHP difference is not observed in the experimental B–C distances which hardly differ in the three compounds owing to their standard deviations [6,9b,10]. We suggest that the relative size of the metallic cage in the three compounds must be at the origin of the difference in the experimental B–C distances. BC_2 units are located in trigonal antiprisms of metal atoms in Al_3BC_3 that are smaller than the elongated cubes of metal atoms that surround the BC_2 chains in Sc_2BC_2. The more important interaction that occurs in the aluminum compound is also shown by the larger occupied DOS peak which lies just below the Fermi level. These bands are notably at the origin of the metal–carbon interaction as shown by the COHP curves sketched in Fig. 4. All the occupied bands are bonding or non-bonding with respect to the Al–C and B–C contacts, whereas vacant bands show antibonding characters of the same bonds. A band gap of ca. 2 eV separates the occupied bands from the vacant ones. Such a band gap is consistent with the yellow color of the Al_3BC_3 crystals. Resistivity measurements were not carried out for Al_3BC_3 but the DOS curve suggests a semiconducting behavior.

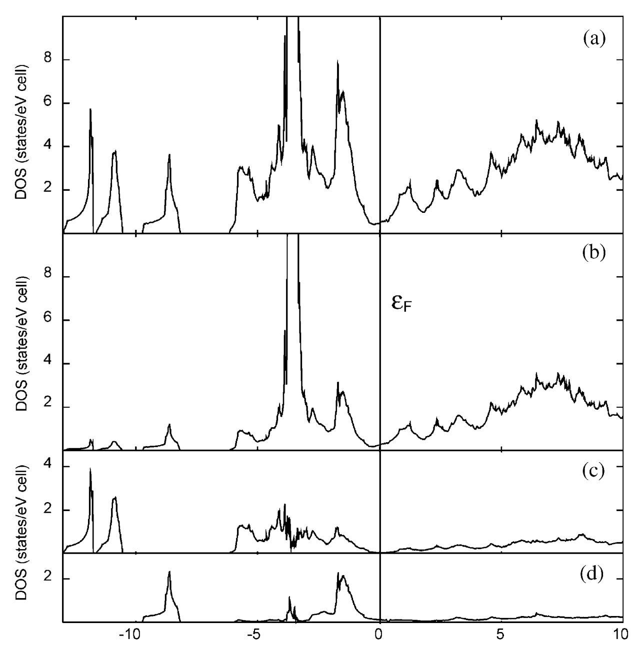

Fig. 5. LMTO calculations for Lu_3BC_3: (a) Total DOS, (b) Lu contribution, (c) BC_2 contribution, (d) C(1) contribution.

As said above, the difference between the crystal structure of Lu_3BC_3 and Al_3BC_3 lies in the metallic environment of the BC_2 chains. Moreover, BC_2 chains

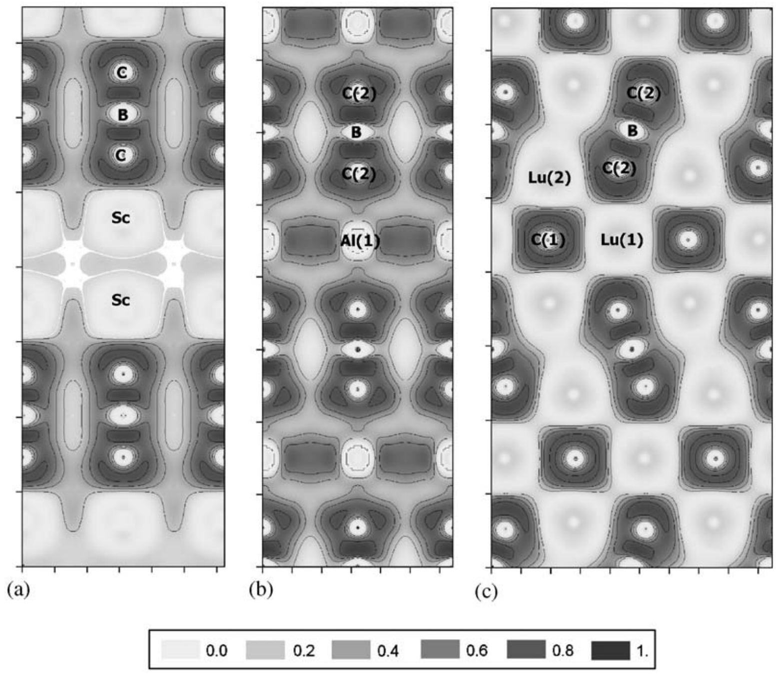

Fig. 6. ELF plots (LMTO) in the (100) planes for: (a) Sc_2BC_2, (b) Al_3BC_3, (c) Lu_3BC_3.

are not parallel to the *c*-axis in Lu_3BC_3. Total and projected DOS curves of Lu_3BC_3 are shown in Fig. 5. Our results are very similar to previous ones obtained using LAPW method [6] and will not be commented in detail here. A significant covalent interaction occurs between rare-earth metal and C atoms (both isolated and from the BC_2 chains) as well as a weak one between Lu atoms and a strong one between main group atoms in the BC_2 chains. LMTO calculations are in agreement with this important interaction. For instance, an ICOHP value of -0.724 Ry/cell is computed between B and C(2) in BC_2 units, and the higher Lu–Lu ICOHP value is equal to -0.004 Ry/cell. Lu-isolated C atoms ICOHP are weaker than Al-isolated C in Al_3BC_3, the strongest interaction exhibits an ICOHP value of -0.137 Ry/cell. All those ICOHP results show a more important ionic character of this compound than the aluminum borocarbide.

Further insight in the nature of the bonding in these compounds can be provided by the electron localization function (ELF) [21]. Being directly related to the electron pair probability density, its graphical representation can contribute to the understanding of electron localization. ELF values vary from 0 to 1, the upper limit corresponding to perfect electron-pair localization. Consequently, high ELF values correspond to regions of space of localized electrons with antiparallel spins. Two-dimensional electron density distribution plots in planes containing the BC_2 units are sketched in Fig. 6 for Sc_2BC_2, Al_3BC_3, and Lu_3BC_3. All plots show an important localization domain between boron and carbon atoms (black areas), demonstrating bonding interactions typical of strong covalent bonds. Localization domains can also be identified around the carbon atoms of the BC_2 entities, typical of lone electron pairs. This supports the (BC_2^{5-}) Lewis model with double B–C bonds and two lone pairs localized on each C atoms.

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