

Portraits of some representatives of metal boride carbide and boride silicide compounds[☆]

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Abstract

Different ternary alkaline-earth and rare-earth metal boron carbide and silicide compounds are examined using the solid-state language of Zintl–Klemm concept, band structures, and density of states, in order to show that the topology of the non-metal sub-lattice is highly dependent on the electron count. It is also shown that the chemistry of rare-earth metal–boron–silicon does not parallel that of rare-earth metal–boron–carbon. B–C bonds are easily formed in the latter, leading to a large variety of different structural arrangements, whereas Si–B bonds are hardly observed in the former, except in insertion compounds.

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1. Introduction

Solid state chemists have shown over the last 30 years or so that the combination of boron and carbon with rare-earth metals (RE) leads to the formation of original ternary compounds with interesting structural arrangements [1,2]. These rare-earth boron carbide compounds are generally prepared by arc-melting technique and are rather difficult to handle. They are moisture sensitive and without care they decompose easily forming metal hydroxides, and hydrocarbon and hydroboron species. A non-exhaustive list of the different ternary compounds characterized either by X-ray or neutron diffraction techniques, is given in Table 1.

It has been shown that these rare-earth metal–boron–carbon compounds can be classified in three different families according to the structural arrangement of the B/C

network, which, indeed, depends upon the *averaged valence electron concentration* (VEC) per main group atom [2]. Given a formula $RE_xB_yC_z$, this number is obtained considering the Zintl–Klemm approach [29], which assumes that the metal transfers completely its valence electrons to the B/C framework. Addition of these electrons to those brought by the boron and carbon atoms, divided by the number of light atoms leads to the VEC. This number increases as the dimensionality of the non-metal framework decreases. With a VEC slightly larger than 4, the B and C atoms form two-dimensional (2D) layers alternating with metallic sheets. With a VEC around 5, B and C atoms depict one-dimensional (1D) infinite zigzag and branched chains running in metallic channels. Finally, for a VEC larger than 5, the B and C atoms form finite (0D) and more or less linear chains trapped into metallic cavities. Indeed, the augmentation of the VEC corresponds to formal population of antibonding orbitals of the B/C network, which leads to breaking of bonds and thus diminishes its dimensionality. Such an ionic approach to “rationalize” the B/C sub-lattice in these compounds must be considered as only approximate since, as we will see below, the metals need not always to be fully oxidized

[☆] Dedicated to the memory of Professor Yu. Paderno in recognition of his important contribution to boron solid state chemistry.

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Table 1
Different $RE_xB_yC_z$ rare earth metal boron carbides structurally characterized. The VEC is calculated assuming trivalent metals

| Structural type | VEC ^a | B–C network | Ref. |
|--|-------------------|---|--------|
| <i>2D networks</i> | | | |
| LaB ₂ C ₂ (Y) | 4.25 | $\frac{2}{\infty} [B_2C_2(B_4C_4)^2]$ | [3–5] |
| CeB ₂ C ₂ (Pr, Nd, Dy, Ho) | 4.25 | $\frac{2}{\infty} [B_2C_2(B_4C_4)^2]$ | [6] |
| ScB ₂ C ₂ | 4.25 | $\frac{2}{\infty} [B_3C_2(B_4C_3)^2(B_3C_2)^2B_4C_3]$ | [7] |
| YB ₂ C (Sc, Tb–Lu) | 4.33 | $\frac{2}{\infty} [B_2C_2(B_3C_2)^2]$ | [4,8] |
| ThB ₂ C (Ce, U ^b , Np, Pu) | 4.33 | $\frac{2}{\infty} [B_6(B_6C_3)^2]$ | [9,10] |
| α -UB ₂ C ^c | 4.33 | $\frac{2}{\infty} [(B_6C_2)^2]$ | [11] |
| Gd ₂ B ₃ C ₂ | 4.60 | $\frac{2}{\infty} [(B_8C_4)^3]$ | [12] |
| Sc ₂ B _{1.1} C _{3.2} | 5.13 | $[C]_{\infty}^2 [(BC_2)^3]$ | [13] |
| <i>Infinite branched chains</i> | | | |
| YBC (Dy, Ho, Er) | 5.00 | $\frac{1}{\infty} [B_2C_2]$ | [4] |
| ThBC | 5.00 | $\frac{1}{\infty} [B_2C_2]$ | [14] |
| UBC (Np, Pu) | 5.00 | $\frac{1}{\infty} [B_2C_2]$ | [15] |
| UB _{0.78} C _{1.22} | 5.11 | $\frac{1}{\infty} [B_2C_2]$ | [16] |
| Th ₃ B ₂ C ₃ | 5.00 ^d | $[C]_{\infty}^1 [B_2C_2]$ | [17] |
| Gd ₄ B ₃ C ₄ | 5.29 | $[BC_2]_{\infty}^1 [B_2C_2]$ | [18] |
| <i>Finite-linear chains</i> | | | |
| La ₁₅ B ₁₄ C ₁₉ | 4.94 | $[B_4C_7][B_5C_6]$ | [19] |
| LaBC (Ce, Pr, Nd, Sm) | 5.00 | $[B_5C_5]$ | [20] |
| Ce ₁₀ B ₉ C ₁₂ (La, Nd) | 5.00 | $[B_3C_8][B_4C_4]$ | [21] |
| Ce ₅ B ₄ C ₅ (La) | 5.22 | $[B_4C_4][B_3C_3][BC_2][C]$ | [22] |
| La ₅ B ₂ C ₆ (Ce, Nd, Gd, Ho) | 5.63 | $[BC_3][C]$ | [23] |
| Sc ₂ BC ₂ (Nd) | 5.67 | $[BC_2]$ | [24] |
| Gd ₅ B ₂ C ₅ (Sm) | 5.86 | $[BC_2][C]$ | [25] |
| Nd ₂₅ B ₁₂ C ₂₈ | 5.57 | $[B_2C_4][B_3C_3][BC_2][C]$ | [26] |
| Lu ₃ BC ₃ | 6.00 | $[BC_2][C]$ | [27] |
| Sc ₃ B _{0.75} C ₃ | 6.20 | $[BC_2][C]$ | [28] |

^aAveraged valence electron count per main group atom.

^bHigh temperature.

^cLow temperature.

^dValue assuming the formal topochemical separation: ThC + 2ThBC + Th₂B₃C₂.

to fulfil the electronic requirements of the anionic B/C network. Moreover, calculating the VEC does not provide any information about the local environment of the boron and carbon atoms in these materials. Therefore, a deeper insight is necessary to get details about the bonding in these materials with the help of quantum chemical methods. This has been done thoroughly on most of the $RE_xB_yC_z$ compounds with various theoretical analyses, particularly in our laboratory over the last years [2]. Recently, we have revisited the *coloring* problem in the REB_2C_2 phases [30], we have speculated on the possible existence of hypothetical REB_2C compounds [2,31], as well as investigated on the electronic structure of new finite B/C chain-containing materials [2,20]. We are now extending the RE –B–C chemistry to that of RE –B–Si.

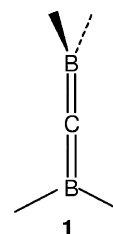
Some of these works are reported or recalled here in order to illustrate how we can rationalize the structural arrangement and some of the physical properties of this kind of compound, how we can understand their bonding in a simple way, which is directly linked to the electron donor ability of the metals to stabilize the electron deficient

boron–carbon networks. We need numbers to do this, numbers generally obtained from various types of band structure calculations.

2. The hypothetical MgB₂C compound

REB_2C layered compounds made of alternate boron–carbon and metallic sheets constitute an important class of rare-earth metal boron carbides. Up to now, three structural types have been reported for the REB_2C phases, namely YB₂C [4], ThB₂C [9], and α -UB₂C [12]. They differ significantly from their topologies within the boron and carbon networks. Tri-connected sp^2 B and C atoms form heptagons and rhombuses, with the metal atoms located above and below the heptagons in YB₂C. In contrast, boron hexagons fused with nine-membered rings of boron and carbon atoms are found in ThB₂C, whereas α -UB₂C phase shows fused eight-membered rings of light atoms. Tri-connected sp^2 boron atoms and two-connected sp carbon atoms are encountered in both ThB₂C and α -UB₂C. Thus the full arrangement of the B/C layers is different, but the local arrangement around the B and C atoms is identical. Both layers can be built from the same linear B–C–B repeat motif. Experimentally measured B–B and B–C distances of ca. 1.8 and 1.5 Å, respectively, are comparable in both compounds and correspond roughly to single and (partial) double bonds, respectively.

Interested in the bonding in these compounds, the first question which arises is the following: what is the formal oxidation state of the B₂C repeat unit which account for such planar arrangements? Previous theoretical works have showed that a planar arrangement with sp^2 B atoms and sp C atoms, encountered in ThB₂C and α -UB₂C is stable for a formal charge equal or close to 4– [31]. Therefore, metals such as Th or U able to have an oxidation state of IV are needed to counterbalance the negative charge. With a trivalent metal such as Y, another arrangement is observed, still planar but with three-connected sp^2 B and C atoms. We may wonder what would happen for a network of linear $(B_2C)^{2-}$ units? Another arrangement is expected. Calculations performed on molecular models mimicking the $(B_2C)^{2-}$ unit have showed that this is an allenic-like system with B–C double bonds, similar to allene C₃H₄ which has a local D_{2d} symmetry [31]. Therefore such a formal charge is not consistent with the two sp^2 boron atoms being coplanar. It is expected to adopt a non-planar geometry instead, in which the boron coordination planes are perpendicular to each other (see 1).



It is possible in turn to construct an MB_2C structure based on the assemblage of allenic-like $(B_2C)^{2-}$ motifs and divalent metals M . As shown in Fig. 1a, a 3D boron–carbon arrangement is obtained with holes in which the M atoms could reside. Assuming typical B–B single bond and B–C double bond distances (ca. 1.8 and 1.5 Å, respectively), the M – M separations would be 3.12 Å. Such short distances preclude using large divalent Eu or Yb RE. A good candidate would be the alkaline-earth metal Mg instead. Another way to look at the B/C network of this hypothetical structure is to consider layers of isolated infinite zigzag boron chains running perpendicular to each other, linked by linear sp carbon atoms.

The geometry of such an arrangement (space group: $I4_1/amd$) was optimized at the DFT level of theory. B–B and B–C computed distances of 1.78 and 1.46 Å are in agreement with formal B–B single bonds and B–C double bonds. This is supported by an electron localization function (ELF) analysis carried out at the TB-LMTO-ASA level (LMTO). ELF which is related to the electron pair probability density [32] indicates basins with bean-like shape between boron atoms and with spherical shape between boron and carbon atoms, corresponding to single and double bonds, respectively (see Fig. 1b). Integration of the valence electron density within these basins gives 2.4 electrons for B–B bonds and 3.6 electrons for B–C bonds. Examination of the B–B and B–C crystal orbital Hamiltonian populations (COHP) [33] shows a change from bonding to antibonding roughly at the Fermi level, indicating that both B–B and B–C interactions are maximized. Integrated COHP (ICOHP) values of -0.373

and -0.682 Ry/cell are computed for B–B and B–C bonds, respectively.

The total and projected DOS and band structure of the hypothetical MgB_2C compound are shown in Fig. 2. Surprisingly, this lattice is expected to be conducting, despite the fact that a localized bonding picture with single and double bonds can be drawn. There is some participation of B, C and Mg at the Fermi level (Fig. 2). Indeed, interaction between the chains is responsible for the metallic properties. Examination of the band structure (not shown here) indicates some anisotropy in the conducting properties. Bands cut by the Fermi level are rather flat along the c direction perpendicular to the zigzag chains and more dispersed along the chains. An electronically and structurally reasonable system seems to emerge from this theoretical analysis. We did not discuss its energy with respect to that of other isomeric forms such as that of the AlB_2 type with planar graphitic-like sheets. Energetic considerations are currently in progress.

It is noteworthy to mention that this B/C arrangement proposed here is identical to one of the numerous hypothetical 3D lattices proposed for elementary carbon

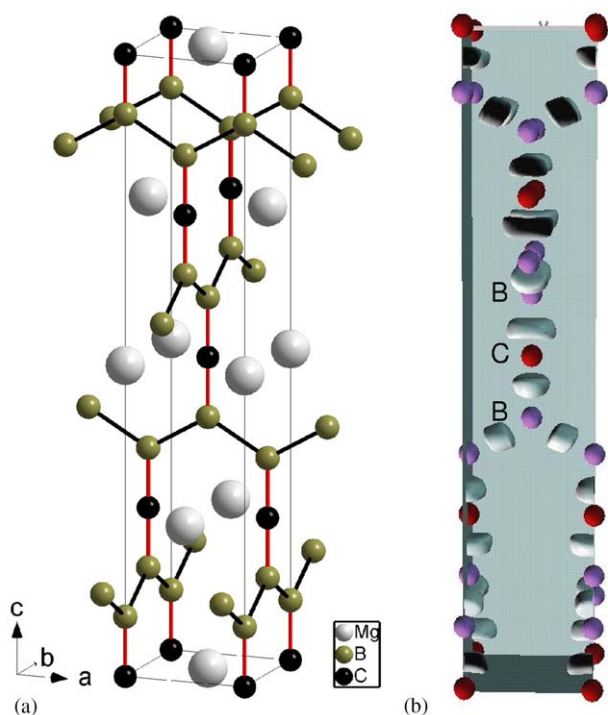


Fig. 1. Hypothetical structural arrangement (a) and LMTO isosurface of the electron localization function ($\eta = 0.8$) (b) of MgB_2C .

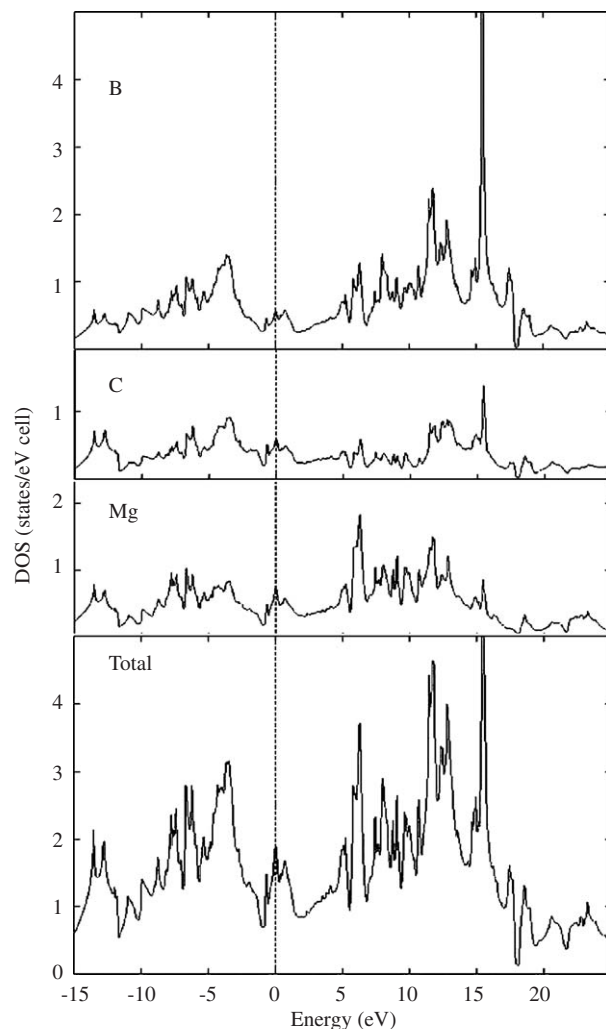


Fig. 2. Total and projected DOS of MgB_2C .

[34]. Assuming C–C single or double bonds, such a material built up of sp and sp^2 C atoms has a density intermediate between that of graphite and diamond. Analogously to MgB_2C , such an arrangement is expected to be metallic in character.

3. Finite linear boron–carbon chains

With VEC values spreading over the range 5–6, the metallic sub-lattice consists of a 3D framework often resulting from a regular or irregular stacking of 2D square nets. Such an arrangement leads to the formation of small holes of different sizes in which finite and roughly linear B_mC_n units are embedded. This is exemplified by LaBC recently characterized during a new investigation of the La–B–C system [20]. 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. 3). These worm-like entities buried in the solid are more or less linear and the measured B–B, B–C and C–C separations, ca. 1.5 Å, correspond roughly to double bonds.

B_5C_5 is not the only kind of finite chain trapped in compounds of this sort. Other chains of different lengths are encapsulated in other phases such as B_4C_7 and B_5C_6 in $La_{15}B_{14}C_{19}$ [19], B_5C_8 in $La_{10}B_9C_{12}$, [21], B_4C_4 and B_3C_3 in $La_5B_4C_5$ [22] or BC_3 in $La_5B_2C_6$ [23] to mention a few.

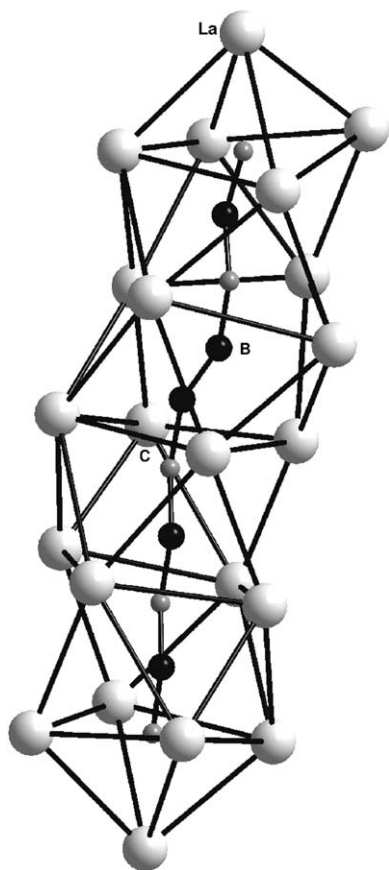


Fig. 3. The B_5C_5 chain in LaBC.

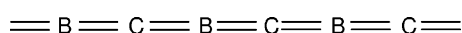
Unambiguous location of B and C atoms is not obvious from X-ray measurements. This is often made based on the chemical environment, the electronegativity and also theoretical considerations. The length of these rods is generally governed by their electronic requirements. With distances corresponding roughly to double bonds, these B/C units can be considered as cumulene-like “molecules” trapped in the solid [35]. EH and DFT calculations have been carried out on one isolated finite B_5C_5 chain in order to have an idea of its oxidation state accounting for the double bond character of the B–B and B–C separations. A formal charge of 9– seems adequate for a cumulenic form with a small energy gap separating the highest occupied MO from the lowest unoccupied MO, both of π type [20]. Although the chain is not strictly linear (a small deviation from linearity is observed), this kind of pseudo-molecule is isoelectronic to a hypothetical cumulenic $(C_{10})^{4-}$ oligomer. With such a formal anionic charge of 9– for the B_5C_5 chain, the metal atoms need not to be fully oxidized (formal ionic limit: $(La^{3+})_5(B_5C_5)^{9-} \cdot 6e^-$). Extra electrons remain in the metallic band and the compound is metallic in character according to LMTO DFT calculations with weak metal–metal bonding [20].

Such an approach which considers anionic B/C chains environed by metal cations may bring the reader to the conclusion that metal–ligand covalency is absent from this kind of compound. Indeed, LaBC has a significant degree of metal–ligand covalent bonding, in which the outer electron clouds of the B_5C_5 anions are polarized towards the metal cations. The computed charge is not 9– for B_5C_5 in the solid, but less, 8.3–. Electron donation occurs from the anionic B/C chains to the metal atoms. Indeed, rare-earth metal boron carbides can be considered as near-Zintl phases in which metal cations transfer their electrons onto the B/C anions which in turn form ideal substructures that can be well rationalized by the octet rule. However, it is essential to take the cations into account when considering their properties. It turns out that all the filled high-lying anion-centered orbitals do not always lie well separated from some of the low-lying empty cation-based orbitals leading to metallic compounds with the E_F crossing the bottom of the metallic band which overlaps with the top of the B/C valence band [2].

4. Towards infinite linear boron carbon chains

B_5C_5 encountered in LaBC is not the longest B/C chain observed in this kind of ternary compound. The longest chain, up to now, is B_5C_8 , mentioned earlier and found in $La_{10}B_9C_{12}$. As for B_5C_5 , it can be considered as a cumulenic-like oligomer $(B_5C_8)^{9-}$ [35]. There is no reason to stop at this length. If stoichiometry, size and electron count can be adjusted, it should be possible to synthesize a compound containing infinite B/C rods with a cumulenic form, that is, with double bonds between B and C atoms (see 2). This would be a model for the hypothetical allotropic 1D phase of carbon called carbyne (karbin) or

chaoite [36]. Theoretical studies predict that carbyne prefers the acetylenic form over the cumulenic form, with alternation of single and triple bonds rather than double bonds because of a Peierls distortion [37]. Indeed, there are examples of organic and organometallic compounds containing pieces of carbyne with such an arrangement, i.e. alternation of single and triple bonds. The recently characterized compound $\{\text{Co}_3(\text{CO})_9\}_2(\mu_3\text{-C}_{16})$ provides a nice example with a linear chain of 16 C atoms spanning two tri-cobalt carbonyl clusters [38]. Characterization of infinite linear B^- rods of acetylenic type in LiB_x some years ago [39], and preparation of infinite boron and boron-carbon chains in ternary Ca-Ge-B or quaternary Ca-Ge-B-C compounds [40] give support for the search of new ternary RE-B-C compounds which would contain 1D $(\text{BC})^-$ rods.



2

5. Rare-earth metal boron silicides

Recent works have shown that substituting silicon for carbon leads to compounds with strongly different structural arrangements [41,42]. Several years ago when we thought about extending the RE-B-C chemistry to that of RE-B-Si, a look at the literature on ternary RE-B-Si compounds showed very few results [43]. We thus decided to explore this area and a research program was launched in our laboratory aiming at the synthesis and characterization of RE-B-Si phases. Our investigations on different ternary phase diagrams reveal that the RE-B-Si chemistry is far to be as rich as that of RE-B-C chemistry. Very few ternary compounds have been found so far. Let us take the example of the Gd-B-Si system for instance. The choice of gadolinium was guided by the fact that it lies at the borderline between light and heavy RE. Exploration of the isothermal section of the ternary Gd-Si-B phase diagram carried out at 1000 °C led to the discovery of only two ternary compounds, namely the Nowotny phase $\text{Gd}_5\text{Si}_3\text{B}_{0.6}$ which results from boron insertion in the binary compound Gd_5Si_3 and $\text{Gd}_5\text{Si}_2\text{B}_8$, a new structural type resulting from the peritectic reaction between the solid GdB_4 and a liquid of composition Gd_5Si_3 [41]. This structural type is also encountered with other light RE [41].

$\text{Gd}_5\text{Si}_2\text{B}_8$ compound can be considered as a two-compound in one (see Fig. 4). One part is made of metal atoms and singly bonded Si-Si pairs, which reminds the U_3Si_2 structure type [44]. The parts above and below the U_3Si_2 -like sheet consist of slabs of ThB_4 structure type [45] with the boron atoms forming 2D layers made of distorted B_6 octahedra linked to each other via tri-connected sp^2 B_2 units (Fig. 4b). All the B-B distances are around 1.8 Å.

An ionic approach is a useful starting point to understand the structural arrangement of the non-metal substructure. The isolated Si_2 pairs should satisfy the octet

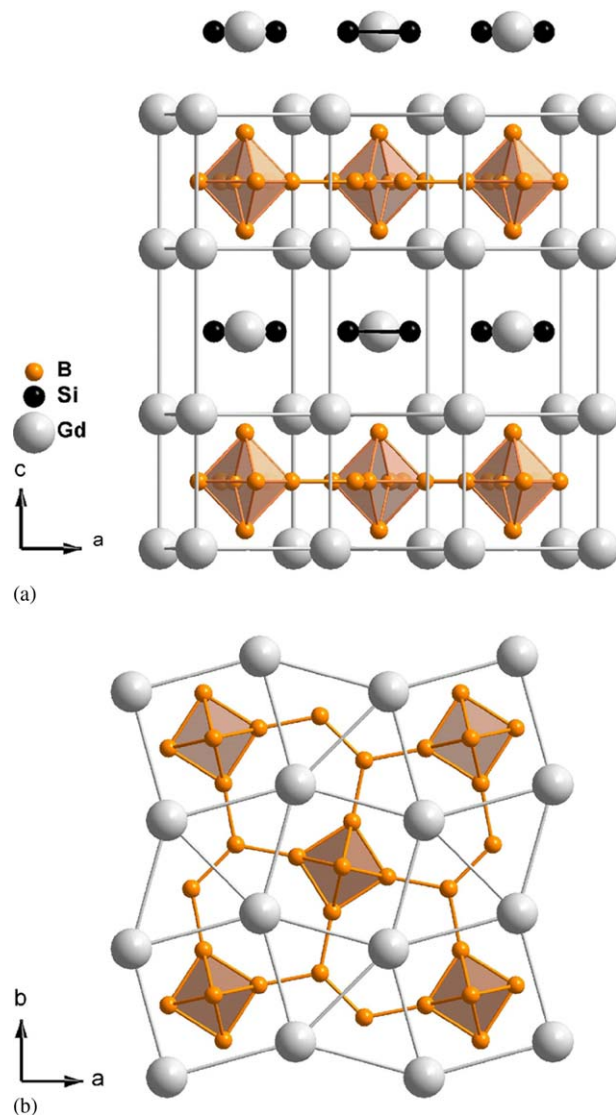


Fig. 4. Crystal structure of $\text{Gd}_5\text{Si}_2\text{B}_8$: 3D view along the c -axis (a) and view of one metal boron layer down the c -axis (b).

rule, i.e., they should be considered as $(\text{Si}_2)^{6-}$ consistent with a single Si-Si bond which is measured (2.362 Å), isoelectronic to ethane, C_2H_6 . Knowing the chemistry of molecular boranes and the Wade's electron rules to which they generally obey [46], the favored electron count for the boron octahedra is $(\text{B}_6)^{4-}$. Why 4-? We can start from thinking of CaB_6 for which every B_6 is formally charged 2- as expected from the Wades rules [46]. In CaB_6 , the octahedra are linked to one another along the three directions. This is not the case in $\text{Gd}_5\text{Si}_2\text{B}_8$ with bond breaking along the c direction. Consequently, the two apical boron atoms need to be "saturated" with lone pairs, leading to a formal charge of 4- per B_6 . Charge assignment of the three-connected sp^2 B_2 units is less straightforward. Assuming two-electron-two-center bonding ($2e-2c$) for the two sp^2 -hybridized coplanar boron atoms of these diatomic entities, they can either obey the sextet or the octet rule. The sextet rule assumes a neutral B_2 unit with a

single B–B bond. This is unlikely with Gd atoms around. The octet rule allows the possibilities for double or single B–B bonds, corresponding to $(B_2)^{2-}$ and $(B_2)^{4-}$, respectively. None of these charge distributions is fully satisfactory, since the former disagrees somewhat with the rather long B–B separation which is 1.80 Å, whereas the latter should lead to a non-planar sp^3 hybridization of the boron atoms. The question about the assignment of the charge of the B_2 unit prevents a clear assignment of the oxidation state of the metals. The same question of formal charge assignment of the B_2 unit arises as well in GdB_4 , which adopts the ThB_4 structural type and therefore shows some relationship with $Gd_5Si_2B_8$ [47]. In order to check which one of these simple pictures is the best starting point to describe the bonding of the B_2 “units” linking boron octahedra to each other in $Gd_5Si_2B_8$, different theoretical tools were employed such as ELF and COHP curves extracted from DFT calculations. Although we did not get a clear answer, it seems that $(B_2)^{2-}$ has to be privileged somewhat, associated with a long B–B double bond with π levels of the B_2 unit weakly bonding but occupied and the π^* levels unoccupied. This would lead to the formal charge distribution $(Gd^{2.4+})_5(Si_2)^{6-}(B_6)^{4-}(B_2)^{2-}$ or $(Gd^{3+})_5(Si_2)^{6-}(B_6)^{4-}(B_2)^{2-}.3e^-$.

Anyhow, both distributions lead to Gd atoms not formally completely oxidized. Therefore the compound should be metallic. This is supported by the DOS computed at the LMTO DFT level. The Fermi level cuts a rather high peak of DOS, showing that the compound should be metallic in character [42]. The different projected DOS indicate participation of all constituting elements, Gd, B_6 , B_2 , and Si_2 , all over the DOS. Again, this reflects some covalent character between the metals and the Si_2 pairs and boron sheets. This predicted metallic behavior is confirmed by resistivity measurements which were made on a single crystal of $Gd_5Si_2B_8$. These measurements indicate that the resistivity decreases below room temperature and that in the low-temperature regime, changes of slope are observed due to complex magnetic ordering [41].

The structural arrangement of $Gd_5Si_3B_x$ ($x \leq 1$), the second ternary compound which was obtained from the exploration of the Gd–B–Si phase diagram, derives from that of the binary phase Gd_5Si_3 (of Mn_5Si_3 type) [48,49] with isolated Si atoms, isolated metal atoms and metal octahedra in which are encapsulated the B atoms (see Fig. 5). The value x would be equal to one if all the octahedral sites were occupied. This is not the case according to X-ray and chemical analysis which propose an occupation of roughly 2/3 of these octahedral sites [49]. We may wonder if there is a relationship between the electron count and the boron content in this phase? Assuming Gd^{3+} , Si^{4-} and B^{5-} should preclude the stoichiometric formula Gd_5Si_3B but rather leads to a fractional content of $B_{0.6}$ to satisfy the electronic requirements of boron. Unfortunately, the boron quantity inserted in this compound has been only defined through crystal structure determinations (within the limits of

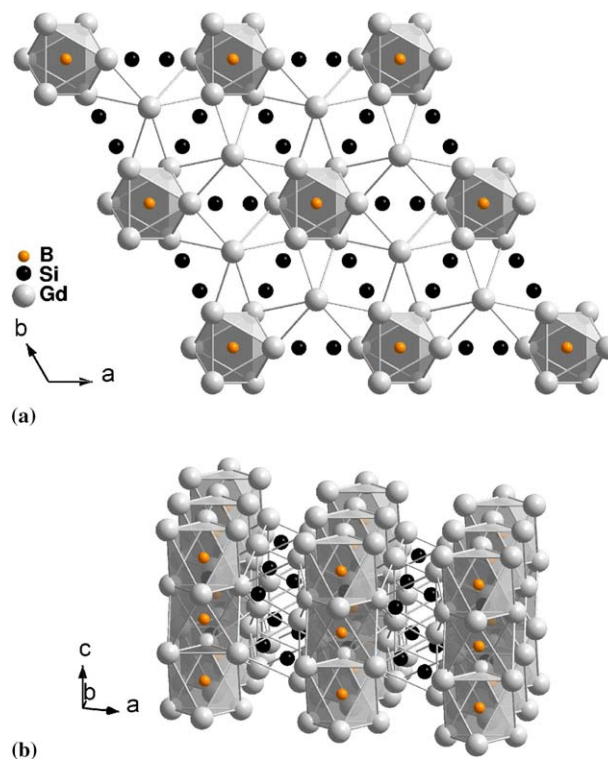


Fig. 5. The 3D view of the crystal structure of $Gd_5Si_3B_x$ along the [001] direction (a) and the [010] direction (b). The boron occupation which is shown corresponds to $x = 1$.

errors). Surprisingly, preliminary experiments with other RE would indicate that the boron content can vary from 0.6 (Y) up to 1 (Dy, Ho or Lu). All we are sure of is that these compounds contain boron. A comparison of their physical properties to those measured for the binary phase Gd_5Si_3 indicate that they differ: higher resistivity for the ternary phase and diminution of the exchange magnetic interactions [49]. There is boron in our compound, but how much?

DFT calculations were carried out on $Gd_5Si_3B_x$, varying x from 0 to 1. The total spin-polarized DOS for the two contents 0.66 and 1 are shown in Fig. 6a and b, respectively. As it can be seen, they look fairly the same at first sight. For both contents, 2/3 and 1, metallic conductivity is expected. No energy gap for any electron count which could indicate a preferred stoichiometry over another one is noticed. At this very moment, our calculations cannot give any clear answer on the exact value of x in these phases. Is it peculiar to boron which is not very electronegative with respect to Gd and Si, which would lead to overlapping of occupied boron energy levels and empty metallic bands?

This compound belongs to the family of the Nowotny phases, which is known to trap everything which can fit in the octahedral holes. Many examples are known with different insertion elements, not only transition metals but also a large variety of main group atoms such as Si, P, Br, etc. [50]. The content in encapsulated light element differs according to its nature, i.e. its electronic requirements.

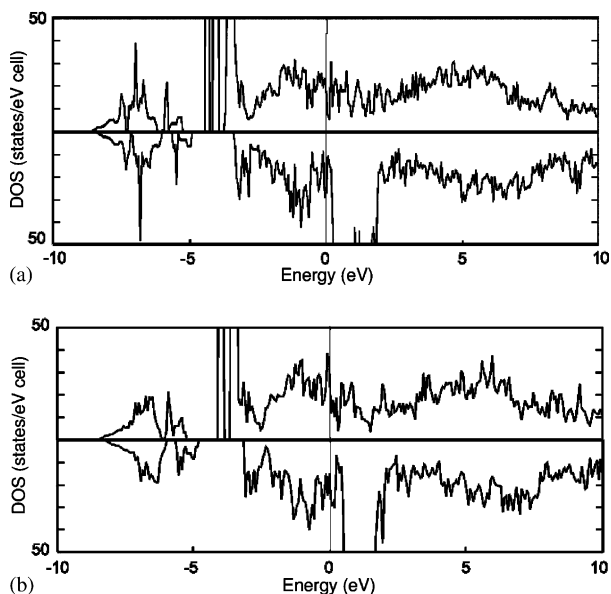


Fig. 6. LMTO total density of states of $Gd_5Si_5B_x$ for $x = 0.66$ (a) and $x = 1$ (b).

Indeed, application of the Zintl–Klemm concept indicates that with Si, C or B, the content in these compounds should be less than one, but can be equal to one with P or Br for instance, as experimentally observed [50]. The electronic conduction properties of these phases are often consistent with this rather simple way of accounting for electrons. La_5Sn_3Br for instance is metallic since metallic electrons remain in the d band once the electronic requirements of Br are satisfied ($(La^{3+})_5(Sn^{4-})_3(Br^-)2e^-$). This has been supported both theoretically and experimentally [51]. On the other hand, J. Corbett has shown that with P, La_5Ge_3P ($(La^{3+})_5(Ge^{4-})_3P^{3-}$) is semi-conducting with a small band gap confirmed both experimentally and theoretically with the Fermi level in a hole of density of states [52].

Interestingly, calculations that we performed recently on the hypothetical phase Gd_5Si_3P , replacing B_x by P, also show a semi-conducting behavior with nearly no density of states at the Fermi level. All these results support the fact that the Zintl–Klemm concept applies to these phases. Why not for boron? With $x = 1$, extra electrons are needed to satisfy the electronic demands of 5–. One way to circumvent this would be to create B–B bonding. The structure $Gd_5Si_3B_x$ was optimized at the DFT level of theory for different contents, 1/3, 2/3 and 1. No distortion for 1/3 and 2/3 and distortion for $x = 1$ were expected. Surprisingly, DFT optimization shows some formation of B–B contacts of roughly 1.7 Å, i.e. isolated B_2 units, for different boron quantity: Not only for one, but also for 2/3. Is it an artifact of the calculations, or is there something real behind? Additional studies are currently in progress.

6. Conclusion

In this paper, we have endeavoured to outline the way that the structural arrangement of the non-metal sub-

lattice of some ternary rare-earth metal boron carbide and silicide compounds could be rationalized using the solid-state language of Zintl–Klemm concept, band structures, and density of states. Interestingly, examination of different categories of compounds shows that the chemistry of $RE-B-Si$ does not parallel that of $RE-B-C$. In the latter, B–C bonds are easily formed and a large variety of topologies are encountered depending upon the electron count, whereas in the former, Si–B bonds are hardly observed, except in insertion compounds.

Appendix A

Density of states and band structure calculations were performed with the tight binding linear muffin–tin orbital method in the atomic spheres approximation including the combined correction (LMTO) using the TB-LMTO-ASA program package [53]. Exchange and correlation were treated in the local density approximation using the von Barth–Hedin local exchange correlation potential [54]. Full optimizations of the atomic positions and cell parameters were carried out using the VASP package [55]. PBE generalized gradient approximation was employed for the exchange and correlation energy term [56].

References

- [1] (a) See for instance, G.-Y. Adachi, N. Imakana, Z. Fuzhong, in: K.A. Gschneidner Jr., L. Eyring (Eds.), Handbook on the Physics and Chemistry of Rare Earths, vol. 15, Elsevier, Amsterdam, 1991, p. 62; (b) A.I. Gusev, Russ. Chem. Rev. 65 (1996) 379; (c) A.L. Ivanovskii, Russ. Chem. Rev. 66 (1997) 459.
- [2] J. Bauer, J.-F. Halet, J.-Y. Saillard, Coord. Chem. Rev. 178–180 (1998) 723 and references therein. See also; (a) J.-F. Halet, in: M.G. Davidson, A.K. Hugues, T.B. Marder, K. Wade (Eds.), Contemporary Boron Chemistry, Royal Society of Chemistry, Cambridge, 2000, p. 514; (b) D. Ruiz, M.T. Garland, J.-Y. Saillard, J.-F. Halet, M. Bohn, J. Bauer, Solid State Sci. 4 (2002) 1173; (c) C. Jardin, H. Hillebrecht, J. Bauer, J.-F. Halet, J.-Y. Saillard, R. Gautier, J. Solid State Chem. 176 (2003) 609.
- [3] (a) P.K. Smith, Ph.D. Thesis, University of Kansas, 1964; (b) P.K. Smith, P.W. Gilles, J. Inorg. Nucl. Chem. 29 (1967) 375.
- [4] J. Bauer, H. Nowotny, Monatsh. Chem. 102 (1971) 1129.
- [5] (a) J. Bauer, O. Bars, Acta Crystallogr. B 36 (1980) 1540; (b) R. Pöttgen, unpublished results 1996.
- [6] (a) T. Onimaru, H. Onodera, K. Ohoyama, H. Yamauchi, Y. Yamaguchi, J. Phys. Soc. Jpn. 68 (1999) 2287; (b) T. Onimaru, H. Onodera, K. Ohoyama, H. Yamauchi, M. Ohashi, Y. Yamaguchi, J. Phys. Chem. Solids 60 (1999) 1435; (c) K. Kaneko, K. Ohoyama, H. Onodera, Y. Yamaguchi, J. Phys. Soc. Jpn. 69 (2000) 3762; (d) J. van Duijn, K. Suzuki, J.P. Attfield, Angew. Chem. Int. Ed. 39 (2000) 365; (e) K. Ohoyama, K. Kaneko, K. Indoh, H. Yamauchi, A. Tobo, H. Onodera, Y. Yamaguchi, J. Phys. Soc. Jpn. 70 (2001) 3291.
- [7] G.S. Smith, Q. Johnson, P.C. Nordine, Acta Crystallogr. 19 (1965) 668.
- [8] J. Bauer, J. Less-Common Met. 87 (1982) 45.
- [9] P. Rogl, P.J. Fischer, Solid State Chem. 78 (1989) 294.
- [10] J. Bauer, D. Ansel, F. Bonhomme, P. Gosselin, J. Less-Common Met. 157 (1990) 109.

- [11] P. Rogl, P.J. Fischer, *Solid State Chem.* 90 (1991) 285.
- [12] F. Wütkar, J.-F. Halet, J.-Y. Saillard, P. Rogl, J. Bauer, *Inorg. Chem.* 33 (1994) 1297.
- [13] (a) Y. Shi, A. Leithe-Jasper, T. Tanaka, *J. Solid State Chem.* 148 (1999) 250;
(b) Y. Shi, A. Leithe-Jasper, L. Bourgeois, Y. Bando, T. Tanaka, *J. Solid State Chem.* 148 (1999) 442;
(c) M. Onoda, Y. Shi, A. Leithe-Jasper, T. Tanaka, *Acta Crystallogr. B* 57 (2001) 449.
- [14] P. Rogl, *J. Nucl. Mater.* 73 (1978) 198.
- [15] L. Toth, H. Nowotny, F. Benesovsky, E. Rudy, *Monatsh. Chem.* 92 (1961) 794.
- [16] P. Rogl, B. Rupp, I. Felner, P.J. Fisher, *J. Solid State Chem.* 104 (1993) 377.
- [17] P. Rogl, *J. Nucl. Mater.* 79 (1979) 154.
- [18] C. Jardin, O. Oeckler, H.j. Mattausch, A. Simon, J.-F. Halet, J.-Y. Saillard, J. Bauer, *Inorg. Chem.* 39 (2000) 5895.
- [19] P. Gougeon, J.-F. Halet, D. Ansel, J. Bauer, *Z. Kristallogr.* 211 (1996) 822.
- [20] V. Babizhetskyy, H.j. Mattausch, A. Simon, R. Gautier, J. Bauer, J.-F. Halet, *Z. Anorg. Allg. Chem.* 631 (2005) 1041.
- [21] (a) P. Gougeon, J.-F. Halet, D. Ansel, J. Bauer, *Z. Kristallogr.* 211 (1996) 823;
(b) V. Babizhetskyy, H.j. Mattausch, A. Simon, *Z. Kristallogr.* 219 (2004) 11.
- [22] (a) P. Gougeon, J.-F. Halet, D. Ansel, J. Bauer, *Z. Kristallogr.* 211 (1996) 824;
(b) V. Babizhetskyy, H.j. Mattausch, A. Simon, *Z. Kristallogr.* 218 (2003) 417.
- [23] (a) J. Bauer, O. Bars, *J. Less-Common Met.* 83 (1983) 17;
(b) O. Oeckler, J. Bauer, H.j. Mattausch, A. Simon, *Z. Anorg. Allg. Chem.* 627 (2001) 779.
- [24] (a) J.-F. Halet, J.-Y. Saillard, J. Bauer, *J. Less-Common Met.* 158 (1990) 239;
(b) Y. Shi, A. Leithe-Jasper, T. Tanaka, *J. Solid State Chem.* 184 (1999) 250.
- [25] E. Bidaud, K. Hiebl, R.-D. Hoffmann, R. Pöttgen, C. Jardin, J. Bauer, R. Gautier, P. Gougeon, J.-Y. Saillard, J.-F. Halet, *J. Solid State Chem.* 154 (2000) 286.
- [26] V. Babizhetskyy, H.j. Mattausch, A. Simon, unpublished results.
- [27] O. Oeckler, C. Jardin, H.j. Mattausch, A. Simon, J.-F. Halet, J.-Y. Saillard, J. Bauer, *Z. Anorg. Allg. Chem.* 627 (2001) 1389.
- [28] (a) Y. Shi, A. Leithe-Jasper, L. Bourgeois, Y. Bando, T. Tanaka, *J. Alloys Compd.* 298 (2000) 99;
(b) T. Mori, Y. Shi, T. Tanaka, *J. Alloys Compd.* 308 (2000) 115.
- [29] (a) E. Zintl, *Angew. Chem.* 1 (1939) 52;
(b) W. Klemm, *Proc. Chem. Soc. London* (1958) 329.
- [30] X. Rocquefelte, S.-E. Boulfelfel, M. Ben Yahia, J. Bauer, J.-Y. Saillard, J.-F. Halet, *Angew. Chem. Int. Ed.* 44 (2005) 7542.
- [31] (a) F. Wütkar, S. Kahlal, J.-F. Halet, J.-Y. Saillard, J. Bauer, P. Rogl, *J. Am. Chem. Soc.* 116 (1994) 251;
(b) G. Frapper, J.-F. Halet, J.-Y. Saillard, F. Volatron, *J. Phys. Chem.* 99 (1995) 12164;
(c) C.-F. Fang, J. Bauer, J.-Y. Saillard, J.-F. Halet, unpublished results.
- [32] A. Savin, H.J. Flad, J. Flad, H. Preuss, H.G. von Schnering, *Angew. Chem. Int. Ed.* 31 (1992) 185.
- [33] (a) R. Dronskowski, P.E. Blöchl, *J. Phys. Chem.* 97 (1993) 8617;
(b) F. Boucher, R. Rousseau, *Inorg. Chem.* 37 (1998) 2351.
- [34] J. Elguero, C. Foces-Foces, A.L. Llamas-Saiz, *Bull. Soc. Chim. Bel.* 101 (1992) 795.
- [35] (a) D. Ansel, J. Bauer, F. Bonhomme, G. Boucekkine, G. Frapper, P. Gougeon, J.-F. Halet, J.-Y. Saillard, B. Zouchoune, *Angew. Chem. Int. Ed.* 35 (1996) 2098;
(b) J. Bauer, G. Boucekkine, G. Frapper, J.-F. Halet, J.-Y. Saillard, B. Zouchoune, *J. Solid State Chem.* 133 (1997) 190.
- [36] (a) F. Diederich, Y. Rubin, *Angew. Chem. Int. Ed.* 31 (1992) 1101;
(b) F. Diederich, *Nature* 369 (1994) 199;
(c) S. Szafert, J.A.G. Gladysz, *Chem. Rev.* 103 (2003) 4175.
- [37] M.J. Rice, A.R. Bishop, D.K. Campbell, *Phys. Rev. Lett.* 51 (1983) 2136.
- [38] A.B. Antonova, M.I. Bruce, B.G. Ellis, M. Gaudio, P.A. Humphrey, M. Jevric, G. Melino, B.K. Nicholson, G.J. Perkins, B.W. Skelton, B. Stapleton, A.H. White, N.N. Zaitseva, *Chem. Commun.* (2004) 960.
- [39] M. Wörle, R. Nesper, *Angew. Chem. Int. Ed.* 39 (2000) 2349.
- [40] Yu. Grin, et al., unpublished results, 2005.
- [41] (a) J. Roger, R. Jardin, V. Babizhetskyy, S. Députier, J. Bauer, R. Guérin, *Z. Kristallogr.-New Cryst. Struct.* 218 (2003) 173;
(b) J. Roger, V. Babizhetskyy, S. Cordier, J. Bauer, K. Hiebl, L. Le Pollès, S.E. Ashbrook, J.-F. Halet, R. Guérin, *J. Solid State Chem.* 178 (2005) 1851.
- [42] V. Babizhetskyy, J. Roger, S. Députier, R. Guérin, R. Jardin, J. Bauer, K. Hiebl, C. Jardin, J.-Y. Saillard, J.-F. Halet, *Angew. Chem. Int. Ed.* 43 (2004) 1979.
- [43] (a) I. Higashi, T. Tanaka, K. Kobayashi, Y. Ishizawa, M. Takami, *J. Solid State Chem.* 133 (1997) 11;
(b) T. Mori, T. Tanaka, *J. Solid State Chem.* 154 (2000) 223;
(c) F.X. Zhang, A. Sato, T. Tanaka, *J. Solid State Chem.* 164 (2002) 361;
(d) J.R. Salvador, D. Bilc, S.D. Mahanti, M.G. Kanatzidis, *Angew. Chem. Int. Ed.* 41 (2002) 844;
(e) T. Mori, F. Zhang, *J. Phys.: Condens. Matter* 14 (2002) 11831;
(f) F.X. Zhang, F.F. Xu, T. Mori, Q.L. Liu, T. Tanaka, *J. Solid State Chem.* 170 (2003) 75;
(g) F.X. Zhang, T. Tanaka, *Z. Kristallogr.* 218 (2003) 26.
- [44] K. Remschnig, T. Le Bihan, H. Noël, P. Rogl, *J. Solid State Chem.* 97 (1992) 391.
- [45] A. Zalkin, D.H. Templeton, *Acta Crystallogr.* 6 (1953) 269.
- [46] K. Wade, *Adv. Inorg. Chem. Radiochem.* 18 (1976) 1.
- [47] (a) M.T. Garland, J.P. Wiff, J. Bauer, R. Guérin, J.-Y. Saillard, *Solid State Sci.* 5 (2003) 705;
(b) M. Ben Yahia, R. Gautier, J.-F. Halet, J.-Y. Saillard, unpublished results.
- [48] B. Aronsson, *Acta Chem. Scand.* 14 (1960) 1414.
- [49] (a) V. Babizhetskyy, J. Roger, S. Députier, R. Jardin, J. Bauer, R. Guérin, *J. Solid State Chem.* 177 (2004) 415;
(b) J. Roger, M. Ben Yahia, X. Rocquefelte, C.-M. Fang, R. Gautier, K. Hiebl, R. Guerin, J.-Y. Saillard, J.-F. Halet, unpublished results.
- [50] J.D. Corbett, E. Garcia, A.M. Guloy, W.-M. Hurng, Y.-U. Kwon, E.A. Leon-Escamilla, *Chem. Mater.* 10 (1998) 2824.
- [51] C. Zheng, H.j. Mattausch, A. Simon, *J. Alloys Compd.* 347 (2002) 79.
- [52] A.M. Guloy, J.D. Corbett, *Inorg. Chem.* 32 (1993) 3532.
- [53] R.W. Tank, O. Jepsen, A. Burkhardt, O.K. Andersen, The Stuttgart TB-LMTO-ASA program, version 4.7, Max-Planck-Institut für Festkörperforschung, Stuttgart, 1999.
- [54] U. von Barth, L. Hedin, *J. Phys. C* 5 (1972) 1629.
- [55] G. Kresse, J. Hafner, VASP program, version 4.4.5, Institut für Materialphysik, Universität Wien, 2000.
- [56] J.P. Perdew, S. Burke, M. Ernernhof, *Phys. Rev. Lett.* 77 (1996) 3865.