Boron carbides from first principles

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Abstract. In this work, we focus on the understanding gained from the investigation of the physical properties of boron carbides with theoretical methods based on density functional theory (DFT). Together with the examination of the DFT total energies of various atomic configurations in the unit cell, comparison with the experiments of the theoretical vibrational or NMR spectra has led to the determination of the atomic structure of $B_4C$ as C-B-C chains linking mostly $B_{11}C$ icosahedra, and a few percents of $B_{10}C_2$ icosahedra. In the icosahedron, the carbon atom is found to be in the polar site ($B_4C^p$). When there are two carbon atoms, they are found to be in antipodal polar positions. At carbon concentrations other than 20%, we find that only four structural models have a negative formation energy with respect to a formation from $\alpha$-boron + diamond. Moreover, they all have a positive formation energy with respect to $B_4C^p$, showing a tendency to decompose into $B_4C^p + \alpha$-boron or $B_4C^p +$ diamond. This metastability explains actual difficulties in the synthesis of clean samples, in particular for $B_{13}C_2$. Finally, the idea of combining high hardness and superconductivity in the same material by doping boron-rich solids has emerged. We show results on the strength of the electron-phonon coupling constant obtained with DFT-based methods in $B_{13}C_2$.

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1. Introduction

Density functional theory (DFT) has become a crucial from-first-principles tool to investigate ground state properties of materials [1, 2, 3]. Theoretical results on boron carbides presented in this paper rely on DFT, and therefore we briefly recall in this introduction the main purpose of DFT and its limitations. DFT maps a system of interacting electrons on a system of noninteracting electrons in an effective potential, which contains the so-called exchange and correlation potential. In fact, DFT relies on assumptions for the exchange and correlation energy, which aim at modeling terms difficult to take into account in the mapping: (i) the difference in kinetic energy between a system of interacting electrons and noninteracting ones; (ii) all many-body electron-electron quantum interactions - such as Pauli’s principle - beyond the Hartree energy (the classical electrostatic energy for interacting charge densities).

In the simplest local density approximation (LDA), each small volume of the system is expected to contribute to the exchange and correlation energy as would do an equal volume of a homogeneous electron gas at the same density [4]. Equilibrium properties calculated within DFT-LDA such as lattice parameters and internal atomic positions usually agree extremely well -within 1%- with experiment. There are however a number of applications in which this accuracy is not high enough. It is worth pointing out, for instance, that most of today’s computational electronic spectroscopy is performed at the experimental lattice constant to avoid the lattice
Exchange and correlation functionals beyond LDA thus become required in order to evaluate the equilibrium volume with a greater accuracy. The generalized gradient approximation (GGA) has been developed with such an objective [6]. It is important for properties which explicitly depend on the equilibrium volume \( V_{eq} \), such as the tensor of elastic constants \( C_{ijkl} \), defined as the second order derivative of the (DFT) total energy \( E \) with respect to the strain tensor \( \varepsilon_{ij} \), where \( i, j, k \) and \( l \) are cartesian indexes

\[
C_{ijkl} = \frac{1}{V_{eq}} \left( \frac{\partial^2 E}{\partial \varepsilon_{ij} \partial \varepsilon_{kl}} \right)_{\varepsilon=0}.
\]  

(1)

In above equation, the explicit dependence on the equilibrium volume \( V_{eq} \) makes the error bar on elastic constants much smaller when calculated within the generalized gradient approximation than within LDA [7]. Nuclear magnetic resonance (NMR) is another type of property which directly probes the local atomic structure through the electronic response to an external magnetic field. For the same reasons, calculations of the chemical shift tensor performed with the GGA do show a better agreement with experiment in comparison with LDA ones [8, 9, 10]. We therefore used GGA for our NMR results spectra presented in subsection 2.4.

Among known limitations of DFT, forbidden energy gaps in insulators and semiconductors are underestimated. For energy gap calculations, theoretical frameworks beyond DFT are required, which take into account the electron-electron interaction beyond the mean-field approximation. Energy gaps are currently computed with a Green’s function approach which allows to calculate the quasiparticle corrections to DFT energies to first-order in perturbation [11, 12, 13].

Excited states also are out of reach of DFT. They are treated either by time-dependent density functional theory (TDDFT) [14, 15], or by the solution of the Bethe-Salpeter equation, when, like in optical absorption, it is necessary to take into account the electron-hole interaction [5, 16]. These methods nonetheless rely on DFT, for the ground state wavefunctions and energies are often (if not always) used in, either as a starting point, or to calculate key quantities like the dielectric tensor.

Finally, it is not yet clear whether the above-mentioned many-body methods based on Green’s functions are sufficient in materials where electronic correlations are of primary importance, like in oxides with multiply occupied 3d orbitals. The dynamical mean field theory presents an alternative method to model the correlations [17]. It should be noted however that both classes of methods have been successfully applied to the electronic spectroscopy of vanadium dioxide [18, 19].

Being sp bonded materials, boron-rich solids (BRS) are expected to have ground state properties well described by DFT based methods. The crystal symmetry of BRS is rhombohedral with \( R3m \) space group. The atomic structure consists in one distorted icosahedron per primitive unit cell (figure 1), eventually plus one multi-atomic chain. Each atom in the icosahedron is the apex of a pentagonal-based pyramid. Two crystallographic sites in the icosahedron are defined by the intericosahedral bonding. In polar site \( p \), one atom is linked by a covalent two-center \( p-p \) bond to one atom in the polar site of a neighboring icosahedron. In the second site \( e \), the equatorial atom is bonded to the chain-end atom of a multiaatomic chain that links neighboring icosahedra. The intericosahedral chain can be absent like in \( \alpha \)-boron. In most of icosahedral solids, there is one chain per unit cell. The chain can be diatomic - like in \( B_{12}P_2 \) and \( B_{12}As_2 \) - or triatomic like in boron carbides (figure 1).

The nature of the bonding makes boron-rich solids widely different from fullerenes, a class of materials with which they are nonetheless often compared. Due to electron deficiency [21, 22, 23], a “standing alone” \( B_{12} \), \( B_{11}C \) or \( B_{10}C_2 \) neutral cluster is unstable. Thus BRS can not be compared to fullerene crystals [24, 25]. The comparison of the respective compressibilities of the intra and interatomic bonds by ab initio methods has proved that neither \( \alpha \)-boron nor
Figure 1. Atomic structure of icosahedral boron carbide from Ref. [20]. Seven distorted icosahedra are shown. The rhombohedral Bravais lattice vectors (not shown) link icosahedra centers. Black balls: atoms at the $p$ polar site. Light grey balls: atoms at the $e$ equatorial site. Dark grey balls: atoms at chain center and chain ends. Polar atoms are shown to be bonded to neighboring icosahedra via the covalent two-center $p-p$ bonds. Equatorial atoms are linked to one atom at the end of the triatomic chain. (Reproduced with permission from [20])

Icosahedral boron carbide with 20% of carbon concentration ($B_4C$) are molecular crystals. They do not form either an inverted molecular crystal, in which the intericosahedral bonds would be “stronger” than the intraicosahedral ones [25, 26, 27]. Icosahedral boron-rich solids form a special case of covalent materials adopting an unusual structure because of the electronic deficiency that is intrinsic to the boron atom.

The icosahedral $sp$ bonding is by far more complex than $sp$ bonding in diamond or other covalent materials with a tetrahedral coordination. Density functional theory is expected to be well suited to explain physical properties related to this complex $sp$ bonding.

2. The atomic structure of $B_4C$ from first principles

In this section, our aim is to review what has been established about the atomic structure of $B_4C$ by comparing experimental data to results computed from first principles.

The atomic structure of $B_12C_3$ ($B_4C$) boron carbide contains 15 atoms in four occupied crystallographic sites (figure 1). Two sites form a distorted icosahedron, the polar and equatorial sites, with 6 atoms per site. The third and fourth sites are respectively the center of the triatomic chain (one atom) and the chain ends (two atoms).

Experimentally, the three carbon atoms are difficult to distinguish from the twelve boron atoms. Indeed, the scattering length of a $^{13}$C nucleus is very close to the scattering length of a $^{11}$B nucleus, and only cell parameters have been measured by neutron diffraction [28, 29]. Atomic positions deduced from X-ray diffraction data indicate that the chain is C-B-C and that
one carbon atom is substituted in the icosahedron [30, 31]. As the X-ray form factor scales like $Z^2$, where $Z$ is the atomic number, the form factors for light neighboring elements like B and C are very close, and it is difficult to distinguish between boron and carbon atoms in the icosahedron. The picture provided by X-ray diffraction is the following one: the third carbon atom is statistically substituted on both polar and equatorial sites, with a predominance for the polar site. The formula is $(B_xC_{1-x})_6(B_yC_{1-y})_6$, in which $0.93 \leq x \leq 1$ for the polar site and $0.74 \leq y \leq 0.86$ for the equatorial site [31, 32].

In order to gain knowledge of the atomic structure of boron carbide with a carbon concentration of 20%, we investigated several structural models with ab initio methods based on DFT, with the purpose of comparing various computed physical properties with available experimental data. Calculations were performed within DFT using the plane-wave pseudopotential method. More details can be found in Refs [20, 24, 25].

2.1. Structural models
In this subsection, all our structural models have a 20% carbon concentration and consist in one unit cell of 15 atoms, periodically repeated by translations of the Bravais lattice vectors. One exception is the bipolar model, which contains thirty atoms to keep the stoichiometry (table 1). In the polar (resp. bipolar) model, the chain is C-B-C and the icosahedron has one (resp. two) carbon atom(s) in the polar site. In the equatorial model, the chain is C-B-C and one carbon atom is substituted in the equatorial site. We have also investigated a unit cell where the chain is C-C-C and the icosahedron is made of pure boron (chain model), or introduced some disorder in the chain, making it C-C-B instead of C-B-C (disordered chain model). A last model consists in a B-rich chain C-B-B (B-rich chain model) (table 1).

The substitution of a carbon atom in the polar site of the icosahedra offers six possibilities, resulting in substitutional disorder. This makes the observed symmetry of the unit cell on average rhombohedral. In our calculations, we do not take explicitly into account the substitutional disorder, as too large supercells would be required. Therefore, the periodic repetition of a carbon atom at a given position in the icosahedron induces a small distortion from the rhombohedral symmetry to a base-centered monoclinic cell. We checked that this approximation does not modify the conclusions of this paper.

2.2. DFT total energy
The total energy obtained within DFT-LDA is reported in table 1. The structure with the lowest energy is the polar model. We take this energy as our reference. The bipolar model comes second, with an energy higher by 0.25 eV per carbon atom change. This energy difference is very significant and corresponds in terms of thermal energy to a temperature larger than 2500 K. Furthermore, the DFT energetics allows to exclude the equatorial model, the chain model, the disordered chain model and the B-rich chain model. It shows that the chain is C-B-C. Exclusion of the equatorial and chain models will be further confirmed by inspecting the lattice dynamics and the NMR spectra. Moreover, the formation energies of disordered chain and B-rich chain models show that these models are unstable (table 5, rows 6 and 7, respectively).

The difference in total energy between our various structural models is much more important than actual accuracy of exchange and correlation functionals. The latter is indeed limited to 3 kcal/mol (10 meV/atom) [33]. As our models differ only by the location of one carbon atom, the exchange-correlation functional limits the accuracy of our calculations to 10 meV per carbon atom change. Crystal phases differing by less than that amount can hardly be distinguished and this may lead to a wrong prediction of the most stable phase. We see that this is not the case in table 1.
Table 1. Total energy (eV) per change of carbon atom location with respect to the polar model within DFT-LDA from Ref. [20, 24, 25].

| Model        | Chain         | Icosahedron | Total energy (eV) |
|--------------|---------------|-------------|-------------------|
| Polar        | C-B-C         | B_{11}C_p   | (0)               |
| Bipolar      | (C-B-C)       | B_{10}C_{2p} + B_{12} | 0.24             |
| Equatorial   | C-B-C         | B_{11}C_e   | 0.53              |
| Chain        | C-C-C         | B_{12}      | 1.05              |
| Disordered chain | C-C-B | B_{11}C_p   | 2.5               |
| B-rich chain | C-B-B         | B_{10}C_{2p} | 3.9               |

Furthermore, the difference in total energy between our structural models is similar in LDA and in GGA (not shown, Ref. [20]) within 20 meV per change of carbon atom. This gives us confidence in the predictive ability of the DFT energetics for our models. We emphasize that LDA and GGA have the same physical content. Nonetheless, we note that by construction there is a cancellation of errors between the exchange energy and the correlation energy in LDA. This cancellation is not built-in in the GGA functionals [34], which makes the computations both in LDA and in GGA worth performing and comparing. Moreover, by construction, GGA functionals tend to decrease the energy of the less dense phase, and hence to favor their stability [35]. Therefore, it is interesting to compute energy differences both in LDA and GGA, in order to obtain an error bar when the crystal density varies among the polymorphs. These differences in the construction of the functionals do not modify the relative stabilities of our structural models (table 1 and Ref. [20]).

Our results for B_{4}C are robust against approximations. Contrastingly relative energies of different crystal structures of pure carbon or of pure boron are much less robust. Graphite is found more stable than diamond by 145 meV/atom in DFT-GGA [36], whereas diamond is found more stable than graphite in DFT-LDA by only 15 meV [36]. Zero-point motion might reverse the most stable phase. Clearly, the determination of the stability of pure carbon polymorphs is beyond the capacity of actual exchange and correlation functionals [37]. This is particularly true for graphite, because Van der Waals interactions are not properly taken into account in LDA nor in GGA [38, 39, 40, 41, 42].

Turning to boron, in calculations for perfect crystals, α-B_{12} has been shown to be more stable than perfect 105-atoms-β-boron in DFT-LDA [43]. Recent calculations performed with a denser sampling of the Brillouin zone of α-boron yielded a total energy difference between α- and β-boron of 68 meV per atom in LDA and of 25 meV per atom in GGA, both predicting that α-B_{12} is more stable [44]. The difference between LDA and GGA is very important in this case. The 43 meV per atom energy difference yields an error bar of the exchange and correlation functionals.

On the other hand, calculations including defects predicted that defected β-boron is the most stable phase [43, 45, 46, 47, 48, 49]. The energy difference with respect to perfect α-boron is at most 20 meV/atom, far below the above-mentioned error bar of 43 meV. Also in this case, calculations reach the limit of exchange and correlation accuracy. We believe that the theoretical determination of the stability of pure carbon or pure boron polymorphs deserves further theoretical breakthroughs to overcome the intrinsic limitation of LDA and GGA functionals.

2.3. Lattice dynamics
Turning to lattice dynamics, we have computed [24] the phonon frequencies at the center of the Brillouin zone for the polar, equatorial and chain models (table 1). We note that in our
case the electronic structure and the lattice dynamics are performed within the same theoretical framework. This implies that variation of both Hartree potential and of exchange and correlation potential are calculated to first-order in perturbation. This response of the screening potential to the perturbing phonon is computed self-consistently, so that at variance with semi-empirical models, the electronic density does not “rigidly shift” with the atomic motion. Compared to e.g. valence-force-field models, our computational scheme for phonon frequencies and displacement patterns does not contain any fitting parameter.

In figure 2, we report the theoretical spectrum [24] for infrared absorption compared with data from Ref [50]. Peak positions are clearly in better agreement for the polar model. With respect to the equatorial model, this is particularly true for the mode observed near 407 cm$^{-1}$. This is a vibration of the chain-center atom perpendicular to the chain axis.

The discrepancy between experimental peak positions and chain model ones is even more pronounced at high frequencies. The peak observed around 1560 cm$^{-1}$ comes from the stretching of the chain, when the chain-end atoms vibrate antisymmetrically (ungerade vibration). The frequency is by far larger when the chain is C-C-C (Panel a) than when the chain is C-B-C (Panels b and c). We therefore conclude that the chain model can be disregarded: stretching of C-C-C chains does not occur in measured infrared spectra.

Turning to peak intensities in the polar model, we show in panel (d) a fit with one single parameter being the proportion between $E_u$ and $A_{2u}$ polarizations. Indeed, this proportion of polarizations is unknown in experiment. Our fit is in good agreement with experiment, showing that the tensor of effective charges is properly accounted for in the calculations.

If not silent, a vibration in B$_4$C is observed either in Raman diffusion or in infrared absorption. This is because the centre of the icosahedron is an inversion centre. The parity of a mode with respect to the inversion center is unique and the mode is either infrared active (ungerade $E_u$ and $A_{2u}$ modes) or Raman active (gerade $E_g$ and $A_{1g}$ modes). Therefore it is interesting to compare our computed phonon frequencies also to the peaks observed by Raman scattering. To our knowledge, only one Raman spectrum measured on a single crystal has been reported in the literature, and it is our reference in figure 3. Observed peaks are broadened by disorder, and in the high frequency range, the theoretical frequencies of all our models [24] coincide with the experiment.

Nonetheless, two vibrational modes at 481 cm$^{-1}$ and 534 cm$^{-1}$ can be singled out. Both modes involve bond bending. The mode observed at 481 cm$^{-1}$ corresponds in our calculations to a rotation of the chain-end atoms around the chain-center. The mode observed at 534 cm$^{-1}$ corresponds to the libration of the icosahedron. This mode has been previously observed in $\alpha$-boron and it was shown to be strongly harmonic [51]. Compared with the disorder-induced broadening of other vibrations, the small widths of the two peaks indicate that the two above mentioned modes are harmonic in boron carbide. The frequency difference between them is therefore a quantity which is expected to be well reproduced in our calculations within the harmonic approximation. Figure 3 shows that the experimental frequency difference is reproduced only by the polar model. This difference is smaller by a factor of 2 in the equatorial model. Therefore the equatorial model can be disregarded as a possible structural model for B$_4$C.

Last but not least, we note that our calculations show no vibrational modes below 400 cm$^{-1}$ (figure 3). The Raman peaks which are observed below 400 cm$^{-1}$ in most of experiments [52, 53, 54] come from a lift of the selection rules for Raman scattering [24]. If $\omega$ is the phonon frequency, the intensity scales like a $\omega^4$ power law at low frequency, which is the signature of a density of states of acoustic phonons. These phonons could be used to check the samples against structural disorder: they are expected to vanish in clean samples.
Figure 2. Infrared spectrum of B$_4$C from Ref. [24]. Dashed line: experiment.[50] Solid line: theoretical spectrum for the *chain* model (panel a); *equatorial* model (panel b); *polar* model (panel c). Panel d: spectrum for the *polar* model where the proportion of E$_u$ and A$_{2u}$ polarizations has been fitted with one single parameter to reproduce the unknown mixing of polarizations in the experiment (see text). (Reproduced with permission from [24])
2.4. Nuclear Magnetic Resonance

In previous subsection, the comparison of the calculated lattice dynamics with experiment allowed to identify the atomic structure of B$_4$C as a C-B-C chain and a B$_{11}$C$^p$ icosahedron with the carbon atom substituted in the polar site. But we have also seen that experimental vibrational spectra do show a large broadening caused by substitutional disorder and/or structural defects. Therefore we have decided to compute NMR spectra, with the aim to learn more about these defects [20].

Three values of the chemical shift of $^{13}$C have been reported in the experimental literature (table 2). Experiments [55, 56, 57] agree with one another about two signals around 1 and 82 ppm. Only one experimental work reports a signal at 101 ppm [55]. We note that this experiment yielded the best resolved spectrum. This additional peak may also be explained by a different route of synthesis of the sample, yielding more structural disorder.

Our calculations show that the polar and bipolar models do explain well the experimental signals. Peaks around 1 and 82 ppm come from chain-end carbon atoms and from carbon atoms in the polar sites of the icosahedra, respectively (polar model). The bipolar model allows to explain the signal at 101 ppm observed in Ref. [55], which comes from a different screening of the magnetic field when two carbon atoms are substituted in the same icosahedron. From the point of view of the total energy, the favorite relative location of two carbon atoms is in antipodal polar positions [20]. Furthermore, we note that a few percents of pure B$_{12}$ icosahedra are necessary to keep the stoichiometry in our calculations.

Turning to the equatorial model, the width of the peak predicted by theory that comes from chain-end carbon atoms is greater than 9.1 ppm (table 2). This is significantly larger than in...
experiment. Moreover, the calculated spectrum of the $^{11}$B nucleus has a shoulder on the side of negative chemical shifts for the equatorial model (figure 4). At variance with this finding, the observed spectrum shows a shoulder on the side of positive chemical shifts, in agreement with the polar model [58]. This allowed us to disregard the substitution of one carbon atom in the equatorial site as a possible structure. Energetics, vibrational and NMR spectra thus agree on this point.

Moreover, a carbon atom at the center of the chain would yield a chemical shift as large as 234 ppm in the $^{13}$C spectrum. Such a signal is not observed (table 2). Energetics, vibrational and NMR spectra agree on the fact that no C-C-C chains are present.

Finally, comparison of computed and observed NMR spectra allows to draw the conclusion that the atomic structure of B$_4$C consists in a C-B-C chain and a B$_{11}$C$_p$ icosahedron with one carbon atom substituted in the polar site. A few percents of icosahedra have a B$_{10}$C$_2$ or a B$_{12}$ atomic structure. We have estimated that 95% of icosahedra are B$_{11}$C$_p$, 2.5% are B$_{10}$C$_2$ and 2.5% are B$_{12}$ ones [20].

**Table 2.** B$_4$C : $^{13}$C NMR chemical shifts, $\delta_{TMS}$ (ppm), and the corresponding peak intensities (in brackets). Experiments from Ref. [55, 56, 57]. Note that the weak resonance at 101.3 ppm is visible only in the experiment of Ref. [55]. Theory : models as in table 1.

| Experiments       | Theory            |
|-------------------|-------------------|
| Ref. [56] | Ref. [57] | Ref. [55] | Bipolar | Polar | Equatorial | Chain |
| 13±15   | -0.6       | 1.0     | -1.7 & -1.1 | -3.9 & 1.3 | 0.8 & 9.9 | 19.9 |
| (66.7%) | (75.6%)   | (66.9%) | (All models : 66.7%) | 81.6 | 79.1 | 233.8 |
| 85±10   | 79        | 81.9    | 101.3 | (These three models : 33.3%) | 100.8 & 104. |
| (33.3%) | (24.4%)  | (31.4%) | (1.7%) | (33.3%) | |

2.5. Conclusions

Inspection of both NMR and vibrational spectra yields the same picture for the atomic structure of B$_4$C : a C-B-C chain and a B$_{11}$C$_p$ icosahedron with one carbon atom substituted in the polar site.

There are no signatures of C atoms at the chain center. This has important consequences : C-C-C chains can not be responsible for the boron carbide amorphization in shock-wave experiments [59].

Lastly, B$_{10}$C$_2$ icosahedra are present as defects in some B$_4$C samples. We have estimated that 2.5% of the icosahedra are B$_{10}$C$_2$. These defects have been experimentally observed. The presence of B$_{12}$ icosahedra is inferred by us from the observed stoichiometry. To our knowledge, there are no direct observations of B$_{12}$ icosahedra in B$_4$C samples.

3. Atomic structure of boron carbides at lower carbon concentrations.

At variance with the case of B$_4$C, knowledge about boron carbides at lower carbon concentrations must be improved both experimentally and theoretically. The atomic structures are not understood, nor are the phase stabilities [60].

We have computed the equilibrium volume and formation energy of several structural models. Calculations were performed within DFT using the plane-wave pseudopotential method. Exchange and correlation energy was computed in the local density approximation. The
Figure 4. $\text{B}_4\text{C} : ^{11}\text{B}$ NMR chemical shift spectrum. Experimental data are from Ref. [58] and theory for the polar, equatorial and chain models from Ref. [20]. (Reproduced with permission from [20])

Pseudopotentials of boron and carbon were developed with the Troullier-Martin scheme [61]. For boron carbides, boron and diamond, plane waves up to a kinetic cutoff of 40 Ry have been included in the basis set. The irreducible wedge of the Brillouin zone has been sampled with 32 points when the unit cell was monoclinic (boron carbides with carbon atoms in the icosahedra), and 10 points when the unit cell was rhombohedral (e.g. for $\alpha$-boron or boron carbides with $\text{B}_{12}$ icosahedra) or cubic (diamond). Cell parameters and atomic degrees of freedom have been relaxed to minimize the total energy at theoretical equilibrium.

3.1. Formation energy
Following present knowledge, $\alpha$-boron (resp. diamond) is the most stable polymorph of pure boron (resp. carbon) within DFT-LDA for defect-free phases (see subsection 2.2). In a first step, formation energies of boron carbides have been computed for a formation from $\alpha$-boron + diamond.

We first considered a structural model as stable at 0 K when its formation energy $E^f$ is negative with respect to a decomposition into $\alpha$-boron + diamond, and when $E^f$ is the smallest one among structures with the same carbon concentration. Among many structural models that have been investigated, only the five models of table 3 are found stable [62]. At 20% carbon
In conclusion, only $B_4^C$ is found to be thermodynamically stable in our calculations. Four other phases are found thermodynamically unstable at ambient conditions because: (i) at 0 K, they are energetically close to a decomposition into $B_4^C + \alpha$-boron (for a carbon concentration lower than 20%) or $B_4^C + \text{diamond}$ (for a carbon concentration greater than 20%). Surprisingly, no phases are found stable against this decomposition in table 4. For $B_{13}C_2$, we found $E_f^{B_{13}C} = 7 \text{ meV/atom}$. Our result is similar to previous calculations, -21 meV/atom at 0 K and -9 meV/atom at ambient temperature [60].

The model combining $B_4^C$ and $B_{13}C_2$ also is marginally unstable ($E_f^{B_{4C}} = 7 \text{ meV/atom}$, table 4). These numbers are however within accuracy of actual exchange and correlation functionals (see subsection 2.2).

Replacing the chain-center atom by a vacancy in $B_4^C$ or in $B_{13}C_2$ yields two models with 21.3 or 14.3% carbon concentration respectively. These crystals with vacancies are found to have a negative formation energy with respect to a formation from $\alpha$-boron + diamond (table 3). They however have a positive formation energy in table 4 and should decompose into $B_4^C + \alpha$-boron or $B_4^C + \text{diamond}$ in thermodynamical conditions.

In conclusion, only $B_4^C$ is found to be thermodynamically stable in our calculations. Four other phases are found thermodynamically unstable at ambient conditions because: (i) at 0 K, they are energetically close to a decomposition into $B_4^C + \alpha$-boron or $B_4^C + \text{diamond}$ (table 4); (ii) entropy effects are expected to further favor this decomposition at ambient temperature. Having however negative formation energies with respect to $\alpha$-boron + diamond (table 3), the four phases could nonetheless exist either in a metastable state, like diamond does; or as defects in an otherwise perfect crystal of $B_4^C$, as $B_{10}C_{12}^p$ does (see subsection 2.4).

At a carbon concentration of 20%, we found negative energies for the $\alpha$-boron + diamond (for a carbon concentration lower than 20%) or $B_4^C + \text{diamond}$ (table 4) and $B_4^C + \alpha$-boron (for a carbon concentration lower than 20%) or $B_4^C + \text{diamond}$ (table 4). The model combining $B_4^C$ and $B_{13}C_2$ also is marginally unstable ($E_f^{B_{4C}} = 7 \text{ meV/atom}$, table 4). These numbers are however within accuracy of actual exchange and correlation functionals (see subsection 2.2).

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subsection 2.2). They can not be produced in a metastable state or as defects. For instance, insertion of carbon atoms in interstitial crystallographic sites is proved to be an inappropriate way of modeling boron-rich boron carbides (table 5, rows 13 and 17). Another model which has been discussed in the literature contains one atom at the centre of the icosahedron [64]. Such a model has a very high positive formation energy (table 5, rows 8 and 14). Therefore we do not expect to observe materials in which boron icosahedra accommodate one atom at the icosahedron centre.

3.2. Discussion

Like $B_4C$, boron carbides at low carbon concentrations probably are mixings of various building blocks. At carbon concentration other than 20%, the numerous structural models of table 5 can be disregarded as possible candidates. Instead, models of table 3 are useful guides towards a determination of actual atomic structures. The common thought that “intrinsic structural defects (...) originate from the energetically more favorable configuration compared to the ideal structures”[65] lacks a theoretical justification. Indeed, the surprise comes from the small number of possible candidates (table 3). Furthermore, the computation of the formation energy shows that these structures are not stable with respect to a decomposition into $B_4C$ boron carbide + $\alpha$-boron or $B_4C$ + diamond (table 4). This metastability explains why physical properties measured on different samples strongly depend on the synthesis route. More precisely, the instability of $B_{13}C_2$ with respect to a decomposition into $B_4C$ + $\alpha$-boron also explains the lack of an actual route to synthesize single crystals of $B_{13}C_2$. Investigation with $ab\initio$ methods of an eventual stabilization under high pressure should shed some light on this question.

NMR data are crucially lacking for boron carbides at low carbon concentrations. To our knowledge, only the experiment of Ref. [55] yielded data on boron carbides at 13.3 and 10% carbon concentrations. This experiment showed two additional signals beside those of $B_4C$. The intensities of these additional peaks however barely vary between 13.3 and 10% atomic carbon concentrations, so that one can not straightforwardly consider them as fingerprints of boron-rich boron carbides. The precision of NMR technique has drastically increased since 1991, and it would be of utmost importance to perform new experiments on boron carbides. DFT-based methods are mature enough to help understanding these experiments.

Finally, one should note that three models of table 3 contain an odd number of electrons per unit cell, and hence are metals in any band theory. Contrastingly, boron carbides are thought to be semiconductors [66]. We think that actual experimental knowledge might be too much sample dependent. A precise measurement of the resistivity on clean samples is lacking, and would be very helpful in discriminating among the models of table 3. We show in the next section that the strength of the electron-phonon coupling combined with the high average vibrational frequency makes boron carbides very interesting if a metallic state can be achieved.

4. Strength of the electron-phonon coupling

Among possible candidates for the role of the main building block for boron carbides at low carbon concentrations, $B_{13}C_2$ is the favourite one. As described in previous section 3, it consists in one $B_{12}$ icosahedron and one C-B-C chain. The odd number of electrons makes it metallic, while $B_4C$ is semiconducting. $B_{13}C_2$ can be viewed as a $B_4C$ crystal doped with one hole per unit cell, and any band theory in general, and DFT in particular, implies that $B_{13}C_2$ is a metal (figure 5). 90% of the states at the Fermi level are icosahedral states. This was our main motivation to investigate electron-phonon coupling in this material, which is a prototype of metallic icosahedral structures.

We have therefore computed the electron-phonon coupling $ab\initio$ [8, 69]. We obtained a coupling parameter averaged around the Brillouin zone equal to 0.8. This quantity is 0.9 in $MgB_2$ [69]. The phonon density of states reported in figure 6, and the Eliashberg function in
Table 3. Formation energy of stable [62] boron carbides at $T = 0$ K, $E_f$ (meV/atom). First column: model name as in table 1. Second column: carbon content. In the third column, excepted for the polar model and the elements, the formula of the icosahedron (resp. chain) is given in (resp. out of) brackets. V stands for a vacancy. This work: $E_f$ is computed in LDA for a formation from $\alpha$-B\textsubscript{12} + diamond. The formation energies of pure carbon or boron phases are also given.

| Model | at. % C | Materials       | This work | Theory | Exp. |
|-------|---------|-----------------|-----------|--------|------|
| 100   | Graphite|                 | -24\textsuperscript{[1]}; 0\textsuperscript{[2]} | -35±10\textsuperscript{[5]} |
| 100   | Diamond |                 | 0         |        |      |
| 21.4  | (B\textsubscript{11}C\textsuperscript{p})C-V-C | -15       | -11\textsuperscript{[2]} |        |
| Polar | 20      | B\textsubscript{4}C\textsuperscript{p} | -121      | -112\textsuperscript{[2]}, -109\textsuperscript{[3][4]} | -88±3\textsuperscript{[6]} (119±24)\textsuperscript{[7]} |
|       |         |                  |           |        |      |
|       |         | (B\textsubscript{11}C\textsuperscript{p})C-B-C+(B\textsubscript{12})C-B-C | -94 | [-92,-84]\textsuperscript{[4]} |      |
|       |         | (B\textsubscript{12})C-V-C | -20 | -35\textsuperscript{[2]}, -33\textsuperscript{[4]} |      |
|       |         | (B\textsubscript{12})C-B-C | -74 | -81\textsuperscript{[2]}, -79\textsuperscript{[4]} |      |
|       |         | $\alpha$-B\textsubscript{12} | 0 | 0\textsuperscript{[2]} |      |

[1] Formation from graphene with Van der Waals forces, Ref. [38].
[2] Formation from graphite and $\alpha$-B\textsubscript{12} in GGA, Ref. [63].
[3] LDA, Ref. [60].
[4] GGA, Ref. [46]. Square brackets indicate an energy range for $E_f$.
[5] Cited in Ref. [38].
[6] Enthalpy of formation at 0 K\textsuperscript{[67]}.
[7] Energy of formation at ambient temperature, Ref. [68].

Table 4. Same as in table 3 with $E_{fB_4C^p}$ computed in LDA for a formation from B\textsubscript{4}C\textsuperscript{p} + diamond for a carbon concentration larger than 20\%, and from B\textsubscript{4}C\textsuperscript{p}+\hbox{$\alpha$-boron} for a carbon concentration lower than 20\%.

| Model | at. % C | Materials       | $E_{fB_4C^p+\alpha-B_12}$ | $\Delta E_{fB_4C^p+\text{diamond}}$ |
|-------|---------|-----------------|---------------------------|-------------------------------------|
| Polar | 21.4    | (B\textsubscript{11}C\textsuperscript{p})C-V-C | -94                       | 104                                 |
|       | 20      | B\textsubscript{4}C\textsuperscript{p} | 0                         | 0                                   |
|       | 16.7    | (B\textsubscript{11}C\textsuperscript{p})C-B-C+(B\textsubscript{12})C-B-C | -94                       | 104                                 |
|       | 14.3    | (B\textsubscript{12})C-V-C | -20                       | -35\textsuperscript{[2]}, -33\textsuperscript{[4]} |
|       | 13.3    | (B\textsubscript{12})C-B-C | -74                       | -81\textsuperscript{[2]}, -79\textsuperscript{[4]} |

figure 7, allow to understand that the magnitude of the electron-phonon coupling mostly comes from a coupling with the vibrations of the icosahedron.

The pioneering theoretical method to compute the superconductivity now allows to compute the screened Coulomb interaction which is required to evaluate the critical temperature.[70, 71] In our calculation, we have instead used a parameter for the Coulomb repulsion in Mc Millan formula [69]. When this parameter is taken equal to the value of MgB\textsubscript{2}, we obtain a critical temperature of 27.6 K, only slightly below the 30.7 K obtained for MgB\textsubscript{2}.

To conclude this section, it has been shown that the critical temperature for metallic B\textsubscript{13}C\textsubscript{2} is comparable to the Tc of MgB\textsubscript{2}, and that superconductivity is linked to B\textsubscript{12} building blocks.
**Table 5.** Unstable [62] boron carbides. Formation energy $E^f$ (meV/atom) from $\alpha$-B$_{12}$ + diamond. Square brackets indicates an energy range for $E^f$. Column 1: model name as in table 1 or row number. Column 2: carbon concentration. Columns 3 and 4: description of the chain and of the icosahedron, respectively. $V$ stands for a vacancy. Column 5 indicates if additional atoms are in interstitial positions, and column 6 indicates if the icosahedron contains one atom at its centre.

| Model or row number | at. % C | Chain | Icosahedron | Interstitial | Ico. center | This work | Theory |
|---------------------|---------|-------|-------------|--------------|------------|----------|--------|
| Bipolar (row 2)     | 20      | C-B-C | B$_{10}$C$_2$ |              |            | 117      | [-117,-81] [-109,-70][1] |
|                      | 20      | (C-B-C)$_2$ | B$_{11}$C$^p$+B$_{11}$C$^{p'}$ |              |            | -113     |        |
| Equivalent chain    | 20      | C-B-C | B$_{11}$C$^p$ |              |            | -84      | -74[1] |
| Disordered chain    | 20      | C-B-B | B$_{10}$C$_2$ |              | C          | 648      |        |
| B-rich chain (row 8)| 20      | C-B-C | B$_{10}$C$_2$ |              |            | 127      |        |
|                      | 18.8    | C-B-C | B$_{12}$      |              |            | 648      |        |
|                      | 15.4    | C-V-V | B$_{11}$C$^p$ |              |            | 144[2]   |        |
|                      | 14.3    | C-B-V | B$_{11}$C$^p$ |              |            | 48[2]    |        |
|                      | 14.3    | B-V-C | B$_{11}$C$^p$ |              |            | 62[2]    |        |
|                      | 13.3    | B-B-C | B$_{11}$C$^p$ |              |            | 45[2]    |        |
| (row 13)            | 12.5    | C-B-C | B$_{12}$      | B            |            | 49       |        |
| (row 14)            | 12.5    | C-B-C | B$_{12}$      | B            |            | 504      |        |
|                      | 12.5    | none  | B$_{11}$C$_2$+B$_{11}$C$_2$ |    |            | 579      |        |
|                      | 11.1    | C-B-C | B$_{11}$C$_2$+B$_{12}$ |    |            | 93       |        |
| (row 17)            | 10.1    | C-V-C | B$_{12}$      | B$_6$        |            | 355      |        |
|                      | 8.3     | none  | B$_{11}$C$^p$ |              |            | 127[2]   |        |
|                      | 7.7     | B-V-V | B$_{11}$C$^p$ |              |            | 212[2]   |        |
|                      | 7.7     | V-B-V | B$_{11}$C$^p$ |              |            | 212[2]   |        |
|                      | 7.4     | C-B-C | B$_{12}$+B$_{12}$ |    |            | 75       |        |
|                      | 7.1     | C-B-V | B$_{12}$      |              |            | 65[2]    |        |
|                      | 7.1     | B-V-C | B$_{12}$      |              |            | 67[2]    |        |
|                      | 7.1     | B-B-V | B$_{11}$C$^p$ |              |            | 119[2]   |        |
|                      | 7.1     | B-V-B | B$_{11}$C$^p$ |              |            | 119[2]   |        |
|                      | 6.7     | C-V-V | B$_{12}$      |              |            | 77[2]    |        |
|                      | 6.7     | C-B-C | B$_{12}$      |              |            | 14[2]; 16[1]; -58[3]; |    |
|                      | 6.7     | B-B-B | B$_{11}$C$^p$ |              |            | 75[2]    |        |

[1] GGA, Ref. [46].
[2] From graphite and B$_{12}$ in GGA, Ref. [63].
[3] LDA, Ref. [60].
The difficulty comes from the synthesis of single crystals (see subsection 3.2). Extrapolating our results to heavily doped $\alpha$-boron, its $T_c$ is expected to be greater than the $T_c$ of heavily doped diamond, silicon or silicon carbide, by more than one order of magnitude.

Figure 5. DFT-LDA band structure of $\text{B}_{13}\text{C}_2$ from Ref. [69]. The energy (eV) is referred to the Fermi level (dashed line). (Reproduced with permission from [69])

5. Conclusion
In this work, we have reviewed actual understanding of the atomic structure of boron carbides gained from ab initio calculations. These computations allowed the unambiguous determination of the atomic structure of $\text{B}_4\text{C}$. Observed vibrational and NMR spectra are well explained by the polar model: one $\text{B}_{11}\text{C}^p$ icosahedron and one C-B-C chain per unit cell. We have shown that the main structural defect, apart from substitutional disorder of the carbon atom in the polar site, is a $\text{B}_{10}\text{C}_2^p$ icosahedron. These defects have been observed in one NMR experiment. Moreover stoichiometry implies the existence of $\text{B}_{12}$ icosahedra.

This good agreement moreover gives us a great confidence in the ability of DFT to accurately predict the formation energies of boron carbides at concentrations other than 20%. We have shown that very few structures can be regarded as possible candidates to be main structural blocks for boron carbides at carbon concentrations lower than 20%. This goes against the widely spread thought that intrinsic structural defects are energetically favourable with respect to ideal structure. Rather, we find a metastability of any model with respect to $\text{B}_4\text{C}^p + \alpha$-boron or $\text{B}_4\text{C}^p + \text{diamond}$. By shedding light on this metastability, we have explained actual difficulties in the synthesis of clean samples of boron carbides with carbon concentrations lower than 20%.

Last, we have shown that the strength of the electron-phonon coupling in a prototype icosahedral metal, $\text{B}_{13}\text{C}_2$, is comparable to electron-phonon coupling in $\text{MgB}_2$. From these considerations, we expect electron-phonon coupling in heavily doped $\alpha$-boron to be more than one order of magnitude greater than that of heavily doped silicon. Combining superconductivity and the known remarkable mechanical properties of boron carbides can lead to materials of high industrial interest.
Figure 6. Phonon density of states of $\mathrm{B}_{13}\mathrm{C}_2$ from Ref. [69]. Solid line : total DOS. Dashed line : contribution from the vibrations of the icosahedron. Dotted line : contribution from the phonon modes of the chain. (Reproduced with permission from [69]).

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Figure 7. Solid line: Eliashberg function from Ref. [69]. Dashed line: average electron-phonon coupling parameter. (Reproduced with permission from [69]).
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