

Atomic Structure of Icosahedral B₄C Boron Carbide from a First Principles Analysis of NMR Spectra

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Density functional theory is demonstrated to reproduce the ¹³C and ¹¹B NMR chemical shifts of icosahedral boron carbides with sufficient accuracy to extract previously unresolved structural information from experimental NMR spectra. B₄C can be viewed as an arrangement of 3-atom linear chains and 12-atom icosahedra. According to our results, all the chains have a CBC structure. Most of the icosahedra have a B₁₁C structure with the C atom placed in a polar site, and a few percent have a B₁₂ structure or a B₁₀C₂ structure with the two C atoms placed in two antipodal polar sites.

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Boron rich solids exhibit a fascinating geometric and electronic structure, unique in the periodic table. They are formed by a packing of B_{12-x}C_x icosahedra. The fivefold axis of the icosahedron can either be preserved up to the micrometer scale, as in the B₁₂O₂ boron suboxide [1], or be lost, as in α -boron or in the B_{12+x}C_{3-x} boron carbides. In all cases, the atoms in the icosahedra are held together by peculiar delocalized three-center bonds. The icosahedra are linked by covalent bonds. There are important analogies between these boron rich solids and other systems that have recently received a lot of attention, namely, the C₂₀ and C₃₆ small fullerene solids, which also contain inter cage covalent bonds [2]. The electrical conductivity of boron carbides exhibits an unusual temperature dependence, which has been explained in terms of a bipolaronic hole mechanism [3].

Among the boron rich materials, B₄C is the hardest [4], and is easily synthesized. It can sustain a high temperature, has a low density, is a semiconductor, and has a high degree of chemical inertness. B₄C is used in nuclear reactors as a neutron absorber, and its use in electronic devices destined for harsh chemical environments has also been suggested [5]. Despite the flourishing field of applications for B₄C, its microscopic atomic structure and, in particular, its substitutional disordering and the nature of its intrinsic defects are still not fully understood.

Until now, both x-ray and neutron diffraction techniques have failed to locate the C atoms in the B₄C structure, since B and C have such similar cross sections [6]. To address this problem, spectroscopic methods have been used [7,8]. Indeed, by comparing the experimental infrared and Raman vibrational spectra with those obtained by first principles calculations [7], the most likely C locations have been identified. However, vibrational spectroscopy sheds no light on the intrinsic defects nor on the type of disorder. NMR is usually expected to be more powerful than the vibrational spectroscopy in determining the local atomic environment. In fact, a number of experiments on the ¹³C

[9–11] and on the ¹¹B [10–13] spectra of B₄C have been carried out, but amazingly no structural information could be deduced. The complexity of the atomic structure as well as the lack of experience concerning the environment created by the atypical three-center bonds has thus far hindered a full interpretation of the data [8,11].

In this paper, we analyze the ¹³C and ¹¹B NMR spectra of B₄C boron carbide using a recently developed density functional approach for the calculation of NMR chemical shifts in solids [14,15]. We obtain a detailed characterization of the atomistic structure of B₄C. Furthermore, we identify the most abundant intrinsic defects of B₄C, which are found in a surprisingly high concentration.

Calculations are performed within density functional theory (DFT). The core-valence interactions are described by norm-conserving pseudopotentials [16] with *s* non-locality and the wave functions are expanded in plane waves with a cutoff of 50 Ry. For the crystalline structures, we sample the Brillouin zone with a 4 × 4 × 4 Monkhorst-Pack mesh. For the cluster calculations, we use cubic supercells with a 25 a.u. lattice constant. The total energy calculations and structural relaxations are performed both within the local density approximation (LDA) and the PW91 generalized gradient approximation (GGA). The geometries and relative total energies computed with the PW91 and LDA functionals are very similar. The NMR chemical shifts are computed using the PW91 GGA, since this functional has been proven to best reproduce the experimental C chemical shifts [17]. The all-electron NMR chemical shifts are computed using the gauge including projector augmented wave (GIPAW) method of Ref. [14], which has been proven to reproduce with high accuracy the results of all-electron NMR chemical shift calculations. For the GIPAW calculations, we use two projectors in each *s* and *p* angular momentum channel for both the C and B atoms [14]. This study is the first application of the GIPAW method to complex solids. The use of GIPAW was found to be essential in this study, as similar methods which do

not take the pseudopotential error into account [15] are not accurate enough for the present application.

To fix the chemical shift scale and to verify the accuracy of our method for B chemical shifts in icosahedral systems, we compute the B and C NMR chemical shifts of the $(B_{12}H_{12})^{2-}$ and $(B_{11}CH_{12})^{-}$ closo-borane clusters (Table I). According to experimental convention, we quote the C chemical shifts δ_{TMS} in parts per million (ppm) relative to the C shift of a liquid sample of tetramethylsilane (TMS). For the B chemical shifts δ_{BTE} , we use liquid B-trifluoroetherate (BTE) as the reference. Instead of fixing the absolute shifts of liquid TMS and BTE by a direct calculation, we ensure that the theoretical B δ_{BTE} of $(B_{12}H_{12})^{2-}$ and the theoretical C δ_{TMS} of $(B_{11}CH_{12})^{-}$ coincide with the experimental ones [21].

In the closo-borane molecules, the B and C atoms are found at the 12 vertices of an icosahedron. The calculated and experimental B δ_{BTE} shifts of $(B_{11}CH_{12})^{-}$ are in good agreement (Table I). In particular, we reproduce the antipodal effect [20], i.e., if we replace a B atom by a C atom in $(B_{12}H_{12})^{2-}$, the B atom diametrically opposite (antipodal) to the C atom is the most strongly affected by the replacement.

The atomic structure of solid B_4C , Fig. 1, consists of an arrangement of 12-atom icosahedra, and of linear 3-atom chains. The periodic unit cell contains 15 atoms, i.e., one icosahedron and one chain. Two crystallographically inequivalent sites exist in the icosahedron. The six atoms which form the top and bottom triangular faces of the icosahedron sit at the *polar* sites, and are directly linked to atoms in neighboring icosahedra by covalent bonds. The other six vertices of the icosahedron form a puckered hexagon, and these symmetry-equivalent sites are called *equatorial* sites. Each one of the six equatorial atoms are linked by a covalent bond to an atom at the end of a chain.

The results of ^{13}C NMR measurements in B_4C [9–11] are summarized in Table II. Note that the intensity of an NMR peak is proportional to the number of atoms which contribute to that peak. All the authors agree with the assignment of the peak near 0 ppm to two C atoms at the

ends of the chain, but the assignment of the peak at 80 ppm is controversial. In Ref. [9] the peak around 80 ppm is assigned to a C atom at the center of the chain. Under this hypothesis, the structure of B_4C would contain B_{12} icosahedra and CCC chains. In Ref. [10] the peak at 80 has been assigned to a C atom in the icosahedron, at a polar site. In this case the structure of B_4C would contain $B_{11}C$ icosahedra and CBC chains. Finally, the peak at 101 ppm is observed but not interpreted [10].

To describe the structure of solid B_4C theoretically, we consider four 15-atom periodic atomic configurations proposed in the literature: (i) the *chain* model with one CCC chain and one B_{12} icosahedron in the unit cell, (ii) the *polar* model with one CBC chain and one $B_{11}C$ icosahedron, the C atom being substituted in a polar site, (iii) the *equatorial* model, with one CBC chain and one $B_{11}C$ icosahedron, the C atom being substituted in an equatorial site, and (iv) the same configuration as the polar one but with one CCB chain. In addition, we consider the possibility that two C atoms lie on the same icosahedron. In this case, to maintain the B_4C stoichiometry and the local charge neutrality, the system should contain either B_{12} icosahedra or CBB chains. In the first case, the unit cell must contain at least 30 atoms: two CBC chains, one B_{12} , and one $B_{10}C_2$ icosahedron.

In Table III we report the LDA and PW91 GGA energies of the different atomic configurations described above. The energies of the polar, equatorial, and chain models agree with those of Ref. [7]. We exclude the possibility that CBB or CCB chains could be found in the experimental samples, given the very high energy of the

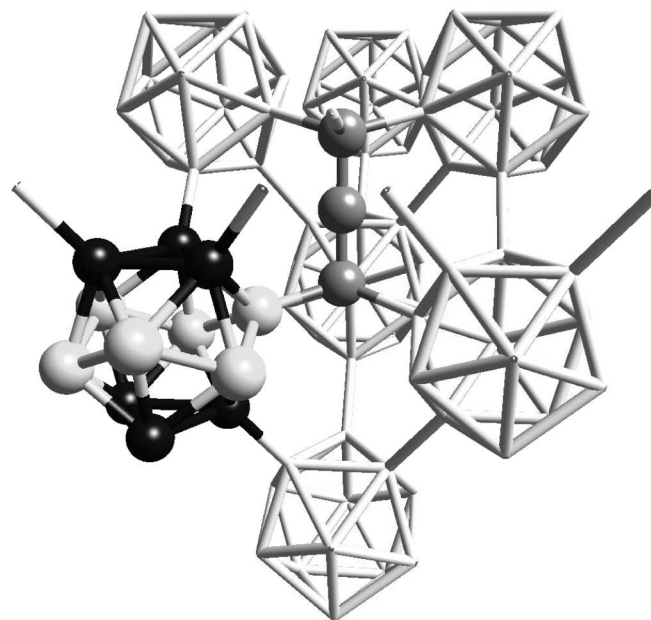


FIG. 1. Atomic structure of B_4C . The black atoms are on the so-called polar sites, bonded to neighboring icosahedra. The white atoms form a puckered hexagon and are in equatorial sites. The grey atoms form the chain, to which the equatorial atoms are bonded.

TABLE I. ^{11}B NMR chemical shifts δ_{BTE} and ^{13}C NMR chemical shifts δ_{TMS} in the closo-borane molecules. By ortho, meta, and antipodal we indicate the B atoms which are 1st, 2nd, and 3rd nearest neighbors of the C atom, respectively.

Molecule	Atomic site	Experiment	Theory
		B δ_{BTE}	B δ_{BTE}
$(B_{12}H_{12})^{2-}$		-14.9 ^a	(-14.9)
$(B_{11}CH_{12})^{-}$	Ortho	-16.3 ^b	-16.2
	Meta	-13.3 ^b	-11.7
	Antipodal	-6.9 ^b	-5.4
		C δ_{TMS}	C δ_{TMS}
$(B_{11}CH_{12})^{-}$		54.6 ^c	(54.6)

^aIn CD_3CN solvent, Ref. [18].

^bIn hexadeuterioacetone, Ref. [19].

^cRef. [20].

TABLE II. B_4C : experimental ^{13}C NMR chemical shifts, δ_{TMS} , and the corresponding peak intensities. Note that the weak resonance at 101.3 ppm is visible only in the best resolved spectrum [10].

Ref. [9]		Ref. [11]		Ref. [10]	
δ_{TMS}	Intensity	δ_{TMS}	Intensity	δ_{TMS}	Intensity
13 ± 15	66.7%	-0.6	75.6%	1.0	66.9%
85 ± 10	33.3%	79	24.4%	81.9	31.4%
				101.3	1.7%

corresponding configurations. The most stable structure is the polar model [22]. Unexpectedly, the second best structure after the polar model is the *bipolar* model, in which two C atoms are substituted on two antipodal polar sites of the same icosahedron. In particular, the bipolar model is energetically favored over the equatorial model and over all other $(CBC)_2-B_{10}C_2-B_{12}$ configurations in which the two icosahedral C atoms are not antipodal.

In Table IV we report the theoretical ^{13}C chemical shifts for the three atomic models proposed in the literature and our bipolar model. Each crystallographic site is characterized by a well-defined range of δ_{TMS} values. By comparing our theoretical results with the experimental data, we conclude the following.

(i) The computed C δ_{TMS} of the polar and equatorial models are in excellent agreement with the two main peaks of the experimental spectra. Indeed, the theoretical chemical shift of the icosahedral C atom is almost independent of the substitutional site [22]. The signals of the chain-end atoms lead to a linewidth smaller in the polar than in the equatorial model, in better agreement with the experiment.

(ii) None of the theoretical C δ_{TMS} of the chain model has any correspondence with the experimental peaks. We conclude that CCC chains are not present in B_4C .

(iii) The calculated C δ_{TMS} of the C polar atoms in the bipolar model are in excellent agreement with the small peaks at 101.3 ppm of the experimental spectrum [10]. Thus $B_{10}C_2$ are present as a defect in B_4C . From the

TABLE III. LDA and PW91 energies of hypothetical solid B_4C . The polar model is the ground state. Other configurations are obtained by changing a C atom location in the polar model. We report the energies required to obtain a given configuration starting from the polar model, per C location change. In this way, the energies are defined as defect formation energies. With C^p (C^e), we indicate a C atom substituted in a polar (equatorial) site. In the bipolar model the icosahedral C atoms are in antipodal positions.

Model	Structure	LDA (eV)	PW91 (eV)
Polar	$CBC-B_{11}C^p$	(0)	(0)
Bipolar	$(CBC)_2-B_{12}-B_{10}C_2^p$	0.24	0.25
Equatorial	$CBC-B_{11}C^e$	0.53	0.54
Chain	$CCC-B_{12}$	1.05	1.07
	$CCB-B_{11}C^p$	2.5	2.5
	$CBB-B_{10}C_2^p$	3.9	4.0

experimental peak intensity, we deduce that about 2.5% of the icosahedra are of $B_{10}C_2$ type. The requirements of stoichiometry and local charge neutrality suggest that a similar percentage of B_{12} icosahedra is also present in the experimental sample of Ref. [10]. As expected, $B_{10}C_2$ defects are fewer in C poor phases: The experimental intensity decreases from 1.7% in B_4C to less than 0.5% in $B_{13}C_2$ and vanishes in B_9C [10].

We now turn to the ^{11}B NMR spectra. The main peak comes from the B atoms in the icosahedra with theoretical δ_{BTE} ranging from -6.7 to 6.3 ppm in the polar, equatorial, and chain models. Since the experimental resolution of ^{11}B NMR spectra makes it impossible to resolve the individual contributions of the B atoms in the icosahedra, we directly compare the experimental [13] and theoretical spectra in Fig. 2. Only the line shape of the polar model bears a close agreement with the experiment. In particular, neither the chain nor the equatorial models are able to reproduce the shoulder around 6 ppm on the left side of the main peak. Interestingly, this shoulder comes from the 6.3 ppm chemical shift of the polar B atom which is antipodal to the polar C atom. The separation between the antipodal shoulder and the main peak is close to what is found in the $(B_{11}CH_{12})^-$ closo-borane molecule (see Table I). Note that, given the experimental resolution, the ^{11}B NMR spectrum cannot be used to detect the presence of substitutional defects.

In addition to the main structure presented in Fig. 2, the signal of the B atom at the chain center is found at 67.3 and 66.1 ppm in the polar and equatorial models, respectively. Occasionally, a small signal is observed at 37 ppm in some experiments [11,13]. This peak could be related to the B atom at the center of the chain. Given the small intensity of the experimental peak and the discrepancy from the theoretical predicted position, a further experimental investigation would be helpful to better identify the δ_{BTE} of the B atom at the chain center.

In conclusion, we have shown that DFT is able to predict the C and B NMR shifts of boron carbide systems with high accuracy. From the DFT energetics and by comparing our results with the experimental NMR spectra, we have determined the detailed atomic structure of the B_4C boron carbide. In particular, for the sample of Ref. [10], we have found that (i) all the chains have a CBC structure, (ii) no C atoms occupy equatorial sites, and (iii) about 95% of the icosahedra have a $B_{11}C$ structure with the C atom

TABLE IV. Theoretical ^{13}C NMR chemical shift, δ_{TMS} .

Carbon site	Structural model			
	Polar	Bipolar	Equatorial	Chain
Chain-end	-3.9	-1.7	0.8	19.9
Chain-end	1.3	-1.1	9.9	19.9
Polar	81.6	100.8		
Polar		104.0		
Equatorial			79.1	
Chain-center				233.8

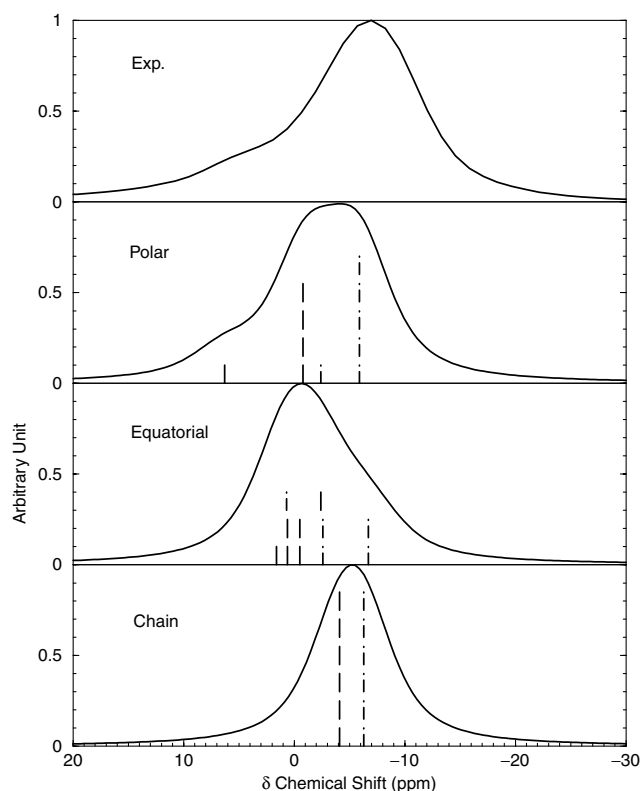


FIG. 2. Experimental ^{11}B NMR chemical shift spectrum from Ref. [13] (upper panel) and theoretical spectra of the icosahedral sites of the polar, equatorial, and chain models. The theoretical spectra are convoluted with a Lorentzian of half-width $\Gamma = 2.5$ ppm and a Gaussian of $\sigma = 1.5$ ppm. Each vertical solid and dash-dotted line indicates the contribution of a polar and of an equatorial atom, respectively.

placed in a polar site, about 2.5% have a B_{12} structure, and about 2.5% have a B_{10}C_2 structure with the two C atoms placed in antipodal polar sites. This very large number of defected icosahedra should have important consequences in the conducting properties of B_4C . In particular, the B_{12} icosahedra, which have a nominal electronic charge of $-2e$, are possible trapping centers for the positively charged bipolaronic-hole carriers [3]. Our investigation also demonstrates that the first principles calculation of NMR chemical shifts and total energies is a powerful complement to experimental measurements.

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 [21] In previous calculations, the B_2H_6 and CH_4 molecules have been used to fix the chemical shift scales. With our reference choice, the theoretical B δ_{BTE} and C δ_{TMS} of B_2H_6 and CH_4 are equal to 25.2 and -16.4 ppm, respectively. The corresponding experimental values are 16.6 and -11.0 ppm.
 [22] In the polar model, the C atoms on neighboring icosahedra are related by translations. Using supercells, we verified that this arrangement has the lowest energy. Among other arrangements, where the C atoms are not related by translations, we found a configuration with an energy comparable to that of the bipolar model. Thus, this kind of translational disorder should be present in B_4C . However, the computed C chemical shifts of the translationally disordered polar configuration are indistinguishable from those of the ordered polar model. Thus, this kind of disorder cannot be detected by NMR.