

Theory of shallow and deep boron defects in 4H-SiC

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Despite advances toward improving the quality of *p*-type 4H-SiC substrates and layers, we still have no model capable of accounting for the multitude of boron-related optical, junction, and paramagnetic resonance experiments available in the literature. A conspicuous puzzle is the observation of two shallow boron defects with rather distinct axial orientations as found by electron paramagnetic resonance (EPR) and electron nuclear double resonance (ENDOR) data. This feature is not observed in material doped with other group-III elements. Another open issue involves conflicting conclusions from photoluminescence and EPR studies of a deeper boron center, which has been linked to rather distinct models, either based on substitutional or vacancy-related boron defects. We unlock these and other problems by means of first-principles calculations, where the temperature-dependent stability, the electronic activity, and the paramagnetic response of boron defects in 4H-SiC are investigated.

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I. INTRODUCTION

Due to its rugged properties, including mechanical, thermal, and chemical stability, a large breakdown field, and the possibility of growing both electronic-grade *n*- and *p*-type layers, 4H silicon carbide (4H-SiC) is nowadays a semiconductor with an important and growing market on power electronics (used in electric vehicles, power supplies, motor control circuits, and inverters) [1,2]. SiC also finds applications in fundamental and emerging fields like high-energy particle detection [3] and quantum technologies [4–7].

The *p*-type dopants are usually boron, aluminum, and gallium. As for the former, there is ample evidence that its incorporation leads to the appearance of two types of acceptors, often referred to as *shallow* and *deep* boron centers, owed to the relative depth of their respective levels within the band gap [8,9]. The two boron species diffuse differently—boron-implanted/diffused layers show heterogeneous incorporation, where the deep center dominates the profile tails [10–12]. While the assignment of the shallow species to substitutional boron on the Si site (B_{Si}) seems consensual, the origin of the deep hole trap has remained elusive. Photoluminescence studies favor a boron atom on the carbon site (B_C) [13], magnetic resonance experiments point to a boron-vacancy complex [14,15], whereas first-principles results suggest either B_C [11,16] or a boron-silicon-antisite pair [17].

Another problem is that boron is often present in the SiC as a contaminant in trace concentrations. The deep species, also referred to as D-center, is of particular concern, especially in *n*-type SiC where it is negatively charged under equilibrium conditions. This state is a potential trap for holes, threatening the functioning of bipolar devices or *n*-type detectors [18].

A possible route for the elimination of the D-center involves thermal oxidation [19–21]. However, the impact of boron-related minority carrier lifetime degradation is not necessarily detrimental. The effect was actually explored to improve the switching time characteristics of *p*-i-*n* diodes, and that was attributed to the effect of a localized lifetime control in the intrinsic layer due to carrier recombination at deep boron traps [22,23].

The D-center is known since early deep level transient spectroscopy (DLTS) studies of B doped 6H-SiC, where two nearly overlapping peaks corresponding to electronic transitions at $E_v + 0.63$ eV and $E_v + 0.73$ eV were revealed [24]. Sutrop *et al.* [8] found that in addition to the deep boron center (measured in that work as a single DLTS peak at $E_v + 0.58$ eV), a hole trap at $E_v + 0.30$ eV was also present, and it was assigned to the shallower boron acceptor.

The presence of the D-center in the 4H polytype was also confirmed using DLTS by Sridhara *et al.* [9]. The level was placed at $E_v + 0.55$ eV (assuming a T^{-2} -corrected cross-section), again without resolving a double peak structure. Although the shallower species could not be found by DLTS (the Si/C ratio of the samples did not favor its formation), admittance spectroscopy measurements of Si-poor samples arrived at an acceptor level for shallow boron in the range 284–295 meV above E_v [9].

Recently, Laplace-DLTS and Laplace-minority carrier transient spectroscopy (Laplace-MCTS) measurements were carried out for studying the shallow and deep boron centers in 4H-SiC [25]. Estimated activation energies for hole emission were respectively 0.27 and 0.60 eV. From Laplace-MCTS, it was shown that the D-center consists of two components, D1 and D2 with nearly 1:1 intensity ratio, respectively estimated at $E_v + 0.49$ eV and $E_v + 0.57$ eV. The pair of traps was assigned to boron at two different carbon sublattice locations in 4H-SiC. The peak of the shallow boron species was structureless. If it corresponded to the superposition of more than one

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point defect (in different sublattice sites), they were indistinguishable as far as the resolution offered by Laplace-MCTS.

Early electron paramagnetic resonance (EPR) studies [26] indicated that the symmetry of the shallow boron species in 6H-SiC experienced a remarkable change upon lowering the temperature. In the 6H phase, two cubic (k_1 and k_2) and one hexagonal (h) sites are available for B_{Si} substitution. While above $T = 50$ K the EPR signals related to all three substitutions show a trigonal pattern, below that temperature the k -related signals lower their symmetry to monoclinic. The h -related signal preserves C_{3v} symmetry for temperatures as low as 5 K.

These findings were confirmed latter by electron nuclear double resonance (ENDOR) spectroscopy [27,28]. The defect structure was interpreted as comprising a B-C broken bond, where boron is threefold coordinated (connected to three C ligands), while the remaining C atom holds a hole that is responsible for 40% of the total spin density. Strikingly, whereas the C radical is aligned along the main crystallographic axes for the case of B_{Si} sitting on the h site, for some reason, boron on the cubic sites leave a C dangling bond aligned along a basal B-C direction. Analogous observations were reported in 4H-SiC samples [29,30].

The deep boron center also has EPR-related signals and several experiments produced rich amounts of data (see Refs. [14,15] and references therein). The defect has a spin-1/2 paramagnetic state, but unlike the shallow boron center, both h - and k -related signals show the same alignment along the hexagonal c axis, with a small basal anisotropy. Minute ^{13}C satellite lines were detected around the main signals, the ^{11}B hyperfine interactions were negligible, and no large ^{29}Si were observed either. However, the spin density was found to be almost 100% localized on Si ligands. Based on the data, a model combining a boron on a silicon position with an adjacent carbon vacancy ($B_{Si}-V_C$) was proposed. The structure comprises an inert boron atom and three Si radicals edging the V_C unit, thus explaining the electronic and magnetic activity [14,15]. An obvious difficulty of this model is that for some reason, the pair would have to be invariably formed with an alignment along the c -axis. Such preferential alignment is not supported by first-principles modeling. In fact, the calculations also show that the lowest-lying level of $B_{Si}-V_C$ is a donor in the upper half of the gap, and therefore, the complex is not compatible with the D-center [16,17].

While early semiempirical Hartree-Fock calculations using small H-terminated SiC clusters predicted that B_{Si} adopts an off-center configuration [31,32], subsequent supercell calculations within the local density approximation (LDA) to density functional theory (DFT) led to ambiguous conclusions. Accordingly, some authors justified the off-site location of B_{Si} with a Jahn-Teller (JT) effect [16,33]. Others found an effective-mass-like defect with no distortion at all [34]. Finally, the authors of Ref. [35] found that the LDA cannot describe the shallow boron state due to overmixing with the valence band. After applying a scissors correction to the band gap during the self-consistent Kohn-Sham method, they obtained a pronounced JT distortion toward C_{1h} symmetry and a prominent ^{13}C -hyperfine interaction due to a C-radical [35]. Although they account for the measured localization of the spin density, these results cannot explain the different

symmetries of k - and h -related boron EPR signals in both 4H- and 6H-SiC.

It is well-known that local and semilocal approximated DFT poorly describes insulator/semiconductor band gaps, making the discussion of defect properties, in particular, those that involve gap states, vulnerable. For instance, several insufficiencies of conventional DFT and advancements in modeling the electronic structure of defects in SiC were presented in Ref. [36]. Among the findings it was shown that hybrid DFT, which replaces a fraction of the local exchange potential by a (possibly screened) Fock exchange contribution, can provide reliable electronic structure of defects in SiC where a local density description fails. We revisited the theory of substitutional boron defects to verify if modern electronic structure calculation methods, in particular hybrid density functional theory, can shed light on the open issues described above. After detailing the methods employed in Sec. II, we report on the physical picture of Si and C replacements by boron in 4H-SiC (Secs. III A and III B). The following three sections connect our findings with photoluminescence and junction capacitance spectroscopies (Sec. III C), with finite-temperature effects on the preferential formation of Si or C substitutions (Sec. III D), as well as with the available EPR/ENDOR measurements (Sec. III E).

We show that B_{Si} and B_C defects nicely explain the optical, capacitance and magnetic measurements related to shallow and deep boron centers in 4H-SiC, respectively. Importantly, it is argued that the *shallow* label attributed to B_{Si} should be interpreted as *shallower* than the deep boron center. In other words, the B_{Si} center has the characteristics of a localized and deep hole trap and not of an effective mass theory (EMT) dopant. The EMT picture for B_{Si} has been advocated based on (semi)local density functional results, but we show that higher level hybrid DFT predicts a strong atomistic relaxation upon hole capture at a ~ 0.3 eV deep trap, making the model compatible with the magnetic resonance observations. We rule out an assignment of deep boron to $B_{Si}-V_C$ based on the calculated g tensor elements. Along the paper, we also solve several problems, most notably we explain the observation of different orientations of g tensor and hyperfine interactions for shallow boron on cubic and hexagonal sites and the distinct temperature dependence of the g tensors of both centers.

II. THEORETICAL METHODS

First-principles calculations were carried out using the density functional Vienna *ab initio* simulation package (VASP) [37–40], employing the projector-augmented wave method, thus avoiding explicit treatment of core states [41]. A basis set of plane-waves with kinetic energy of up to 400 eV was used to describe the Kohn-Sham states. Total energies were evaluated self-consistently, using the hybrid density functional of Heyd-Scuseria-Ernzerhof (HSE06) [42,43] with a numerical accuracy of 10^{-7} eV. When compared to generalized gradient approximated (GGA) calculations [44]—which underestimate the band gap of SiC by a factor of nearly one half—the HSE06 functional has the main advantage of predicting a Kohn-Sham band gap width of 3.17 eV for 4H-SiC. This figure should be compared to the experimental value of 3.27 eV [45].

Defect energies were found using 400-atom (defect-free) supercells of 4H-SiC (with hexagonal shape), obtained by replication of $5 \times 5 \times 2$ primitive cells, into which boron defects were inserted. The equilibrium (calculated) lattice parameters of 4H-SiC were $a = 3.071$ Å and $c = 10.052$ Å. These are close to the experimental values of $a = 3.079$ Å and $c = 10.081$ Å [46].

Defect structures were firstly optimized within the HSE06 approximation using $\mathbf{k} = \Gamma$ to sample the Brillouin zone (BZ), until the largest force became lower than 0.01 eV/Å. On a second step, electronic total energies of the obtained structures were found from single-point calculations with the band structure sampled at a Γ -centered $2 \times 2 \times 2$ mesh of $\mathbf{k}$ points (also within HSE06). In line with Gerstmann *et al.* [35], we found that structural optimizations of B_{Si} defects within the GGA led to erroneous results due to overmixing of gap states with the valence band top. An analogous effect attributed to the overmixing of a carbon interstitial (C_i) level, in this case with the SiC conduction band bottom, was also pointed out by Gouveia and Coutinho [47], and that will be further discussed below.

Electronic transitions of boron defects were calculated by finding the Fermi energy at crossing points of formation energies for different charge states q . Defect formation energies (E_f) were obtained as a function of the chemical potential of the “sample” constituents, according to the usual formalism (see, for instance, Refs. [48,49]),

$$E_f(\mu_i, \mu_e; q) = E_{\text{elec}}(q) - \sum_i n_i \mu_i - n_e \mu_e. \quad (1)$$

The first term on the right-hand side of Eq. (1) is given by $E_{\text{elec}}(q) = \tilde{E}_{\text{elec}}(q) + E_{\text{corr}}(q)$, and refers to the electronic energy of the periodic calculation $\tilde{E}_{\text{elec}}$ shifted by E_{corr} to remove the effect of the artificial and infinite array of localized charges when the charge state is $q \neq 0$. For that we use the method proposed by Freysoldt, Neugebauer, and Van de Walle [50], generalized for anisotropic materials by Kumagai and Oba [51]. The method uses the axial and transverse dielectric constants of 4H-SiC, calculated as $\epsilon^{\parallel} = 10.65$ and $\epsilon^{\perp} = 9.88$, respectively [52]. See Ref. [53] (and also, Refs. [50–52,54–56]) for convergence tests to the formation energy of boron defects upon varying the boundary conditions. The second and third terms sum up the chemical potentials μ_i of the n_i neutral atomic species and $n_e = -q$ extra electrons (with respect to the neutral state) that form the problem. The electronic chemical potential is $\mu_e = E_v + E_f$, where E_v and E_f are the valence band top and Fermi energies, respectively. The former is obtained as the highest occupied state in a bulk supercell, whereas the latter is an independent variable.

Chemical potentials for $i = \{Si, C\}$ were calculated as

$$\mu_i = \mu_i^0 + (1 - f_i) \Delta E_{SiC}^f, \quad (2)$$

where μ_i^0 are energies per atom in pure silicon or carbon (diamond phase), ΔE_{SiC}^f is the heat of formation of SiC estimated as $\Delta E_{SiC}^f = \mu_{SiC}^0 - \mu_{Si}^0 - \mu_C^0 = -0.62$ eV, with μ_{SiC}^0 being the energy per SiC formula unit in a perfect 4H-SiC crystal. This result is close to the enthalpy of formation $\Delta H_{SiC}^f = -0.72$ eV measured at standard conditions [57]. Eq. (2) allows for a variation of the chemical potentials in the range $\mu_i^0 + \Delta E_{SiC}^f \leq \mu_i \leq \mu_i^0$ subject to $0 \leq f_i \leq \sum_i f_i = 1$, with

the upper limit representing i -rich conditions during the material growth. We will calculate the relative energy of different boron defects, all of which possessing a single boron atom. Although being an irrelevant quantity for this purpose, the chemical potential of boron (μ_B) was found from the α -rhombohedral ground state phase [12 atoms per unit cell with $R\bar{3}m$ space group (group No. 166)], with equilibrium lattice parameters $a = 5.029$ Å and $\alpha = 58^\circ$ [58].

We also examined the relative stability of boron acceptors on different lattice sites at finite temperatures. The range of temperatures close to those experienced during epitaxial growth are of particular importance. In this case intrinsic conditions apply, and for acceptors with levels in the lower part of the gap the relevant charge state is the negative one. The difference in the Helmholtz free energy of formation between two boron dopants replacing different crystalline species is obtained as,

$$F(B_{Si}^-) - F(B_C^-) = \Delta F_{\text{elec}} + \Delta F_{\text{vib}} + \mu_{Si} - \mu_C. \quad (3)$$

In the above, $\Delta F_{\text{elec}} = F_{\text{elec}}(B_{Si}^-) - F_{\text{elec}}(B_C^-)$ is the electronic free energy difference between the two defects, where F_{elec} is replaced by the stationary solution of the electronic problem, E_{elec} (obtained within hybrid density functional theory). This approximation essentially neglects electronic entropy, and it is justified by the depth of the electronic levels and the negligible density of defect states at the Fermi level under intrinsic conditions [59]. The second term on the right-hand side of Eq. (3) accounts for the vibrational free energy difference between the defects, and for each we have

$$F_{\text{vib}}(T) = k_B T \sum_{i=1}^{3N-3} \ln \left[2 \sinh \left(\frac{\hbar \omega_i}{2k_B T} \right) \right]. \quad (4)$$

The summation above runs over $3N - 3$ vibrational modes of the N -atom defective supercell, with respective angular frequencies ω_i . Symbols k_B and $\hbar$ refer to the Boltzmann and reduced Planck constants, respectively. It is noted that Eq. (4) already accounts for zero-point motion. Chemical potentials in Eq. (3) were found from Eq. (2), after adding a vibrational term F_{vib}/N to μ_{Si}^0 and μ_C^0 , obtained from respective supercells of silicon and diamond made of $N = 64$ atoms, and with the temperature set to $T = 273.15$ K. Analogously, a vibrational free energy term $2F_{\text{vib}}/N$ was added to μ_{SiC}^0 . For further details regarding the calculation of defect free energies, we direct the reader to Refs. [59–61] and references therein.

The vibrational mode frequencies of 4H-SiC cells containing boron defects were evaluated in $N = 72$ -atom cells ($3 \times 3 \times 1$ primitive cells). We considered the participation of all atoms in the dynamical matrix, whose elements were found from the force derivatives with respect to the atomic positions [61].

The g tensor and hyperfine (HF) interactions of paramagnetic boron defects were calculated using the gauge including projector augmented wave (GIPAW) method [62] as implemented in the QUANTUM ESPRESSO package [63,64]. The GIPAW method is based on self-consistent density functional perturbation theory, describing the applied magnetic field and spin-orbit couplings as perturbations. The current implementation pertaining the g tensor calculation is limited to local and semilocal functionals. Hence, for these calculations, the

Kohn-Sham states were found within the GGA [44]. We used hexagonal supercells of 256 atoms, a Γ -centered BZ sampling mesh of $2 \times 2 \times 2$, and a plane-wave cutoff $E_{\text{cut}} = 612$ eV (45 Ry). The computation of reciprocal space derivatives to obtain spin currents in linear magnetic response, makes the calculation of g tensors rather sensitive to $\mathbf{k}$ -point sampling [65]. Convergence issues can be especially severe for states whose g values show large deviations from that of the free electron. For that reason, we also tested a denser $3 \times 3 \times 3$ grid in the evaluation of g values for neutral B_{Si} .

Due to erroneous geometries obtained for B_{Si} defects within GGA, atomistic structures for the GIPAW calculations were found within HSE06 level (using the VASP code). Such combined approach was successfully used in a recent study of defects in Ga_2O_3 [66].

As for the HF coupling tensors A , they describe the interaction between the electron spin of a paramagnetic state with magnetic nuclei at the defect core. For an axial state along an arbitrary principal direction 3, transverse principal values $A_1 = A_2$ and the HF tensor can be described by isotropic (a) and anisotropic (b) hyperfine constants, which relate to the diagonalized tensor components as $a = (2A_1 + A_3)/3$ and $b = (A_3 - A_1)/3$ [27]. The evaluation of the HF tensors rely on the accurate computation of the spin density embedding the nuclei of interest, and for the case of the isotropic term (also known as Fermi contact), it involves the description of the electron density within the core region. Therefore the use of pseudopotentials implies a core reconstruction from the pseudo-wave-functions [67].

III. RESULTS

A. Boron on the silicon site: Shallow boron

We start by looking at the boron impurity on the Si site. In the neutral charge state, the boron atom was clearly displaced from the perfect lattice site after optimizing the energy with respect to the atomistic geometry. Essentially, boron formed three B-C bonds, leaving an unsaturated C radical. The on-site structure was metastable with a small ~ 0.1 eV barrier along the way toward the off-site ground state structure.

4H-SiC has two distinct sublattice sites, namely, cubic (k) and hexagonal (h), and for each, substitutional boron atoms can form two types of C radicals, namely, those polarized along the hexagonal axis of the crystal (labeled with “a” and standing for “axial”) and those polarized along the basal bond directions (labeled with “b” and standing for “basal”). This leads to a total of four possible defect configurations to consider.

Among all structures, those depicted in Figs. 1(a) and 1(b), namely, $B_{\text{Si}}(k_b)$ and $B_{\text{Si}}(h_a)$, were the most stable at k and h sites, respectively. The B atom in both structures displays threefold coordination, where three short (1.65 Å) B-C bonds contrast with the ~ 2.42 Å long separation between B and the C radical (see dashed lines in Fig. 1). See Ref. [53] (and also Ref. [68]), which provides further geometrical details of the structures. While B-C bond lengths are essentially the same for all configurations, the longer B-C distance can vary by about 0.04 Å, depending on the specific site and orientation. The energies of the two most stable neutral states, namely,

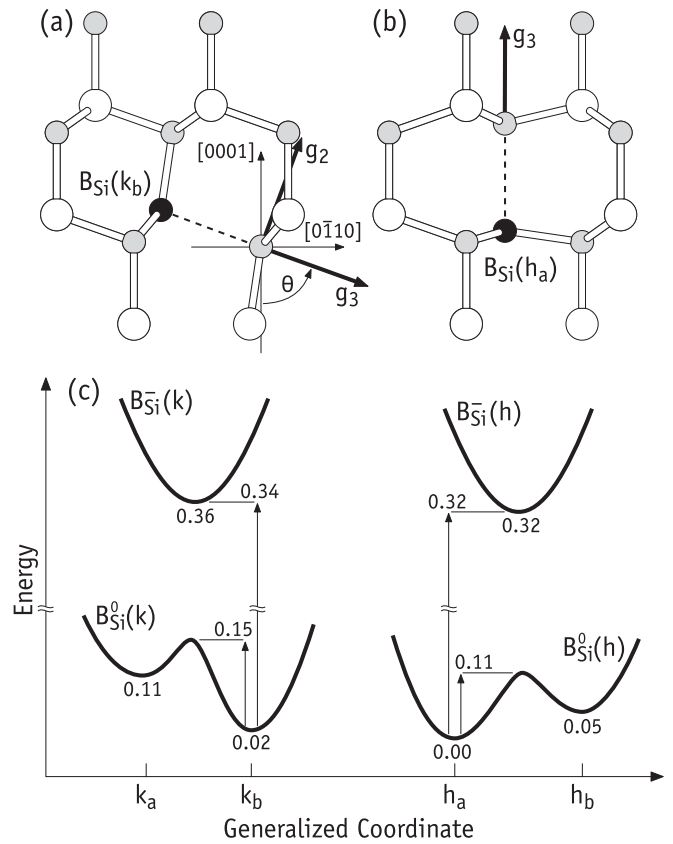


FIG. 1. Low-energy structures of neutral B_{Si} at (a) k and (b) h sites of 4H-SiC, respectively, and configurational coordinate diagram of neutral and negatively charge states (c). g tensor principal directions of neutral states are also shown. Boron, carbon and silicon are shown in black, gray and white, respectively. All energies in the diagram are in eV. Energies located below the energy minima are relative to the $B_{\text{Si}}^0(h_a)$ ground state. Energies next to arrow heads are relative to the state next to the arrow base. See Ref. [53] for details regarding the barrier calculations.

$B_{\text{Si}}^0(k_b)$ and $B_{\text{Si}}^0(h_a)$, differ by 0.02 eV only, whereas $B_{\text{Si}}^0(k_a)$ and $B_{\text{Si}}^0(h_b)$ are metastable, respectively at 0.11 and 0.05 eV above the ground state $B_{\text{Si}}^0(h_a)$. The reason for the breaking of the B-C bond along different directions for $B_{\text{Si}}(k)$ and $B_{\text{Si}}(h)$ will become evident when we discuss the electronic structure of the center further below. We summarize the above results in the lower part of the configurational coordinate diagram represented in Fig. 1(c).

The above threefold coordinated B_{Si} defects are markedly different from those found from previous local density functional calculations. B_{Si} in 3C-SiC was essentially reported as a fourfold coordinated center, showing only slightly different B-C bond lengths due to a weak JT driven C_{3v} distortion [16,33]. Fourfold coordination was also found for B_{Si} in 4H-SiC [34]. The neutral state was in this case interpreted as a shallow acceptor, binding a diffuse hole with the character of an EMT state. These conclusions are clearly at variance with our results—we find that (1) the paramagnetic B_{Si}^0 state is a singlet, showing the highest symmetry allowed by the crystalline host, i.e., it is immune to the JT effect, and (2) is strongly localized on the carbon radical next to boron, which is not in line with an EMT state.

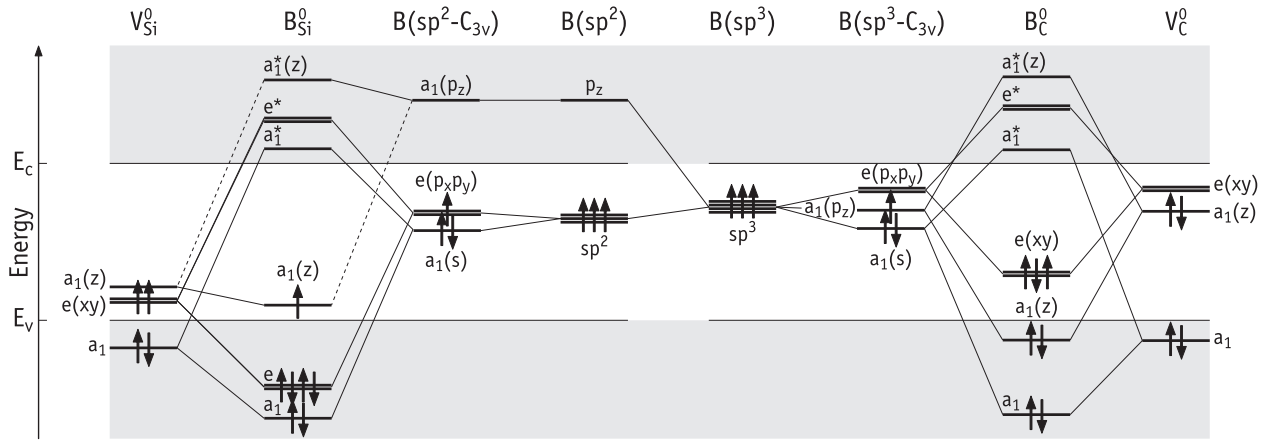


FIG. 2. Schematic one-electron models of B_{Si}^0 (left) and B_C^0 (right) impurities in 4H-SiC constructed by hybridization of valence states from sp^2 and sp^3 atomic boron (middle-left and middle-right) with states from the silicon and carbon vacancies (left and right), respectively. Labeling of states is according to the C_{3v} point group, except for isolated atoms in the middle. Some labels include the direction of the wave function polarization within parentheses. The diagrams are spin-averaged with upward/downward arrows indicating the level occupancy.

An explanation for the above conflict was put forward by Gerstmann *et al.* [35], who interpreted the prediction of an effective-mass character for B_{Si} as a failure of LDA, and as a corollary, a failure to describe the measured ^{13}C hyperfine data: “like the well-known underestimation of the fundamental band gap, the localization of this defect state is also strongly underestimated”. Accordingly, the LDA gap is about 50% narrower than the measured value, and for that reason, the C dangling bond state becomes artificially over-mixed with the SiC valence states. On the other hand, the nonlocal HSE06 functional predicts a 3.2 eV wide gap for 4H-SiC, allowing the singlet acceptor state to emerge above the valence band top.

An analogous effect was found by Gouveia and Coutinho [47] for C_i in 3C-SiC, but in this case involving the mixing of a gap level with the conduction band. Based on analysis of the Kohn-Sham data of structures ranging between the D_{2d} (ground state with spin-1) and C_{1h} (metastable and diamagnetic) structures of C_i^0 , an overestimated mixing between the C_i highest occupied level and the conduction band states, was attributed to the narrow (semi-)local approximated band gap, which favored the incorrect C_{1h} structure. Besides the exchange-correlation treatment, this effect may depend on other factors, most notably the dispersion of the defect state (the mixing could be k -point dependent), the sampling of the BZ, or the size/shape of the supercells. The authors of Ref. [47] used 512-atom cubic cells with the Brillouin zone sampled at Γ . More recently, Schultz *et al.* [69] found that upon improving the sampling to $2 \times 2 \times 2$ (using identical supercells and GGA-level exchange-correlation treatment), the correct spin-1 D_{2d} state could be recovered. In Ref. [36], it was noted that the C_{1h} metastable structure of C_i^0 , was the most stable when using 216-atom cells with Γ -sampling even at hybrid-DFT level. However, upon adding k -points away from Γ to the sampling mesh (where the gap is wider), the correct D_{2d} configuration was also recovered. The result of Ref. [70], where the C_{1h} structure was originally proposed as the most stable, was therefore attributed to errors related to calculation settings.

One could ask if, for the case of B_{Si} , the above effect results from poor sampling of the Brillouin zone. In Ref. [53], we clearly demonstrate that the valence band edge overmixing of B_{Si} at the GGA-level is a stable result and was found even for high-density k -point samplings (up to $4 \times 4 \times 4$).

From inspection of the band structure of defective supercells, we arrived at the orbital model for B_{Si}^0 depicted on the left hand side of Fig. 2. It consists of a schematic diagram without spin resolution. Upward/downward arrows simply reflect the electron occupancy. The model postulates how the $sp^{2\uparrow\uparrow}$ states of atomic $B(sp^2)$ unfold under the effect of a trigonal crystal field of $B(sp^2-C_{3v})$, and how these hybridize with the silicon vacancy states (V_{Si}^0) to produce the electronic structure of B_{Si}^0 . Accordingly, three short B-C bonds of B_{Si} are formed with the participation of six electrons on low-energy bonding states $a_1 + e$. These result from overlap of a_1 and $e(xy)$ states localized on three C atoms edging V_{Si}^0 , with $a_1(s)$ and $e(p_x p_y)$ of threefold coordinated $B(sp^2-C_{3v})$. Both $a_1 + e$ and corresponding antibonding states $a_1^* + e^*$ of B_{Si}^0 are resonant with the valence and conduction bands, respectively. The weak interaction between $a_1(z)$ (localized on the fourth carbon radical of V_{Si}^0) with the $a_1(p_z)$ state from the displaced boron atom, leaves the former within the gap and semioccupied. The $a_1(z)$ state is the C radical responsible for the acceptor activity of B_{Si} , the short covalent B-C bonds naturally explain the off-site distortion without JT effect.

A picture close to that of Fig. 2 was discussed in the literature nearly three decades ago by Bratus and coworkers [31]. From analysis using a linear combination of atomic orbitals (LCAO), it was argued that the $sp^2 + p_z$ hybridization of boron on the Si site was more stable than sp^3 simply because (1) the covalent radius of B is much smaller than that of Si and (2) the three bonds of $B(sp^2)$ with carbon (~ 1.6 Å long) are considerably shorter than the host Si-C bonds (~ 1.9 Å). Among the main conclusions was also the description of B_{Si}^0 ground state as a singlet, and consequently, that the observed displacement of B from the perfect crystalline site could be explained without a Jahn-Teller effect.

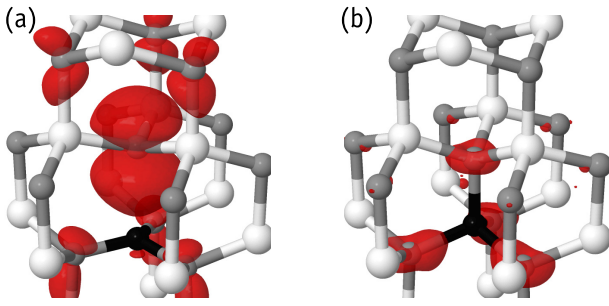


FIG. 3. Spin-density isosurface (cutoff $0.003 \text{ e}/\text{\AA}^3$) of neutral B_{Si} defects at the h site of 4H-SiC. (a) Off-site threefold coordinated ground state configuration obtained within HSE06. (b) Fourfold configuration as found from a GGA-level calculation. Si, C and B atoms are shown in white, gray and black, respectively.

Subsequent studies of Petrenko *et al.* [32], now using a semiempirical modified neglect of diatomic overlap method, also supported a pronounced off-site location for B_{Si} in SiC. The crystalline host was approximated as a hydrogen saturated spherical cluster of ~ 90 SiC atoms (3C phase). With the emergence of first-principles local density functional supercell calculations, a fourfold coordinated structure for B_{Si} with effective-mass character became favored, suggesting that the findings of Ref. [32] resulted from limitations of the method employed. For instance, one could argue that due to quantum confinement and underscreening effects, the band gap of the small clusters was rather wide. That effect could have eliminated the mixing of $a_1(z)$ with the valence, thus favoring the sp^2 -like bonding of boron. Another argument cautioning against the off-site location of B_{Si} is the fact that such relaxations are often overestimated when modeling defects in H-terminated clusters.

On the contrary, we argue that the (semi)local density functional results for neutral B_{Si} are spurious, that hybrid DFT finds the correct off-site location of the B atom, and the LCAO-based arguments of Bratus *et al.* [31] were essentially correct after all. Figure 3 depicts the spin-density in the vicinity of neutral $B_{Si}(h)$ in 4H-SiC as found for (a) the off-site ground state configuration within hybrid-DFT/HSE06 and (b) the on-site ground state configuration within conventional DFT/GGA. Both isosurfaces have the same spin-density cutoff ($0.003 \text{ e}/\text{\AA}^3$). They depict the border within which the magnitude of the spin density is above the specified threshold. Figure 3(a) shows that the amplitude of the spin density near the core of threefold coordinated B_{Si}^0 is much larger than in the fourfold coordinated configuration. In the latter case, many isosurface *bubbles* (with that specific spin density magnitude) are scattered across the supercell volume, hidden behind the spheres and cylinders used to represent atoms and bonds. Upon decreasing the cut-off by half, no spin density isosurface could be seen for the fourfold coordinated boron, while the p -like state of threefold coordinated boron was well visible. This is consistent with deep threefold and shallow fourfold states, respectively. Clearly, the DFT/GGA approximation predicts a diffuse state with very little localization at the core of the defect.

Still regarding the bonding character of B_{Si}^0 in SiC, we note that this center is isovalent to substitutional nitrogen

on the Si site of SiC (N_{Si}) [71] as well as substitutional nitrogen in diamond (N_s) [72]. Within a simple Lewis picture, B_{Si}^0 can be represented as $[\equiv B_{Si} \cdot C \equiv]$, where each horizontal bar stands for a single C-B or C-Si bond, and the bullet is an unpaired electron. Analogously, N_{Si}^0 in SiC and neutral substitutional N in diamond can be described as $[\equiv N_{Si} : \bullet C \equiv]$ and $[\equiv N_s : \bullet C \equiv]$, respectively, where the dots “ $\cdot$ ” represent a lone-pair of electrons tightly bound to nitrogen and deep within the valence band. Like the B species in the Si site of SiC, N atoms with four carbon nearest neighbors become threefold coordinated next to a paramagnetic C radical. However, unlike B_{Si} , local and semilocal density functional calculations account well for their off-site structure [71,73,74]. Although an explanation for such behavior is outside the scope of the present work, we speculate that short C-N bonds combined with Coulomb repulsion between the N lone pair and the unpaired electron on the C dangling bond could be important ingredients for the stabilization of the off-site configuration. A strong indication in favor of this argument is that while the C-radical of B_{Si}^0 in SiC induces a semioccupied state low in the gap, C-radicals of N_{Si} in SiC and N_s in diamond lead to semioccupied states in the upper half of the gap, suggesting a stronger repulsion of the unpaired electron in the N-related defects.

The semioccupied $a_1^\uparrow(z)$ singlet of B_{Si}^0 in 4H-SiC is represented in Fig. 2 just above the valence band top. A spin-averaged calculation of $B_{Si}^0(h_a)$ reveals that this level is located 0.52 eV above the highest occupied Kohn-Sham level from the bulk. On the other hand, in a spin-polarized calculation the spin-up $a_1^\uparrow(z)$ level lies within the valence band (the highest occupied state is bulklike), while the spin-down component of $a_1(z)$ is 1.47 eV above the E_v level. This picture is indicative of deep acceptor activity.

Upon atomic relaxation of negatively charged defects (B_{Si}^-), we found that independently of the lattice site and initial configuration, the boron atom moved to the perfect substitutional site, thus forming four nearly equivalent 1.77 Å long B-C bonds. Concurrently, the $a_1(p_z)$ state of boron increased its mixing with $a_1(z)$ from V_{Si} to form the fourth B-C bond. The resulting $a_1(z)$ bond state from B_{Si}^- became resonant with the valence, and the Kohn-Sham band gap was left clean. This does not imply that B_{Si}^- cannot capture a hole to become neutral. It does not imply that it is a shallow acceptor either. As will be shown in Sec. III C, hole capture is accompanied by reconfiguration to the threefold coordinated structure, making the hole trap relatively deep. As summarized in Fig. 1(c), the energy of $B_{Si}^-(h)$ was found slightly lower (0.04 eV) than that of $B_{Si}^-(k)$.

Now we look at the origin of the site-dependent alignment of B_{Si}^0 in 4H-SiC (the arguments discussed below apply to other polytypes as well). The analysis is best followed with help of Fig. 4. In 4H-SiC, the stacking of SiC dimers along the c -axis occurs according to a A-B-C-B sequence, where A and C are hexagonal bilayers and B are cubic bilayers. Importantly, while hexagonal SiC dimers (type A and C) are replicated in steps of length c along the main crystallographic direction (where c is the axial lattice parameter), cubic bilayers (type B) are repeated every $c/2$ -long steps. This results in a *wavier* electrostatic potential and a stronger electric field in crystalline regions along type B columns (see Fig. 4).

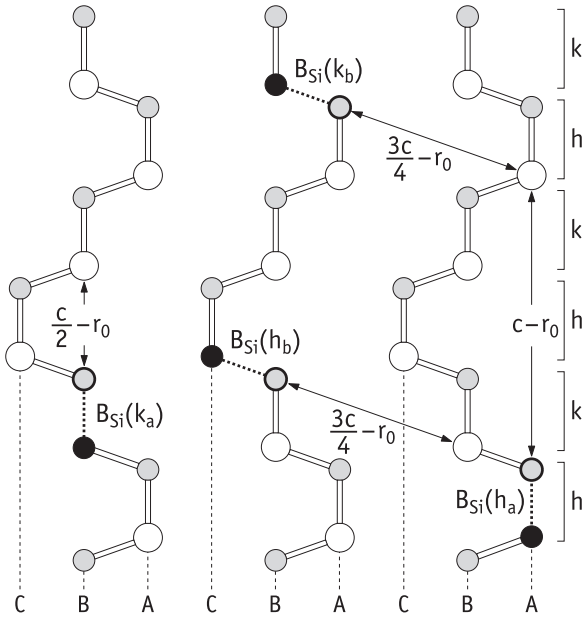


FIG. 4. Location and possible alignments of B_{Si} defects on the $\{11\bar{2}0\}$ plane of 4H-SiC. Silicon and carbon atoms are shown in white and gray. Boron and carbon at the core of the defect are represented as black and gray-haloed circles. For the sake of clarity, all atomic positions are those of the perfect crystal. The C-B broken bond of the neutral state is represented as a dotted line. Relevant distances are indicated next to arrows, where c and r_0 are the axial lattice parameter and the Si-C bond length, respectively. Stacking (A, B, C) and site (k , h) indexes are also indicated.

The $a_1^\uparrow(z)$ state on the C radical of $B_{Si}^0(k_a)$ interacts with the extensive $3sp^3$ valence electrons of the nearest Si atom along the axis, only $c/2 - r_0 = 3.14$ Å away from carbon, where r_0 is the Si-C bond length (see left hand side of Fig. 4). This repulsion effectively raises the energy of $B_{Si}^0(k_a)$ by 0.11 eV with respect to $B_{Si}^0(h_a)$. In the latter case, the Si atom on the back of the $C \cdots B_{Si}(h_a)$ unit is $c - r_0 = 8.17$ Å away from C (see right hand side of Fig. 4).

Due to symmetry reasons, the above analysis cannot be strictly applied to $B_{Si}^0(k_b)$ and $B_{Si}^0(h_b)$ defects (with C radicals polarized along Si-C basal bonds). However, analogous conclusions may be drawn by inspecting the amount of empty space between the carbon radical and the nearest atom along the $B \cdots C$ direction. As depicted in the middle of Fig. 4, in a pristine 4H-SiC crystal, that distance is $3c/4 - r_0 = 5.64$ Å for both k and h sites, thus lying right between the lower and upper limits of the axially distorted configurations. This is consistent with the energy ordering found for $B_{Si}^0(h_a) < B_{Si}^0(k_b) \sim B_{Si}^0(h_b) < B_{Si}^0(k_a)$.

The reorientation barrier between basal and axial distortions of neutral B_{Si} defects, was found from a batch of nudged elastic band (NEB) calculations encompassing five intermediate structures between initial and final states. See Ref. [53] (and also Ref. [75]) for details of the barrier calculations. From the results we find activation barriers of 0.04 and 0.06 eV for $k_a \rightarrow k_b$ and $h_b \rightarrow h_a$ reorientations. These jumps involve a return from metastable to lowest energy structures of B_{Si}^0 in k and h sites, respectively. These figures are reflected in the diagram of Fig. 1(c). Given the above meV-range barriers,

the metastable states are probably not formed, even at liquid-He temperature.

The reorientation of the C radical of $B_{Si}(k)$ between equivalent basal orientations was also investigated using the NEB method. We found that $B_{Si}(k)$ has to surmount a barrier of 0.09 eV to perform a $k_b \rightarrow k_b'$ jump between neighboring alignments with the same energy. Hence, above a certain (low) temperature, $B_{Si}(k)$ is likely to roam around all equivalent k_b distortions, showing effective thermally averaged C_{3v} symmetry.

B. Boron on the carbon site: Deep boron

Regarding the boron replacement of carbon (B_C), we found that the boron impurity sits very close to the crystalline site. Very small B-C bond distortions were obtained when symmetry breaking was allowed during the relaxations. From inspection of the Kohn-Sham band structure we found that the on-site configuration (with C_{3v} symmetry) introduces a deep doublet state in the gap. In a spin-averaged calculation of a trigonal $B_C^0(h)$ defect, a pair of doubly degenerate Kohn-Sham states occupied by three electrons appear at 0.29 eV above the highest occupied level from the bulk. On the other hand, in a spin-polarized calculation of the same structure the spin-up $e^{\uparrow\uparrow}(xy)$ level lies at 0.06 eV above E_v , whereas the spin-down counterpart $e^{\downarrow}(xy)$ is 0.44 eV above the E_v . Note that these figures neglect any Jahn-Teller relaxation and electron-phonon coupling effects (the occupation of the doublets was fixed—not variational).

A simplified bond orbital model for neutral B_C is shown on the right half of Fig. 2. It represents the conversion of atomic boron $B(sp^3)$ states under the effect of a trigonal crystal field, $B(sp^3-C_{3v})$, and the hybridization of the later with $a_1^{\uparrow\downarrow} + a_1^{\uparrow\downarrow}(z) + e(xy)$ states of the carbon vacancy (where boron is sitting). The Si radicals edging the V_C defect are considerably more diffuse than the C radicals in V_{Si} , and therefore their overlap with boron is significant for all states. The result is the formation of bonding $a_1^{\uparrow\downarrow} + a_1^{\uparrow\downarrow}(z)$ and antibonding $a_1^* + a_1^*(z)$ singlets within the valence and conduction bands, respectively, while a partially occupied $e^{\uparrow\downarrow\downarrow}(xy)$ doublet is left in the gap. The a_1 and $a_1(z)$ states are respectively located on basal and axial B-Si bonds, while the components of $e(xy)$ are B-centered p_x - and p_y -like states overlapping basal bonds only. It is clear that any electronic activity of B_C must be ascribed to the $e(xy)$ state.

Upon monoclinic distortion (C_{1h} symmetry), the $e^{\uparrow\downarrow\downarrow}(xy)$ neutral state can either split into $a''^{\uparrow\downarrow}(x) + a'^{\uparrow}(y)$ or $a'^{\uparrow\downarrow}(y) + a''^{\uparrow}(x)$ states with net spin $S = 1/2$. Here a' and a'' are respectively symmetric and antisymmetric with respect to a $\{2\bar{1}\bar{1}0\}$ mirror plane. While a'' is a p_x -like state with a node coincident with the mirror plane, a' is p_y -like with a node on the boron atom and polarized along $\langle 01\bar{1}0 \rangle$. Irrespectively of the lattice site, we found that the most stable JT-distorted configuration of B_C^0 involved a minute (~ 0.06 Å) displacement of boron along $\langle 01\bar{1}0 \rangle$, leading to two shorter B-Si bonds (and a slightly elongated one). That configuration corresponds to the electronic state $a'^{\uparrow\downarrow} + a''^{\uparrow}$. The alternative $a''^{\uparrow\downarrow} + a'^{\uparrow}$ state was metastable by 15 meV only. In overall, $B_C^0(k)$ was more stable than $B_C^0(h)$ by 39 meV.

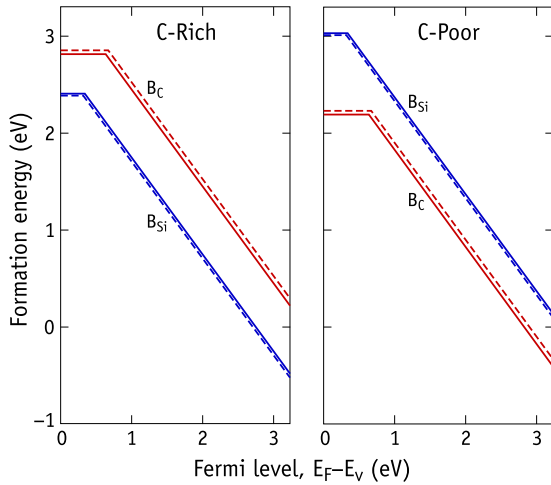


FIG. 5. Formation energy diagrams of B_{Si} (blue lines) and B_C (red lines) in 4H-SiC. Solid and dashed lines represent formation energies of boron defects located at k and h sites, respectively.

Interestingly, and despite the minute JT-driven bond deformations, the relaxation energy with respect to the high-symmetry (C_{3v}) state was about 0.25 eV for both $B_C^0(k)$ and $B_C^0(h)$. This is a surprisingly large value, and as far as we could find, it is not an artifact. The electronic occupancy of the high symmetry state (at the JT singularity) was not variational during the self-consistent cycle, and each pair of spin components of the doublet kept equal occupancy.

While the JT relaxation energy is a considerable barrier to surmount at liquid-He temperature, the question is—how likely is boron able to jump between neighboring off-axis configurations and show a dynamic Jahn-Teller effect? There are in total 6 possible JT displacements of boron away from the perfect C-site. They comprise alternating $a'^{\uparrow\downarrow} + a''^{\uparrow}$ and $a''^{\uparrow\downarrow} + a'^{\uparrow}$ states around the hexagonal axis of the crystal, dephased by a rotation angle of $\pi/3$. Jumping between neighboring structures involves a displacement of the B atom of only 0.04 Å. Although the barrier was not calculated with a proper transition-state method, it was estimated from the energy of the structure at mid-way between two neighboring $B_C^0(k)$ and $B_C^0(h)$ states. The small traveling distance of the B atom justifies this simple approach. Accordingly, we found that the rotation barrier is about 15 meV for both $B_C^0(k)$ and $B_C^0(h)$. Such minute figure is smaller than the zero-point energy of an oscillating B-Si bond, suggesting that the B_C^0 defects effectively roam around the c axis, thus showing a dynamic-JT effect even at liquid-helium temperature.

In the negative charge state, the doublet becomes fully occupied and B_C^- recovers the full trigonal symmetry of the C site. In this charge state, the impurity at the k site is 76 meV more stable than at the h site.

C. Connection with optical and junction spectroscopy

The formation energy of boron impurities, obtained according to Eq. (1), is shown in Fig. 5. There we show the results for the formation energy of B_{Si} and B_C defects in 4H-SiC under carbon rich and poor conditions (left- and right-hand side diagrams, respectively), as a function of the Fermi

energy (referred with respect to the valence band top). Solid and dashed lines refer to boron defects located at k and h sites, respectively.

Clearly, and in agreement with previous findings [16,33], in carbon rich material, where depletion of Si is favored, B_{Si} has lower formation energy than B_C . The opposite is found for C-poor material. At growth temperatures, where the Fermi level can be assumed to be at mid-gap, the formation energy of B_{Si} is 0.74–0.85 eV lower than that of B_C in C-rich samples. On the other hand, B_C is more stable than B_{Si} by 0.36–0.48 eV in C-poor samples. The ranges result from considering k and h sites for each impurity.

Figure 5 shows that both B_{Si} and B_C are single acceptors. The defects adopt a negative charge state for a wide range of Fermi levels, and we did not find donor transitions or additional acceptor transitions within the gap.

Considering the lowest-energy configurations of neutral B_{Si} defects at k and h sites, we place the acceptor levels of $B_{Si}(k)$ and $B_{Si}(h)$ at $E_v + 0.34$ eV and $E_v + 0.32$ eV, respectively. These results are shown graphically in Fig. 1(c), and they indicate that the binding energy of the hole to B_{Si} is almost independent of the lattice site, despite the adoption of rather distinct crystalline alignments by neutral $B_{Si}(k_b)$ and $B_{Si}(h_a)$ ground states.

These results are in line with the observation of a single peak by DLTS and Laplace-DLTS related to a hole trap of shallow boron at $E_v + 0.27$ eV [8,18,25]. Despite the agreement, we note that the calculated difference between the acceptor levels of B_{Si} at k and h site (20 meV), is smaller than the typical error of the method employed for the calculation. Additionally, the detection of a single peak by the Laplace-DLTS technique suggests that the difference could be even smaller, or that one of the configurations is dominant. The calculated relative energies of $B_{Si}(k)$ and $B_{Si}(h)$ do not support the second possibility.

An important question relates to the mechanism behind the capture of holes by B_{Si}^- . After all, the band structure of a supercell with this defect state shows a clean band gap. Our findings indicate that the mechanism involves a strong electron-phonon coupling, much like in a polaronic trapping effect [76]. Essentially, the off-site distortion of B_{Si}^- raises an occupied level above the valence band top, which is then stabilized upon hole capture. The first stage (level raising above E_v) translates into the surmounting of a capture barrier, estimated to be of the order of 0.1 eV. See Ref. [53] (and also Refs. [77–81]) for details regarding the raising of the level above E_v and the estimation of the capture barrier.

Regarding boron on the carbon site, we find $(-)/0$ transitions at $E_v + 0.63$ eV and $E_v + 0.67$ eV for $B_C(k)$ and $B_C(h)$, respectively. Neutral ground states with electronic configuration $a'^{\uparrow\downarrow} + a''^{\uparrow}$ were considered in our calculations. These figures agree well with early and recent measurements in 6H- and 4H-SiC [8,9,18,24,25], which indicate a transition of deep boron in the range 0.5–0.7 eV above the valence band top.

The separation between calculated levels of $B_C(k)$ and $B_C(h)$ is small, ≈ 40 meV, but about twice larger than the analogous figure obtained for B_{Si} . Again, this difference is lower than the error of the calculations, and therefore should be considered with due care. Considering that the signal of the D center was recently shown to comprise two equally intense

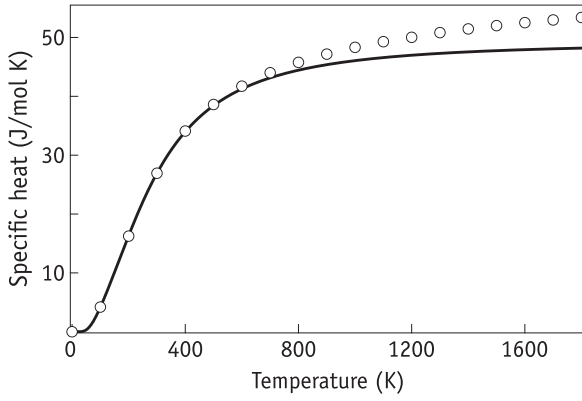


FIG. 6. Specific heat of 4H-SiC calculated at constant volume within the harmonic approximation (solid line). Circles represent measured data for α -SiC, obtained under constant pressure conditions as reported in Ref. [82]. The calculation employed Eq. (5) and considered a total of 213 vibrational frequencies from a 72-atom 4H-SiC supercell.

peaks separated by nearly 0.1 eV, our results support the view that these peaks arise from two nearly equivalent deep boron acceptors: A “shallower” configuration sitting at the cubic carbon site and a “deeper” one replacing the hexagonal site. These correspond to measured transitions at $E_v + 0.49$ eV and $E_v + 0.57$ eV, respectively [25].

D. Finite temperature calculations

Up until now, our results refer to zero temperature conditions, not even accounting for differences in zero-point motion between B_{Si} and B_C species. However, at high temperatures the effect of entropy to the relative stability of B_{Si} and B_C can be relevant. To strengthen our conclusions, we evaluated their respective free energies of formation at high temperatures, in particular under intrinsic conditions. For the sake of testing the methodology, we calculated the specific heat at constant volume for bulk 4H-SiC as

$$c_v(T) = -T \left(\frac{\partial^2 F_{vib}}{\partial T^2} \right), \quad (5)$$

and the result is shown in Fig. 6. In that plot, we also report several data points recorded during experiments at constant pressure for α -SiC (6H-SiC) [82].

The calculated specific heat describes the measurements very well up to nearly $T \sim 800$ K, when anharmonic effects start to gain importance, and beyond which the calculated free energy and its derivatives become more qualitative. In Ref. [61], we demonstrated that these calculations cannot be improved by enlarging the supercells. Also important, is the fact that the constant volume calculations match well the constant pressure measurements across a wide range of temperatures. The reason is hinted by the minute thermal expansion of crystalline SiC, which is about $5 \times 10^{-6} \text{ K}^{-1}$ for temperatures as high as 1000 °C [46].

The calculated difference in the free energy of formation $\Delta F(k) = F(B_{Si}^-(k)) - F(B_C^-(k))$, is shown in Fig. 7(a) in the temperature range $T = 600$ –1800 K. The quantity represented refers to impurities located in cubic sites. For boron defects at

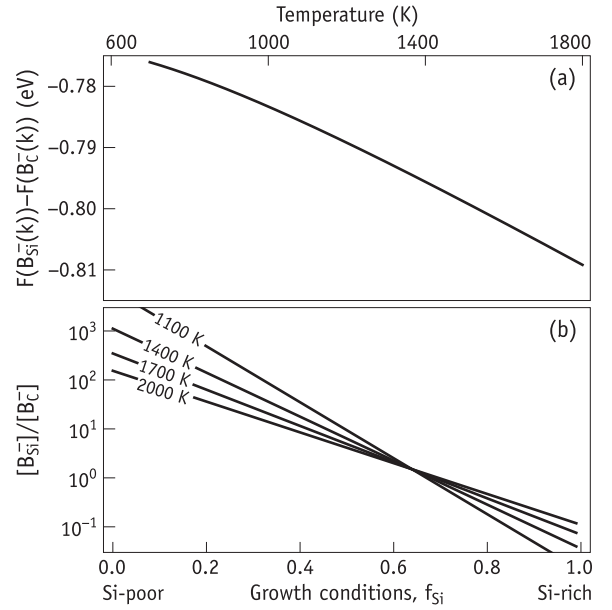


FIG. 7. (a) Free energy of $B_{Si}^-(k)$ with respect to that of $B_C^-(k)$ in 4H-SiC as a function of temperature under Si-poor conditions. The Fermi level was considered to be located at midgap. (b) Concentration ratio of B_{Si}^- to that of B_C^- as a function of the stoichiometric growth conditions (represented by f_{Si}), for selected temperatures.

the hexagonal sites the T -dependence of the analogous quantity was almost identical, although its magnitude increased by about 0.1 eV. Figure 7(a) shows that B_{Si}^- increases its relative stability with respect to B_C^- by almost 0.05 eV when raising the temperature from 1000 K to 2000 K. The implication of this result is illustrated in Fig. 7(b) where we plot the concentration ratio of B_{Si}^- to B_C^- defects as a function of the stoichiometric conditions (represented by f_{Si}), at different temperatures. Under equilibrium, the concentration ratio is given by

$$\frac{[B_{Si}^-]}{[B_C^-]} = \exp \left(- \frac{\Delta F(k) - \Delta F(h)}{k_B T} \right), \quad (6)$$

where $\Delta F(k)$ and $\Delta F(h)$ are free energy differences $F(B_{Si}^-) - F(B_C^-)$ pertaining k and h sites, respectively [as represented in Fig. 7(a)]. For chemical vapor deposition grown material, reactors typically run at temperatures of about 1600–1650 °C ($T \sim 1900$ K) [83]. Under these conditions we estimate $[B_{Si}^-]/[B_C^-] \approx 200$ and about 0.1 for a Si-poor and Si-rich stoichiometry, respectively. It is evident that even for the limit of Si-poor growth, which is the most favorable for introduction of the B_{Si} , thermodynamics imposes the formation of deep boron centers with a concentration about two orders of magnitude below that of the shallow counterpart. Figure 7(b) shows that even at $T = 1700$ K the $[B_{Si}^-]/[B_C^-]$ ratio is nearly 350, and probably the elimination of B_C cannot be achieved during growth.

We finally note that from the calculated vibrational mode frequencies, we could not find boron-related modes outside the spectrum of the crystalline density of states. Therefore any boron vibrational mode must be resonant, and most certainly hard to detect experimentally.

TABLE I. Calculated principal values (g_1 , g_2 , and g_3) of the gyromagnetic g tensor of paramagnetic boron-related defects at k and h sites of 4H-SiC. Assignments of experimental values from EPR signals of shallow (top) and deep (bottom) boron centers are indicated by their location in the table. For trigonal states (C_{3v}), g_3 is parallel to the main crystallographic c axis. For monoclinic states (C_{1h}), g_1 is perpendicular to the $\{2\bar{1}\bar{1}0\}$ symmetry plane, while g_2 and g_3 are rotated by an angle θ away from $\langle 0\bar{1}10 \rangle$ and $\langle 0001 \rangle$ directions, respectively. Dynamic trigonal states (labeled with a subscripted “dyn”) refer to averaged g tensors involving three symmetrically equivalent C_{1h} states (see text). Also indicated are the temperatures of the measurements.

	T (K)	Sym	g_1	g_2	g_3	θ ($^\circ$)
$B_{Si}^0(k_b)$		C_{1h}	2.0068	2.0078	2.0028	70
EPR [29]	4.2–45	C_{1h}	2.0059	2.0069	2.0025	69
$B_{Si}^0(k_{dyn})$		C_{3v}	2.0051	2.0051	2.0073	0
EPR [29]	61–83	C_{3v}	2.0046	2.0046	2.0064	0
$B_{Si}^0(h_a)$		C_{3v}	2.0089	2.0089	2.0022	0
EPR [29]	4.2–83	C_{3v}	2.0070	2.0070	2.0019	0
$B_{Si}(k)-V_C^0(k)$		C_{1h}	2.0041	2.0065	2.0028	78
$B_{Si}(k)-V_C^0(k_{dyn})$		C_{3v}	2.0035	2.0035	2.0063	0
$B_C^0(k)$		C_{1h}	2.0050	2.0205	2.0279	13
$B_C^0(k_{dyn})$		C_{3v}	2.0129	2.0129	2.0275	0
EPR [14]	4	$\sim C_{3v}$	2.0	2.0	2.029	~ 0
$B_C^0(h)$		C_{1h}	2.0056	2.0173	2.0246	13
$B_C^0(h_{dyn})$		C_{3v}	2.0116	2.0116	2.0240	0
EPR [14]	4	$\sim C_{3v}$	2.0	2.0	2.024	~ 0

E. Connection with EPR

Figure 1 readily explains the rather distinct EPR signals of shallow boron at k and h sites, as well as their temperature dependence [26]. While $B_{Si}^0(h)$ finds its ground state forming a paramagnetic p-like orbital on the C atom of a broken B-C bond along the main crystalline axis, the $B_{Si}^0(k)$ lowest energy configuration has an analogous p orbital (and a B-C broken bond) but it is now along the direction of a basal bond of the crystal.

The upper part of Table I records the calculated g tensors of shallow B_{Si}^0 defects in 4H-SiC, along with the corresponding quantities measured by EPR [29]. For trigonal states (C_{3v} symmetry), the main g_3 component is assumed to be parallel to the main crystallographic c axis. For monoclinic states (C_{1h} symmetry), g_1 is perpendicular to the $\{2\bar{1}\bar{1}0\}$ symmetry plane, while g_2 and g_3 are rotated by an angle θ away from $\langle 0\bar{1}10 \rangle$ and $\langle 0001 \rangle$ directions, respectively. Figures 1(a) and 1(b) show this convention graphically for $B_{Si}^0(k_b)$ with a broken B-C bond on the $(2\bar{1}\bar{1}0)$ mirror plane and for $B_{Si}^0(h_a)$, respectively.

Ground-states $B_{Si}^0(k_b)$ and $B_{Si}^0(h_a)$ have a calculated main g tensor component $g_3 \sim 2.002$ along the C radical, making an angle with the $[0001]$ direction of $\theta = 70^\circ$ and 0° , respectively (see also Fig. 1). The g tensors are nearly or perfectly axial for both static $B_{Si}^0(k_b)$ and $B_{Si}^0(h_a)$ structures, resulting from the conspicuous alignment of the spin density on the carbon radical as Fig. 3(a) clearly displays. The match with the measurements carried out at low temperature ($T \lesssim 45$ K) is excellent, both in terms of magnitude (error

$\lesssim 0.0005$) and monoclinic angle (error $\sim 1^\circ$). The error bar of the components perpendicular to the C-radical (g_1 and g_2) is about 4 times larger, but still, the agreement is deemed very good, especially considering that both calculated and observed g values show identical trends in terms of axial character and anisotropy: $g_2 - g_1 = 0.0010$ for $B_{Si}^0(k_b)$ and $g_3 - g_1 = -0.0067$ for $B_{Si}^0(h_a)$.

The calculated g tensor components of Table I were found by sampling the band structure over a $2 \times 2 \times 2$ mesh of $\mathbf{k}$ -points. A denser $3 \times 3 \times 3$ -mesh calculation for $B_{Si}^0(h_a)$ gave $g_1 = g_2 = 2.0083$ and $g_3 = 2.0015$, which deviate from the results with the coarser mesh by 0.0007. Most importantly, the relative magnitude of the axial and transverse components is similar in both calculations and match very well the observations.

As discussed at the end of Sec. III A, the activation energy for rotation of the broken bond of $B_{Si}^0(k_b)$ around $[0001]$ was estimated at about 0.1 eV, allowing the structure to jump between all three equivalent alignments at rather low temperatures. This result is consistent with the observed raise of symmetry of the EPR signal assigned to shallow boron in cubic sites, from monoclinic to trigonal above $T \sim 45$ K. We argue that above this temperature, the $B_{Si}^0(k)$ defect jumps between three equivalent monoclinic configurations at a rate much faster than the inverse of the EPR recording time. The result is the observation of a “dynamic” state with effective C_{3v} symmetry (hereafter labeled with a “dyn” subscript), whose g tensor is estimated by averaging over all three equivalent C_{1h} orientations. The calculated axial component $g_3 = 2.0073$ of $B_{Si}^0(k_{dyn})$, now along $[0001]$, mostly inherits contributions from $g_2 = 2.0078$ of static $B_{Si}^0(k_b)$ configurations [see Fig. 1(a)], thus becoming the largest component. This contrasts with g_3 of $B_{Si}^0(h_a)$ which is the smallest component of this configuration. The magnitude of the calculated g values of $B_{Si}^0(k_{dyn})$ agrees very well with those assigned to shallow boron on the cubic site measured in the temperature range $T = 61$ –83 K (error < 0.001). The calculated anisotropy $g_3 - g_1 \approx 0.002$ for $B_{Si}^0(k_{dyn})$ differs from the measurements by 0.0004 only.

The coupling of the unpaired spin of B_{Si}^0 defects with ^{13}C and ^{11}B magnetic isotopes quantifies the magnitude and shape of the spin density at the core of the defect. ^{11}B and ^{13}C hyperfine data was recorded experimentally at 3.4 K [26] and 1.5 K [28] by EPR and ENDOR, respectively. Under these conditions B_{Si}^0 defects are static and the HF signals could be resolved. The calculated principal values of the HF tensors due to interactions with ^{13}C and ^{11}B elements at the broken C-B bond of B_{Si}^0 defects (k_b and h_a structures) are reported in Table II. Also reported are the isotropic and anisotropic HF constants (a and b , respectively), which assume an axial character for the wave function of the unpaired electron. The upper and lower halves of the table show the results for boron located on cubic and hexagonal sublattice sites, respectively. The experimental data accompanying the calculations relate to boron defects in 6H-SiC samples [26,28].

The calculations confirm that the paramagnetic state is essentially axial along direction 3 (see principal directions and monoclinic angle θ in Fig. 1). Differences between A_1 and A_2 were always lower than 1 MHz. Both theory and experiments indicate a relatively large and close ^{13}C Fermi contact

TABLE II. Calculated principal values of the hyperfine tensors (A_1 , A_2 , and A_3) for ^{13}C and ^{11}B species located in the broken C-B bond of $\text{B}_{\text{Si}}^0(k)$ and $\text{B}_{\text{Si}}^0(h)$ defects in 4H-SiC. Isotropic and anisotropic HF constants (a and b) are also shown and they assume an axial state pointing along direction 3. For the trigonal $\text{B}_{\text{Si}}^0(h)$ defect, directions 1 and 2 are along the basal plane. For the monoclinic $\text{B}_{\text{Si}}^0(k)$ defect, B_1 is the component perpendicular to the $[2\bar{1}10]$ mirror plane, while B_2 and B_3 are rotated by an angle θ away from $\langle 0\bar{1}10 \rangle$ and $\langle 0001 \rangle$ directions, respectively (see Fig. 1). EPR data from ^{13}C -enriched samples (^{13}C -EPR) [26] and ^{11}B -ENDOR [28] are also included for comparison. These were obtained in 6H-SiC and pertain to boron defects at k_1 (k_1 and k_2 data are very similar) and h sites. All HF couplings are in MHz.

Defect	A_1	A_2	A_3	a	b	θ ($^\circ$)
$^{13}\text{C}-\text{B}_{\text{Si}}(k_b)$	34	34	183	84	50	72
^{13}C -EPR [26]	48	48	169	88	40	~ 70
$\text{C}^{11}\text{B}_{\text{Si}}(k_b)$	0	0	6	2	2	74
^{11}B -ENDOR [28]	-6.78	-6.78	2.40	-3.72	3.06	~ 70
$^{13}\text{C}-\text{B}_{\text{Si}}(h_a)$	30	30	182	81	51	0
^{13}C -EPR [26]	48	48	173	90	42	0
$\text{C}^{11}\text{B}_{\text{Si}}(h_a)$	2	2	8	4	2	0
^{11}B -ENDOR [28]	-3.88	-3.88	4.85	-0.97	2.91	0

($a \sim 80\text{--}90$ MHz), reflecting the large localization on the C radical. The calculated anisotropic ^{13}C HF constants ($b \sim 50$ MHz) are also in fair agreement with the EPR data ($b \sim 40$ MHz). Although not statistically meaningful, the error bar of the calculated HF constants (considering the measurements reported in Table II) is estimated as $\lesssim 10$ MHz. We also note that the isotropic HF constants slightly underestimate previous calculations based on the local density approximation (LDA) [35]. This is interpreted as a tendency of GGA to underlocalize the electron density in comparison to the overlocalization of the LDA.

Regarding the ^{11}B HF interactions, like their measured analogues, the amplitudes are very small (few MHz). Unlike the calculations, the measured Fermi contact is negative. Still, the discrepancy is well within the estimated error. Hence, along with the g tensors, the HF calculations provide compelling support for the assignment of B_{Si}^0 to the EPR/ENDOR data as reproduced in Tables I and II.

The above HF interaction calculations were carried out using the GIPAW code within the GGA to the exchange-correlation potential. We performed test calculations at the HSE06 level (using the VASP code) and found that the Fermi contact terms were about a factor of two larger. The HSE06-level dipolar terms were similar to those found using the semilocal functional. Such discrepancy was also reported in Ref. [66] for the evaluation of isotropic coupling constant using semilocal and hybrid functionals, and that calls for further investigations.

Regarding the deep boron species, among the arguments behind its assignment to a $\text{B}_{\text{Si}}-\text{V}_{\text{C}}$ structure were the negligible ^{13}C and ^{11}B hyperfine satellites next to the main signal, as well as a pronounced localization of the spin density on Si atoms [14,15]. Unfortunately, the dynamic Jahn-Teller effect makes any comparison between the measurements and the static HF calculations rather difficult—unlike the Zeeman effect, the ^{29}Si HF interactions are intermittent due to rotation of the nodal wave function.

We calculated the g tensor for neutral $\text{B}_{\text{Si}}(k)-\text{V}_{\text{C}}^0(k)$, with both the B atom and the vacancy aligned along the crystalline main axis. The ground state structure involves an electronically inert threefold coordinated B atom next to three

Si radicals edging the C-vacancy, two of which reconstruct to form an elongated bond due to JT effect (see Ref. [15] and references therein). Most spin density of this complex is localized on a single Si dangling bond polarized toward the center of the vacancy and the B atom. Although the distance between B and the Si radical is approximately the separation between second neighbors of the crystal, Si radical states are rather extended in space. In fact, considering its symmetry and character, the paramagnetic state must have a finite amplitude on B atom, and that feature does not favor the $\text{B}_{\text{Si}}-\text{V}_{\text{C}}^0$ model.

The calculated g tensor of $\text{B}_{\text{Si}}-\text{V}_{\text{C}}^0$ allows us draw more definite conclusions. The static JT distorted state of $\text{B}_{\text{Si}}(k)-\text{V}_{\text{C}}^0(k)$ with C_{1h} symmetry has a main g_3 component along the Si dangling bond, which makes an angle of $\theta = 78^\circ$ with $[0001]$ —this was not observed at a temperature as low as $T = 4$ K. Accordingly, two nearly axial EPR signals with a main axis along $[0001]$ were reported [14]. The magnitude of the calculated g values also differ markedly from the observed ones. Even considering a dynamic JT state (with effective C_{3v} symmetry), the calculated effective g value of $\text{B}_{\text{Si}}(k)-\text{V}_{\text{C}}^0(k_{\text{dyn}})$ along the c axis ($g_3 = 2.0063$) is too small when compared to its measured counterpart ($g_3 = 2.029$) [14].

In Sec. III B, it was shown that the paramagnetic state of B_{C}^0 has spin-1/2, and that it derives from a partially occupied JT distorted $e(xy)^{\uparrow\downarrow\uparrow}$ doublet. Also as detailed on the right hand side of Fig. 2, this manifold derives from the boron p_{xy} states, which are nodal on the boron atom as well as along the c axis. The spin density of the JT distorted configurations $a''^{\uparrow\downarrow} + a'^{\uparrow}$ and $a'^{\uparrow\downarrow} + a''^{\uparrow}$ is depicted in Figs. 8(a) and 8(b). Such a shape anticipates a very small spin localization on the B atom. For the $a'^{\uparrow\downarrow} + a''^{\uparrow}$ ground state, the amplitude is zero on boron and high on two basal Si ligands (Si_2 and Si_3).

The spin density of the ground state $a'^{\uparrow\downarrow} + a''^{\uparrow}$ configuration of $\text{B}_{\text{C}}^0(k)$ is zoomed in Fig. 8(c). The case of $\text{B}_{\text{C}}^0(h)$ is analogous and a similar discussion applies. The figure also depicts the principal directions of the g values with respect to the crystalline axes. Like it was considered for the shallow boron defect, trigonal (C_{3v}) states have its main g_3 component along the $[0001]$ hexagonal axis. Also, monoclinic (C_{1h}) states

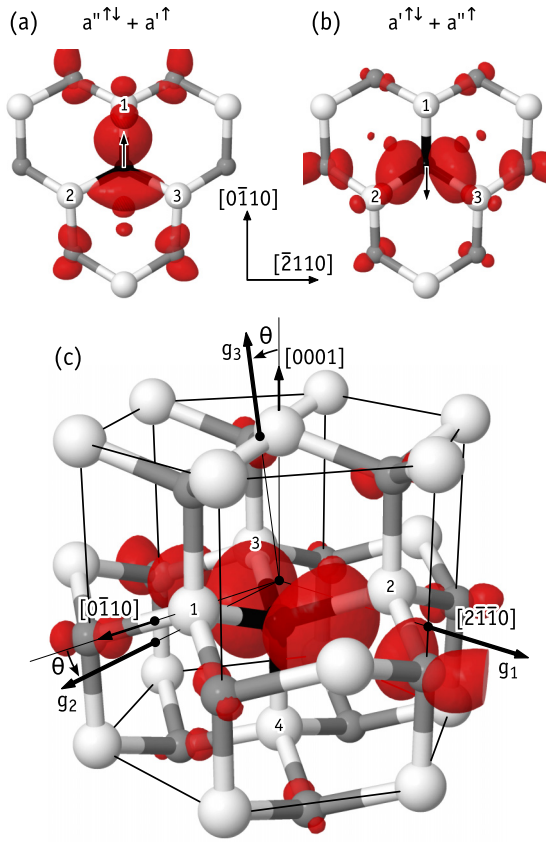


FIG. 8. Spin-density isosurface (cutoff $0.02 \text{ e}/\text{\AA}^3$) of a neutral B_C defect at the k site of 4H-SiC. (a) and (b) depict two alternative Jahn-Teller distorted states, namely $a''\uparrow\downarrow + a'\uparrow$ (metastable) and $a'\uparrow\downarrow + a''\uparrow$ (ground state), which lead to opposite displacements of the B atom along $[01\bar{1}0]$ (see arrows). In (c), we depict the $a'\uparrow\downarrow + a''\uparrow$ ground state along with the principal directions of the calculated g tensor (see text). Si, C, and B atoms are shown in white, gray and black, respectively.

have g_1 perpendicular to the $\{2\bar{1}\bar{1}0\}$ plane, while g_2 and g_3 are rotated by an angle θ away from $\langle 0\bar{1}10 \rangle$ and $\langle 0001 \rangle$, respectively.

Let us first consider the case of static JT distorted configurations. These correspond to monoclinic states with calculated g values of $g_1 \approx 2.005$, $g_2 \approx 2.017\text{--}2.020$, and $g_3 \approx 2.024\text{--}2.028$. The latter is rotated away from $[0001]$ by $\theta = 13^\circ$ only. Although the magnitude of g_3 is not far from the measured axial g values, the monoclinic rotation angle was not observed.

Considering that B_C^0 is predicted to show a dynamic JT effect, the effective g values are better estimated via averaging over symmetrically equivalent alignments. Hence, we find $g_1 = g_2 \approx 2.012$ for both $B_C^0(k_{\text{dyn}})$ and $B_C^0(h_{\text{dyn}})$, whereas $g_3 \approx 2.028$ and 2.024 for $B_C^0(k_{\text{dyn}})$ and $B_C^0(h_{\text{dyn}})$, respectively. As reported in Table I, the calculated main g_3 values are in excellent agreement with the axial g values observed for deep boron defects in 4H-SiC [14]. The basal g values also compare well with the corresponding measured figures (~ 2.0), although these are accompanied by relatively large error bars due to random g -strain broadening effects [15].

The nodal state shown in Fig. 8(c) strongly overlaps with two of the Si atoms connected to boron (Si_2 and Si_3). The two other Si ligands are nodal (Si_1 and Si_4) and have no overlap with the spin density. We suggest that the dynamic JT effect on this defect could be responsible for an intermittent localization on all atoms, thus explaining the weak and broad hyperfines detected for ^{11}B , ^{13}C , and ^{29}Si . Finally, we also note that the dynamical nature of the ground-state of B_C^0 , and a possible occupancy of both $a''\uparrow\downarrow + a'\uparrow$ and $a'\uparrow\downarrow + a''\uparrow$ states above few tens of degrees Kelvin, could explain the broadening and quenching of the EPR main signals of deep boron above $T \approx 30 \text{ K}$ [14].

IV. CONCLUSIONS

We reported on first-principles hybrid density functional calculations of boron defects in 4H-SiC. Besides defect structures and electronic transition levels, defect free energies at finite temperatures, g tensor calculations and hyperfine coupling constants were also reported. The vibrational contribution to the free energies, as well as the one-electron states for the calculation of the paramagnetic properties, were found within a semilocal approximation to the electronic exchange and correlation interactions.

We support the assignment of the shallow boron species to B_{Si} . In the neutral state, these defects possess a threefold coordinated B atom next to an unsaturated C radical. We mind the reader that this structure was obtained when the atomistic relaxation was performed within hybrid DFT. Lower level GGA calculations led to fourfold coordinated boron atoms. In line with arguments already reported [35], the erroneous GGA structure derives from the overmixing between the acceptor state of boron and the valence band top of the crystal. However, unlike Ref. [35], we conclude that the neutral B_{Si} defect adopts a singlet state. The axially distorted structure of this defect (along the c axis) conserves the maximum point group symmetry of the 4H-SiC crystal (C_{3v}). The displacement from the perfect lattice site can be explained by the host crystal field. Hence, the off-site structure cannot be justified by a Jahn-Teller effect—it is simply driven by the short covalent radius of boron compared to that of Si.

As a word of caution, we note that the relative energy of on-site and off-site B_{Si}^0 states cannot be easily obtained with the present method. If the fourfold coordinated B_{Si}^0 is a diffuse effective-mass-like state, it could be disfavored due to the artificial confinement effect of the supercell approximation [79]. Still, even if that was the case, only the off-site threefold coordinated B_{Si}^0 model (and not the EMT model) could account for the measurements.

The C radicals on cubic and hexagonal B_{Si} defects are polarized differently, i.e., along basal and axial bond directions of the crystal, respectively. This feature has been previously detected by EPR but left unexplained. We demonstrate that it results from distinct crystal fields acting on each sublattice site.

Substitutional boron on the carbon site (B_C^0) is a dynamic Jahn-Teller system with a “Mexican hat” like potential. The potential ripples for rotation around the symmetry axis of the undisturbed state are 15 meV high only. This figure is lower than the zero-point energy of the defect, implying that

is shows effective trigonal symmetry, even at liquid-helium temperature.

B_{Si} and B_C are both single acceptors. Despite adopting rather different alignments in the crystal, the acceptor levels of $B_{Si}(k)$ and $B_{Si}(h)$ are estimated in a narrow range $E_v + (0.34-0.32)$ eV. This could explain the observation of a single transition by Laplace-DLTS for shallow boron. The acceptor level of B_C is anticipated at $E_v + (0.63-0.67)$ eV, in excellent agreement with the D-center transition level measured in the range 0.5–0.7 eV above E_v . Our results suggest that recently reported Laplace-DLTS experiments unfolding the D-center signal into two components, relate to a “shallower” configuration sitting at the cubic carbon site and a “deeper” one replacing the hexagonal site.

From the calculated free-energies of B_{Si} and B_C , we found that under typical growth temperatures, the equilibrium concentration ratio $[B_{Si}]/[B_C] \approx 200$ and about 0.1 for a Si-poor and Si-rich stoichiometry, respectively. This leads us to the conclusion that formation of B_C cannot be avoided during growth when boron is present, and contamination of n-type layers with boron could limit the mobility and lifetime of holes due to trapping and recombination at deep B_C acceptors.

We demonstrated that the EPR measurements of shallow boron can be described by a site- and temperature-dependent g tensor of B_{Si} . Below ~ 50 K, neutral B_{Si} defects at k and h sites show static C_{1h} and C_{3v} symmetry, with comparable g values along the carbon radical p-state, respectively $g_3 = 2.0028$ and 2.0022. These figures compare very well with 2.0025 and 2.0019 from the measurements, respectively. Above ~ 50 K, the EPR signal related to the hexagonal species remains unchanged. However, the B-C broken bond in $B_{Si}(k)$ can reorient by surmounting a barrier of about 0.1 eV, and the estimated *thermally averaged* g_3 value (now parallel to $[0001]$) increases to 2.0073 (to be compared to 2.0064 from the measurements).

Calculations of the gyromagnetic tensor are complemented with calculations of the most prominent ^{13}C and ^{11}B hyperfine splitting interactions involving core atoms at the threefold coordinated B_{Si}^0 defects. The results agree well with the measurements both in terms of magnitude and axial direction of the interactions.

Our results rule against the assignment of a $B_{Si}-V_C$ complex to the deep boron defect. Both directions and magnitude of the calculated g values for this complex, differ markedly from the observations. Combining with previous calculations which concluded that $B_{Si}-V_C$ is a donor without levels in the lower half of the gap [17], we can definitely abandon the idea of a relation between the deep boron center and $B_{Si}-V_C$.

Instead we assign deep boron to B_C . The calculated g values for B_C show excellent agreement with the measurements for deep boron if we account for the dynamics of the defect. We argue that the dynamic Jahn-Teller effect, along with the nodal shape of the paramagnetic state, could explain the weak and broad hyperfine signals related to ^{11}B , ^{13}C and ^{29}Si . Additionally, by considering B_C as being responsible for the deep boron spectra, and hence ruling out the $B_{Si}-V_C$ model, we naturally avoid having to justify the inexplicable formation of $B_{Si}-V_C$ defects with exclusive axial orientations as observed by EPR.

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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