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Theoretical and electron paramagnetic resonance studies of hyperfine interaction in nitrogen doped 4H and 6H SiC

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Motivated by recent experimental findings on the hyperfine signal of nitrogen donor (N_C) in 4H and 6H SiC, we calculate the hyperfine tensors within the framework of density functional theory. We find that there is negligible hyperfine coupling with ^{29}Si isotopes when N_C resides at h site both in 4H and 6H SiC. We observe measurable hyperfine coupling to a single ^{29}Si at k site in 4H SiC and k_1 site in 6H SiC. Our calculations unravel that such ^{29}Si hyperfine coupling does not occur at k_2 site in 6H SiC. Our findings are well corroborated by our new electron paramagnetic resonance studies in nitrogen doped 6H SiC. © 2014 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4866331>]

I. INTRODUCTION

Silicon carbide (SiC) is a promising semiconductor for high-temperature, high-power electronic devices. The most common dopant in SiC is nitrogen (^{14}N , natural abundance: 99.6%, nuclear spin: $I = 1$), which introduces shallow donor levels in the band gap causing n -type conductivity.¹ Recently, it has been found that SiC is able to host solid state quantum bits² and single photon emitters.³ Awshalom's group has showed that the most common polytypes (3C, 4H, 6H) of SiC can possess coherent and optically manipulable defect spin states.⁴ The coherence time may be reduced by N donors with $S = 1/2$ spin. For these reasons, it is essential to understand deeply the electronic and magnetic properties of the N donor in SiC.

The N donor impurity in SiC is a complex problem since N might reside at carbon (C) or silicon (Si) sites. Moreover, N can substitute several inequivalent lattice sites: In 4H SiC, there are two inequivalent sites, the hexagonal (h) and the quasi-cubic (k), denoted as $N_C(h)$ and $N_C(k)$, respectively, when N substitutes carbon atom in SiC lattice. 6H SiC has three inequivalent sites, namely the hexagonal (h) and two quasi-cubic (k_1 and k_2), denoted as $N_C(h)$, $N_C(k_1)$, and $N_C(k_2)$, respectively. The ionization energy of N on the hexagonal site (in 4H SiC 66 meV, in 6H SiC 100 meV) is much shallower than that of center on the quasi-cubic site (in 4H SiC 124 meV, in 6H SiC 155 meV).⁵ The *ab initio* calculated ionization energies for N_C s are in good agreement with the above mentioned data, supporting the fact that N preferentially resides at the C sites and not the Si sites.⁶ This statement is also confirmed by previous density functional theory calculations predicting that N_C is favorable over N_{Si} by more than 5 eV, so the concentration of N_{Si} is negligible.^{7–9}

Studying the spin density of the N donor in hexagonal SiC is the key to understand the physical properties of the system. The spin density distribution can be mapped by electron paramagnetic resonance (EPR) or electron-nuclear double resonance (ENDOR) by means of the interaction between the donor electron spin and the nuclear spin of ^{13}C (1.1%, $I = 1/2$) and ^{29}Si (4.7%, $I = 1/2$) isotopes. This results in hyperfine (hf) signals, which reveals the distribution of the electron spin density around the N donor. The hf interaction with N was first reported in Ref. 10: In both 4H and 6H SiC, this interaction is weak for $N_C(h)$, and strong when N resides at the quasi-cubic sites. However, the previous results about the hf structure of N donor for proximate ^{13}C and ^{29}Si isotopes in 4H and 6H SiC (Refs. 10–14) are contradictory. In 4H SiC for $N_C(k)$, Duijn-Arnold *et al.*¹² find that the hf interaction with Si atoms is larger than that with C atoms; whereas in a later study,¹¹ considerably large hf interaction can be found for a single Si atom along the c axis and for C atoms located in the outer shells. For $N_C(h)$, experimental results on Si or C atoms were not available because the EPR signals for ENDOR measurement were too weak. In 6H SiC, Duijn-Arnold *et al.*¹² observe that the spin density is localized mainly on C atoms not only for the quasi-cubic sites but also for the $N_C(h)$, and no strong hf interaction is found with Si atoms. For the quasi-cubic N donors, Savchenko *et al.*¹³ find the strongest hf interaction with Si atoms close to the N donor, however considerable hf interaction is obtained for C atoms too. In their later study,¹⁴ large hf splitting is found for several Si atoms for $N_C(h)$ and $N_C(k_1)$. For N substituting the k_2 site, they find that the hf interaction with C is much stronger. From this result, they conclude that the N donor at k_2 site incorporates at Si site. We note that unambiguous distinction between quasi-cubic sites were reported only in Ref. 14. These contradictory results need in-depth investigation.

In this work, we present hf calculations related to N_C in 4H and 6H SiC and new EPR measurements in 6H SiC.

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Our calculations reveal that both in 4H and 6H SiC considerable hf interaction (larger than 5 MHz) occurs with more C than Si atoms. Moreover, for $N_C(k)$ in 4H SiC and $N_C(k_1)$ in 6H SiC, the hf structures are similar: well observable hf interaction occurs with the third Si neighbour atom along the c axis. The result for $N_C(k)$ in 4H SiC is in good agreement with Son *et al.*'s study.¹¹ For $N_C(k_2)$ in 6H SiC, the interaction with the third neighbour Si along the c axis disappears, the spin density is mostly localized on C atoms, which does not mean that N donor resides at Si site. Our new EPR measurements corroborated our *ab initio* results in 6H SiC confirming ~ 23 MHz hyperfine signal on one ^{29}Si when N substitutes one of the quasi-cubic sites.

II. METHOD OF THE CALCULATION

In order to calculate the hf constants, we used 5.3.3 version of Vienna *Ab Initio* Simulation Package (VASP).^{15,16} Since we had to calculate the electron spin density close to the nuclei accurately, the all-electron projector augmented wave method (PAW)^{17,18} was applied together with plane wave basis set. We utilized the standard PAW-projectors provided by the VASP package. Plane wave cut-off of 420 eV was used, which was sufficient to obtain convergent spin density and hf constants (A_{xx} , A_{yy} , A_{zz}). For modeling the defects, large 576-atom and 432-atom supercells were applied for 4H and 6H SiC, respectively. For these supercells, the Γ -point sampling of the first Brillouin zone sufficed. In 4H SiC, the conduction band minimum (CBM) is at the M point; and in 6H SiC, this minimum lies between the M and L point called U point where the conduction band is relatively flat at the minimum.⁶ Since the M point was projected into the Γ -point, the corresponding Bloch-states are well sampled to build up the donor wave functions. In 6H SiC, the results may be less accurate due to smaller number of atoms. However, we focus rather the *distribution* of the donor wave function and the trend of the relative magnitudes in hf interactions that should be well-captured in our calculations.

It was shown recently¹⁹ that for the calculation of the hf constants related to point defects in semiconductors, e.g., in SiC, the non-local Heyd-Scuseria-Ernzerhof hybrid functional (HSE06)^{20,21} provides the accurate results with taking the contribution of the spin polarization of the core electrons to the Fermi-contact term into account. However, we applied the semi-local Perdew-Burke-Ernzerhof functional (PBE)²² for geometry optimization of N donors since the spin density of the shallow donor states can be well-described by PBE. We carried out the geometry optimization until the force acting on the atoms was below 0.01 eV/Å. These PBE optimized geometries were used for the HSE06 hf calculations. According to Ref. 19, this approximation caused less than 3% error in the calculated hf constants.

The EPR measurements were performed on an X-band (~ 9.4 GHz) E500 Bruker spectrometer equipped with a continuous He-flow cryostat, allowing the regulation of the sample temperature from 4 to 295 K. The sample was commercial n -type substrate 6H SiC with concentration of nitrogen $\sim 3.3 \times 10^{17} \text{ cm}^{-3}$.

III. RESULTS AND DISCUSSION

Now, we provide and discuss our results in detail. The hf values related to N and relevant Si atoms are listed in Table I. The hf values obtained for 30 C atoms (on the average) for each center in 4H and 6H SiC are in the range of 10 and 25 MHz. These C atoms are arranged in groups containing 3–6 atoms, and they reside in the second (~ 4 – 5 Å far from N), fourth (~ 6 – 8 Å far from N), and sixth (~ 10 – 12 Å far from N) shells. The maximum hf values for these C atoms located in the second, fourth, and sixth shells are ~ 25 MHz, ~ 20 MHz, and ~ 15 MHz, respectively, and they are isotropic, namely, A_{xx} , A_{yy} , and A_{zz} are almost equal. The hf interaction with C atoms placed between these shells is weak, thus the spin density does not continuously decrease with increasing distance from the N donor but it oscillates. The reason why small hf values can be found for most of Si atoms is the appearance of the floating states in the interstitial channels around the Si atoms.²³ Because of this phenomenon, the effective mass approximation used in Refs. 10, 12, and 14 is not valid and it might result in false assignment of the measured spectrum. In addition, in high-frequency ENDOR, it is not too easy to detect Si atoms with hf constant of larger than ~ 12 MHz because of the overlap with C signals.⁶ This fact increases the probability of the false identification. Hereinafter, we analyze each defect one by one.

First, we deal with the N donor in 4H SiC. In Fig. 1, the spin density is depicted for $N_C(h)$ and $N_C(k)$, respectively. For

TABLE I. The calculated principal values (in MHz unit) of the hf tensors for ^{14}N and ^{29}Si in $N_C(h, k)$ in 4H and in $N_C(h, k_1, k_2)$ in 6H SiC. The labelled numbers are the measured values. Other assignments in Ref. 14 to ^{29}Si are given in the text. The distances (d) between the N atom and proximate nuclei are also given. The signs cannot be determined in the measurements.

	Center	Atoms	d (Å)	A_{xx}	A_{yy}	A_{zz}
4H	$N_C(h)$	N		7.57	7.57	8.06
				2.82 ^a	2.82 ^a	3.06 ^a
	$N_C(k)$	Si $\times 3$	6.72	−11.23	−11.24	−11.08
		N		46.45	46.45	46.50
				50.97 ^a	50.97 ^a	50.98 ^a
		Si $\times 3$	1.93	−5.56	−5.56	−13.20
				5.06 ^b	5.94 ^b	14.25 ^b
		Si $\times 1$	3.18	−39.34	−39.34	−38.66
				41.31 ^b	41.31 ^b	41.07 ^b
	$N_C(k_2)$	N		2.00	2.00	2.76
				2.33 ^a	2.33 ^a	2.74 ^a
6H	$N_C(h)$	N		2.00	2.00	2.76
				2.33 ^a	2.33 ^a	2.74 ^a
	$N_C(k_1)$	N		32.86	32.86	32.85
				33.56 ^a	33.56 ^a	33.58 ^a
				33.77 ^c	33.77 ^c	33.77 ^c
		Si $\times 3$	1.93	−2.70	−2.67	−8.29
		Si $\times 1$	3.18	−18.40	−18.40	−17.92
				23.26 ^c	23.26 ^c	22.77 ^c
	$N_C(k_2)$	N		32.60	32.60	32.71
				33.22 ^a	33.22 ^a	33.23 ^a
				33.20 ^c	33.20 ^c	33.20 ^c
		Si $\times 3$	1.93	−2.59	−2.69	−9.79

^aExperimental data are taken from Ref. 10.

^bExperimental data are taken from Ref. 11.

^cOur EPR measurement.

FIG. 1. Calculated spin density for N_C at h and k sites in $4H$ SiC (isovalues: $0.0031 \text{ 1/\AA}^3$ and $0.0020 \text{ 1/\AA}^3$ for h and k sites, respectively). Floating states appear in the internal channel of Si atoms in both cases.

$N_C(h)$, the hf interaction is notable mainly with C atoms. However, three Si atoms ($\text{Si} \times 3$) can be found with ~ -11 MHz isotropic hf values, as well as additional Si atoms with 6–8 MHz of isotropic hf values. The numbers of these Si atoms are about the half of those of the C atoms on which the spin density is localized. The hf interaction with N atom is slightly anisotropic and weak, and ~ 2.5 times larger than the measured value found in Ref. 10 (see Table I). For $N_C(k)$, we find strong isotropic hf interaction with N donor (~ 46 MHz) and with a Si atom ($\text{Si} \times 1$, ~ -39 MHz) along the c axis. Besides, anisotropic hf interaction occurs with three nearest neighbour Si atoms ($\text{Si} \times 3$) located in the basal plane (see Table I). Our results on hf signals of ^{29}Si , ^{13}C , and ^{14}N agree the measured data reported in Refs. 10 and 11 within 10%. Contrarily, Ref. 12 reports anisotropic interaction with Si atoms (largest hf constants: $A_{xx} = A_{yy} = 5.28$ MHz, $A_{zz} = 9.06$ MHz), and mainly isotropic hf interaction with C atoms (~ 5 MHz of maximum value). They cannot find as large hf values as in Ref. 11 neither for Si nor for C atoms since they analyzed only the lower ENDOR frequency range, thus the Si and C shells close to the N donor are not detected.¹¹ In conclusion, our result for $N_C(k)$ supports the measurements and interpretation of hf signals in Ref. 11.

Next, we study the hf signals of N_C in $6H$ SiC. Fig. 2 shows the distribution of the spin density for $N_C(h)$, $N_C(k_1)$, and $N_C(k_2)$. For $N_C(h)$, considerable isotropic hf constants occur for C atoms and small, slightly anisotropic hf values for N atom (see Table I). The interaction with Si atoms is anisotropic and $A_{zz} < 3$ MHz. In the case of $N_C(k_1)$ as for $N_C(k)$ in $4H$ SiC, we find strong isotropic hf interaction with N (~ 33 MHz) and with the third neighbour Si atom ($\text{Si} \times 1$, ~ -18 MHz) along the c axis, and anisotropic interaction with three nearest Si atoms in the basal plane. For $N_C(k_2)$, the hf constant for N is isotropic, and the value of it is almost

the same as that for $N_C(k_1)$. However, large hf value for $\text{Si} \times 1$ is missing. The strongest hf interaction with Si occurs for three nearest neighbour Si atoms ($\text{Si} \times 3$, $A_{xx} \approx A_{yy} \approx -2.6$ MHz, $A_{zz} \approx -9.8$ MHz). The lack of the hf interaction with $\text{Si} \times 1$ atom is due to the long distance ($\sim 8.2 \text{ \AA}$) of this Si atom from the N donor along the c -axis. Isotropic hf interaction showing toroidal spin density (see $N_C(k)$ in Fig. 1 or $N_C(k_1)$ in Fig. 2) can be found for three equivalent Si atoms at $\sim 6.7 \text{ \AA}$ far from N but not along c -axis. The isotropic hf interaction seems to move from $\text{Si} \times 1$ to that three Si atoms, however, the value of the hf splitting is small, only ~ 3.2 MHz.

Comparing our results with previous experimental findings in $6H$ SiC, we can conclude the followings. For $N_C(h)$, the results in Ref. 12 are similar to ours, however the highest hf constant for C atom is only ~ 10 MHz, and for Si atoms is less than 3 MHz according to their interpretation of the measured EPR spectrum. Our results on Si go opposite to those in Ref. 14: isotropic hf values of ~ 11 MHz and ~ 14 MHz are reported for Si located in the first and the second shell of $N_C(h)$ donor. For $N_C(k_1)$ in Ref. 14, two large isotropic hf splittings (~ 23 and ~ 15 MHz) were assigned to Si atoms located in the first or third shell of N. In contrast, we can find considerable hf interaction only with a single Si atom ($\text{Si} \times 1$). For $N_C(k_2)$ in Ref. 14, they reported spin density localized on C atoms, and only small isotropic hf interaction (~ 5 MHz) was reported for Si atoms. Since the largest hf interaction was observed on C atoms, they concluded that this center was $N_{\text{Si}}(k_2)$, i.e., N would substitute Si atom in SiC lattice. Our calculation reveals that this conclusion was not well grounded since large hf splitting on Si nuclei is missing for $N_C(k_2)$. For the two unresolved quasi-cubic sites, Ref. 10 reported isotropic hf values for Si with less than 7 MHz and for C atoms with less than 5 MHz. In contrast, in Ref. 12, less than 4 MHz isotropic hf constants were obtained for Si and less than 10 MHz for C atoms. They explained this contradiction by the strong overlap of the Si and C signals. The results in Ref. 12 are closer to our findings, however unambiguous conclusion cannot be made since the quasi-cubic sites were not resolved.

Our findings on $N_C(k_1)$ and $N_C(k_2)$ are validated by our new EPR measurements. Fig. 3 shows the EPR spectra of the shallow N donors in $6H$ SiC measured at 55 K for $\mathbf{B} \perp c$. Two hf lines of $N_C(k_1)$ with splittings of $A_{xx} = A_{yy} = 23.26$ MHz and $A_{zz} = 22.77$ MHz were observed. Their intensity ratio with the main line of $\sim 5\%$ indicates that they are from the hf interaction with one ^{29}Si atom on the bond along to the c axis. For

FIG. 2. Calculated spin density for N_C at h , k_1 , and k_2 sites in $6H$ SiC (isovalues: $0.0031 \text{ 1/\AA}^3$, $0.0011 \text{ 1/\AA}^3$, $0.0024 \text{ 1/\AA}^3$ for h , k_1 , k_2 sites, respectively). Floating states appear in the internal channels around Si atoms.

FIG. 3. EPR spectrum of the shallow N donor in 6H SiC measured for $\mathbf{B} \perp c$ and the simulated spectrum of $N_C(k_1)$ and $N_C(k_2)$ with assuming the hf interactions with one ^{29}Si (~ 23.26 MHz) for $N_C(k_1)$ and 6 (~ 18.40 MHz) and 3 equivalent ^{13}C (~ 14.63 MHz) atoms for $N_C(k_2)$ with Lorentzian lineshape and a linewidth of 0.62 G. The middle line of the simulated spectrum is smaller than that of the experimental one since the $N_C(h)$ line is not included in the simulation. The broad shoulder at low magnetic field in experimental spectrum is due to the overlapping with smaller splitting hf lines of ^{13}C and ^{29}Si , which are not included in the simulated spectrum.

$N_C(k_2)$, two pairs of hf lines were observed for $\mathbf{B} \perp c$ with hf splittings of ~ 18.40 MHz and 14.63 MHz, which are in good agreement with previous ENDOR study.¹⁴ As shown in Fig. 3, these C hf structures are best fitted with assuming the hf interactions with 6 and 3 equivalent ^{13}C atoms, respectively, as predicted from the calculations (~ 20.4 MHz for six C-atoms and ~ 14.6 MHz for three C atoms). The agreement between EPR and calculations in the Si hf structure of $N_C(k_1)$ and the C hf structures of $N_C(k_2)$ supports the conclusion that the missing of the Si hf structure of $N_C(k_2)$ can be explained by the nature of the floating states, i.e., the spin density is distributed in the interstitial channels around the Si atoms, and it does not require the model of N substituting Si atom at k_2 site in 6H SiC.

IV. SUMMARY

In summary, we studied the hf structure of N_C at different lattice sites in 4H and 6H SiC. We show that the spin density appears mainly on C atoms and in the interstitial channels around Si atoms. Hexagonal and quasi-cubic N donors can be distinguished by means of the hf value for the N donor. Moreover, the two quasi-cubic sites in 6H SiC can also be resolved since hf value of ~ 23 MHz can be observed for a single ^{29}Si isotope located on the c axis only for $N_C(k_1)$. Based on the agreement with results in Ref. 11 for 4H SiC and with our new EPR data for 6H

SiC, we conclude that N donor definitely substitutes C sublattice in hexagonal SiC. The interpretation and/or the assignments in the other EPR/ENDOR studies^{10,12,14} need further investigations.

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- ¹Properties of Silicon Carbide, edited by G. Harris, EMIS datareviews series (INSPEC, Institution of Electrical Engineers, 1995).
- ²W. F. Koehl, B. B. Buckley, F. J. Heremans, G. Calusine, and D. D. Awschalom, *Nature* **479**, 84 (2011).
- ³S. Castelletto, B. C. Johnson, V. Ivády, N. Stavrias, T. Umeda, A. Gali, and T. Ohshima, *Nature Mater.* **13**, 151 (2014).
- ⁴A. L. Falk, B. B. Buckley, G. Calusine, W. F. Koehl, V. V. Dobrovitski, A. Politi, C. A. Zorman, P. X.-L. Feng, and D. D. Awschalom, *Nat. Commun.* **4**, 1819 (2013).
- ⁵M. Ikeda, H. Matsunami, and T. Tanaka, *Phys. Rev. B* **22**, 2842 (1980).
- ⁶N. T. Son, J. Isoya, T. Umeda, I. G. Ivanov, A. Henry, T. Ohshima, and E. Jánzn, *Appl. Magn. Reson.* **39**, 49 (2010).
- ⁷A. Gali, P. Deák, N. T. Son, and E. Jánzn, *Appl. Phys. Lett.* **83**, 1385 (2003).
- ⁸R. Rurali, P. Godignon, J. Rebollo, E. Hernández, and P. Ordejón, *Appl. Phys. Lett.* **82**, 4298 (2003).
- ⁹M. Bockstedte, A. Mattheusch, and O. Pankratov, *Appl. Phys. Lett.* **85**, 58 (2004).
- ¹⁰S. Greulich-Weber, *Phys. Status Solidi A* **162**, 95 (1997).
- ¹¹N. T. Son, E. Jánzn, J. Isoya, and S. Yamasaki, *Phys. Rev. B* **70**, 193207 (2004).
- ¹²A. v. Duijn-Arnold, R. Zondervan, J. Schmidt, P. G. Baranov, and E. N. Mokhov, *Phys. Rev. B* **64**, 085206 (2001).
- ¹³D. V. Savchenko, E. N. Kalabukhova, V. S. Kiselev, J. Hoentsch, and A. Pöpl, *Phys. Status Solidi B* **246**, 1908 (2009).
- ¹⁴D. V. Savchenko, E. N. Kalabukhova, A. Pöpl, and B. D. Shanina, *Phys. Status Solidi B* **249**, 2167 (2012).
- ¹⁵G. Kresse and J. Hafner, *Phys. Rev. B* **49**, 14251 (1994).
- ¹⁶G. Kresse and J. Furthmüller, *Phys. Rev. B* **54**, 11169 (1996).
- ¹⁷P. E. Blöchl, *Phys. Rev. B* **50**, 17953 (1994).
- ¹⁸G. Kresse and D. Joubert, *Phys. Rev. B* **59**, 1758 (1999).
- ¹⁹K. Szász, T. Hornos, M. Marsman, and A. Gali, *Phys. Rev. B* **88**, 075202 (2013).
- ²⁰J. Heyd, G. E. Scuseria, and M. Ernzerhof, *J. Chem. Phys.* **118**, 8207 (2003).
- ²¹A. V. Krukau, O. A. Vydrov, A. F. Izmaylov, and G. E. Scuseria, *J. Chem. Phys.* **125**, 224106 (2006).
- ²²J. P. Perdew, K. Burke, and M. Ernzerhof, *Phys. Rev. Lett.* **77**, 3865 (1996).
- ²³Y.-i. Matsushita, S. Furuya, and A. Oshiyama, *Phys. Rev. Lett.* **108**, 246404 (2012).