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Electronic structure of the nitrogen donors in 6H SiC as studied by pulsed ENDOR and TRIPLE ENDOR spectroscopy

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The nitrogen (N) donors in 6H SiC were investigated by field sweep electron spin echo (FS ESE), pulsed electron nuclear double resonance (ENDOR) and pulsed General TRIPLE ENDOR spectroscopy. The ²⁹Si and ¹³C superhyperfine (shf) lines observed in the FS ESE and ENDOR spectra of N in n-type 6H SiC were assigned by pulsed General TRIPLE resonance spectroscopy to the specific carbon (C) and silicon (Si) atoms located in the environment of N donors residing at two quasi-cubic lattice sites (N_{k1} , N_{k2}) in 6H SiC. As a result, the largest value of the shf interaction was found with Si atoms for the N donors at the hexagonal (N_h) and quasi-cubic site N_{k1} , while for N_{k2} the largest value of the shf interaction was found with C atoms. It gives us the argument to consider that N substitute

different lattice sites in 6H SiC lattice. The relative signs of the shf interaction (shfi) constants for N_{k1} and N_{k2} with ²⁹Si and ¹³C nuclei located in the nearest-neighbor, next nearest-neighbor, and outer shells are found from the TRIPLE ENDOR spectra to be positive for C atoms and negative for Si atoms. From the comparison of the experimentally obtained shfi constants with the theory, the electronic spin-density distribution over the ²⁹Si and ¹³C nuclei located in the nearest neighbor shells of N donors has been obtained taking into account the Kohn–Luttinger interference effect. The position of the conduction band minimum along the ML-line was determined to be at $k_{0z}/k_{\max} = 0.2 \pm 0.05$.

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1 Introduction Nitrogen (N) and phosphorus (P) are the major paramagnetic donor impurities in silicon carbide (SiC) polytypes. However, the reason for the different behavior of N and P as n-type dopants in SiC remains unknown. In contrast to P, which incorporates on both substitutional lattice sites (P_{Si} and P_C) [1, 2], N preferentially resides at the carbon (C) sites (N_C).

The current point of view, that N exclusively substitutes C in SiC originates from electron paramagnetic resonance (EPR) and electron nuclear double resonance (ENDOR) experiments, which were initiated more than 50 years ago. Firstly, only one set of hyperfine (hf) triplet lines from ¹⁴N ($I = 1$, 99.6%) of a paramagnetic center with electron spin $S = 1/2$ was observed in the EPR spectrum at 9 GHz of n-type 6H SiC [3].

Further investigation of the ¹⁴N EPR spectrum in 6H SiC at 14 GHz allowed to resolve two triplet lines of different intensities from two distinct centers [4]. Taking into account that there are three inequivalent lattice sites in 6H SiC, two quasi-cubic (“k1,” “k2”) and one hexagonal (“h”) site, the different intensities of the two hf triplets and the different g tensors belonging to them, lead to an assignment of the triplet lines with the lower intensity to N substituting hexagonal sites (N_h) and those with the higher intensities to N substituting two quasi-cubic sites (N_{k1} , N_{k2}). But first ENDOR measurements performed at 9 GHz in 6H SiC did not support this claim because the observed ENDOR signals were not assigned to the central ¹⁴N hyperfine interactions (hfi) of the N donors and ¹⁴N hfi constants have not been obtained [5]. However it was suggested at the same time, that

N substitutes C sites by comparing the spin-lattice relaxation time of the remote ^{29}Si ($I = 1/2$, 4.68%) and ^{13}C ($I = 1/2$, 1.07%) nuclei which have a small superhyperfine interaction (shfi) with the donor electron.

Only later high-frequency EPR measurements performed at 142 GHz allowed to resolve three distinct spectra from nitrogen donors in 6H SiC, which could be identified with the three inequivalent positions in the lattice [6]. Two sets of ^{14}N hf triplet lines with very similar hfi constants were attributed to N_{k1} and N_{k2} while a third EPR line with an unresolved hf structure was attributed to N_h [6].

However, a further confirmation of this assignment made from high-resolution EPR measurements by other methods such as ENDOR was required. Especially it was necessary to prove that the single line with anisotropic width and possible small unresolved hf structure found in the high-resolution EPR spectra is due to N_h . This task was successfully resolved by measurements of the ^{14}N ENDOR spectrum at 9 GHz [7–10]. The central ^{14}N hfi for the inequivalent lattice sites were determined in 6H, 4H, and 3C SiC polytypes. It was proved that N_h has small anisotropic hfi constants in 6H and 4H SiC. In addition, a series of ENDOR lines from ^{29}Si and ^{13}C nuclei in the region of their respective Larmor frequencies (ν_n) were observed in the ENDOR spectra of 6H SiC and 4H SiC polytypes. These lines were identified with the shfi of N donors with ^{29}Si and ^{13}C nuclei located around N atoms. However, the observed ^{29}Si and ^{13}C ENDOR lines could not be assigned to the inequivalent lattice sites. The ^{29}Si and ^{13}C shfi constants as determined from ENDOR spectroscopy differed only slightly, so that it was not possible to conclude if Si or C atoms are next neighbors to the N donors. Only the larger number of ^{29}Si ENDOR shf lines in the investigated frequency range compared to those for ^{13}C ENDOR shf lines was served as argument in favor for N substituting C sites with a ^{29}Si next-neighbor environment.

The next investigation of the ^{14}N ENDOR spectra in 4H SiC and 6H SiC polytypes was undertaken at 95 GHz [11]. The aim of the work was to determine the spatial distribution of the electronic wave function of N donors at the three inequivalent lattice sites from the investigation of the shfi of the unpaired electron spin of the donor with the ^{29}Si and ^{13}C nuclei. The shfi constants deduced from ENDOR measurements at 95 GHz were comparable to the results obtained previously at 9 GHz because the ^{14}N ENDOR spectra were only studied in the low-frequency region around Larmor frequencies of ^{29}Si and ^{13}C nuclei in both experiments [7–10]. Therefore, there was no reason to change the current point of view that N substitutes for C atom in the SiC lattice. Further interest in ENDOR studies of the N donors in SiC was triggered by the shf satellite lines found in the highly resolved EPR spectra of N donors in 4H SiC [12] and in EPR spectrum of 4H SiC with a modified isotopic composition [13] with corresponding shfi constants of one order in magnitude larger than those observed previously in the ^{14}N ENDOR spectra of 4H SiC.

Additional pulsed ENDOR measurements on the N donor centers in 4H SiC at 9 GHz in a higher frequency range revealed a series of new ENDOR lines due to shfi of N donors with neighboring ^{29}Si and ^{13}C nuclei having shfi constants considerably larger than those obtained in previous ENDOR studies [14]. The shf satellite lines found in the high-resolution EPR spectra were identified as due to the ^{29}Si nuclei. The fact that the largest value of shfi constants were found for the ENDOR lines belonging to the ^{29}Si nuclei indicates that Si atoms locate in the nearest-neighbor shell of the N at quasi-cubic sites and, thus, N substitutes C sites in 4H SiC.

With the aim to find the shf lines with the larger constants just as obtained for 4H SiC, N donors were studied by EPR [13], field sweep electron spin echo, (FS ESE) and pulsed ENDOR methods in 6H SiC [15]. Shf satellite lines were also found in ^{14}N EPR and FS ESE spectra, which correspond to shfi constants significantly larger than those observed previously in the ENDOR spectra of 6H SiC and confirmed in that way that a careful pulsed ENDOR study in the high-frequency range is also required for this polytype. Indeed, new ^{29}Si and ^{13}C ENDOR lines belonging to four silicon and three carbon atoms, which were not observed previously, could be detected at higher frequencies. The angular dependencies of these signals measured in a plane perpendicular to the crystallographic (0001) plane of 6H SiC revealed almost isotropic shf couplings for all nuclei with large isotropic shf coupling parameters ranging from 23 to 10 MHz for ^{29}Si and 18 to 13 MHz for ^{13}C . The observed largest shf splitting (23.12 MHz), was attributed to Si atoms located along the *c*-axis in nearest-neighbor positions of N on the quasi-cubic sites, which unambiguously confirms that N substitutes C lattice sites in 6H SiC.

But despite of the conclusion made on the basis of this ENDOR study of N donors some fundamental questions related to the spatial distribution of the electronic wave function of the isolated N donors residing at the two quasi-cubic sites in 6H-SiC were not well understood yet. A major obstacle in previous ENDOR studies of the N donors at cubic sites [15] was that the ^{29}Si and ^{13}C ENDOR signals could not be unambiguously assigned to either the N_{k1} or N_{k2} site. Furthermore the shf lines observed in the EPR and ENDOR spectra could not be ascribed to specific C and Si atoms located around the N_{k1} and N_{k2} sites in 6H SiC as well as the relative sign of the shfi constants for N donors were not obtained yet. As the result, the spatial distribution of the electronic wave function of N_{k1} and N_{k2} could not completely be established. The lack of these necessary experimental data is possibly due to the limited capabilities of the EPR and ENDOR methods, which were used so far for the investigation of the ligand shf structure.

It is well known that the General TRIPLE ENDOR technique [16, 17] allows to obtain the relative signs of the shfi constants from the changes of the relative amplitudes of the high- and low-frequency ENDOR transitions. At the same time, this method can be used to distinguish between ENDOR lines resulting from different species because only

the lines originating from the same paramagnetic species are affected.

In this work, FS ESE, pulsed ENDOR, and General TRIPLE ENDOR spectroscopy have been employed to determine the relative sign of the shfi constants for N donors in 6H SiC and to assign specific C and Si atoms with the N_{k1} and N_{k2} donor sites. It was found that N_{k1} and N_{k2} in 6H SiC having comparable isotropic ^{14}N hfi constants ($a_l(N_{k1}) = 33.564 \text{ MHz}$, $a_l(N_{k2}) = 33.221 \text{ MHz}$) have a different environment. Si atoms are located in the nearest neighborhood of the N_{k1} while C atoms are located in the nearest neighborhood of N_{k2} indicating that N_{k1} and N_{k2} reside at two distinct atom sites in the 6H SiC lattice. The comparison of the experimentally obtained ^{13}C and ^{29}Si shfi constants with the theory of the donor states developed by Kohn and Luttinger [18] allow us to establish the spatial distribution of the electronic wave function of the isolated N donors over the neighbored ^{13}C and ^{29}Si nuclei and to fix the position of the conduction band minimum along the ML-line at $k_{0z}/k_{\text{max}} = 0.2 \pm 0.05$.

2 Experimental methods A series of n-type 6H-SiC wafers grown by the modified Lely method with donor concentration of about $(N_D - N_A) \approx 10^{17} \text{ cm}^{-3}$ were investigated by pulsed magnetic resonance methods. The X-band FS ESE, pulsed Davies ENDOR, and General TRIPLE ENDOR measurements were performed on Bruker ELEXSYS E580 spectrometer at $T = 6 \text{ K}$.

The FS ESE spectra were measured using Hahn echo pulse sequence: $\pi/2 - \pi - \tau - \pi - \text{echo}$. The typical pulse lengths and delays for FS ESE measurements were: $t_{\pi/2} = 100 \text{ ns}$, $t_\pi = 200 \text{ ns}$, and $\tau = 1000 \text{ ns}$.

Figure 1 depicts the pulse sequences for Davies ENDOR and General TRIPLE ENDOR experiments. The detailed description of General TRIPLE ENDOR pulse sequence and its effect on populations of EPR and ENDOR transitions for the system with $S = 1/2$ and $I = 1/2$ is given in Ref. [19]. Pulsed ENDOR and General TRIPLE ENDOR spectra were measured using additional radiofrequency (RF) π pulse after echo detection that helps the total spin system to recover to the thermal equilibrium in a much shorter time limited

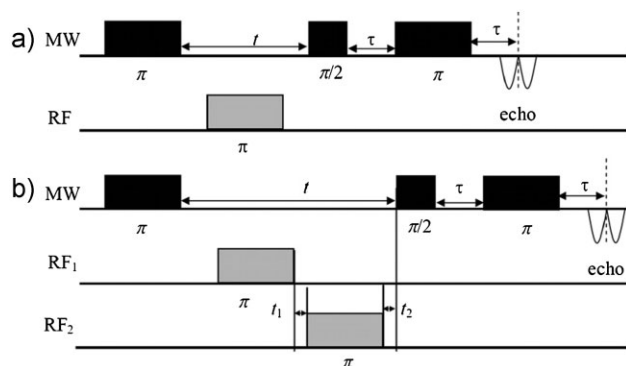


Figure 1 Davies ENDOR (a) and General TRIPLE ENDOR (b) pulse sequences.

only by the spin-lattice relaxation time instead of nuclear spin-lattice relaxation time as in case of the original Davies ENDOR experiment as was proposed in Ref. [20]. The typical pulse lengths and delays for Davies ENDOR and General TRIPLE ENDOR measurements were: $t_{\pi\text{RF}} = 16 \mu\text{s}$, $t = 30 \mu\text{s}$, $t_{\pi/2} = 100 \text{ ns}$, $t_\pi = 200 \text{ ns}$, and $\tau = 1000 \text{ ns}$.

The FS ESE and ENDOR spectra of ^{14}N can be analyzed using the following spin-Hamiltonian, which includes the electron, nuclear Zeeman interactions, hf, shf, and quadrupole interactions:

$$H = \frac{\mu_B \mathbf{B} g \mathbf{S}}{\hbar} - \frac{g_n \mu_n \mathbf{B} \mathbf{I}}{\hbar} \sum_i \mathbf{S} \mathbf{A}_i \mathbf{I}_i + \mathbf{I} \mathbf{P} \mathbf{I}, \quad (1)$$

where μ_B is the Bohr magneton of the electron; $\mathbf{B} = (0, 0, B_0)$ the externally applied magnetic field; g the electron g -tensor; \mathbf{S} the electron spin operator; $\hbar = h/2\pi$ the Plank constant; g_n the nuclear g -factor (for ^{14}N : $g_n = 0.40347$, for ^{29}Si : $g_n = -1.1106$, for ^{13}C : $g_n = 3.74795$); μ_n the nuclear magneton; \mathbf{I}_i the nuclear spin operator (of i -th nucleus); \mathbf{A}_i the tensor of hfi/shfi of i -th nucleus ($i = 1$ – hfi with its own nucleus, $i > 1$ – shfi with surrounding nuclei in the lattice) and \mathbf{P} is the ^{14}N nuclear quadrupole interaction tensor with its largest principal value: $P_z = e^2 q Q / [2I(I-1)\hbar]$ ($e q$, electrical field gradient; Q , electrical quadrupole moment).

The spin-Hamiltonian terms for the hfi/shfi can be written as the sum of isotropic Fermi-contact and electron–nuclear dipole–dipole interactions: $\mathbf{S} \mathbf{A}_l \mathbf{I}_l = a_l \mathbf{S} \mathbf{I}_l + \mathbf{S} \mathbf{T}_l \mathbf{I}_l$, where a_l is the isotropic hfi/shfi constant of l -th atom, \mathbf{T}_l the traceless tensor with principal values $(-b_l; -b_l; 2-b_l)$ of the dipole–dipole interaction between the electron spin and the nuclear spin \mathbf{I}_l . Here, b_l is the anisotropic hfi/shfi constant of l -th atom. For the system with axial symmetry it follows that $A_{||} = a_l + 2b_l$ and $A_{\perp} = a_l - b_l$ (b_l – anisotropic hfi/shfi constant of l -th atom).

Figure 2 shows the energy level scheme for a N donor with an electron spin $S = 1/2$ taking into account first and second order effects in the ^{14}N hfi, the ^{14}N nuclear quadrupole interaction, and the shfi of the donor center with ^{29}Si or ^{13}C nuclei having different signs of shfi constants and corresponding ENDOR and General TRIPLE ENDOR spectra.

3 Results and discussion

3.1 Experimental results Figure 3(1) shows the first derivative of the X-band FS ESE spectra observed in n-type 6H-SiC wafers with donor concentration of about $(N_D - N_A) \approx 10^{17} \text{ cm}^{-3}$ at $T = 6 \text{ K}$ for the orientation $\mathbf{B} \perp \mathbf{c}$. The X-band FS ESE spectrum consists of two overlapping hfi triplets corresponding to N_{k1} and N_{k2} , a single line due to N_h coinciding with the central line of the N_{k1} and N_{k2} triplets, which has a small unresolved hf splitting, and a further triplet from N_x centers caused by spin-coupling between N_h and N_{k2} [15]. The triplet lines due to the N_{k1} and N_{k2} are accompanied by two weak shf satellites lines with a large splitting of 0.83 mT corresponding to 23.2 MHz , which has been

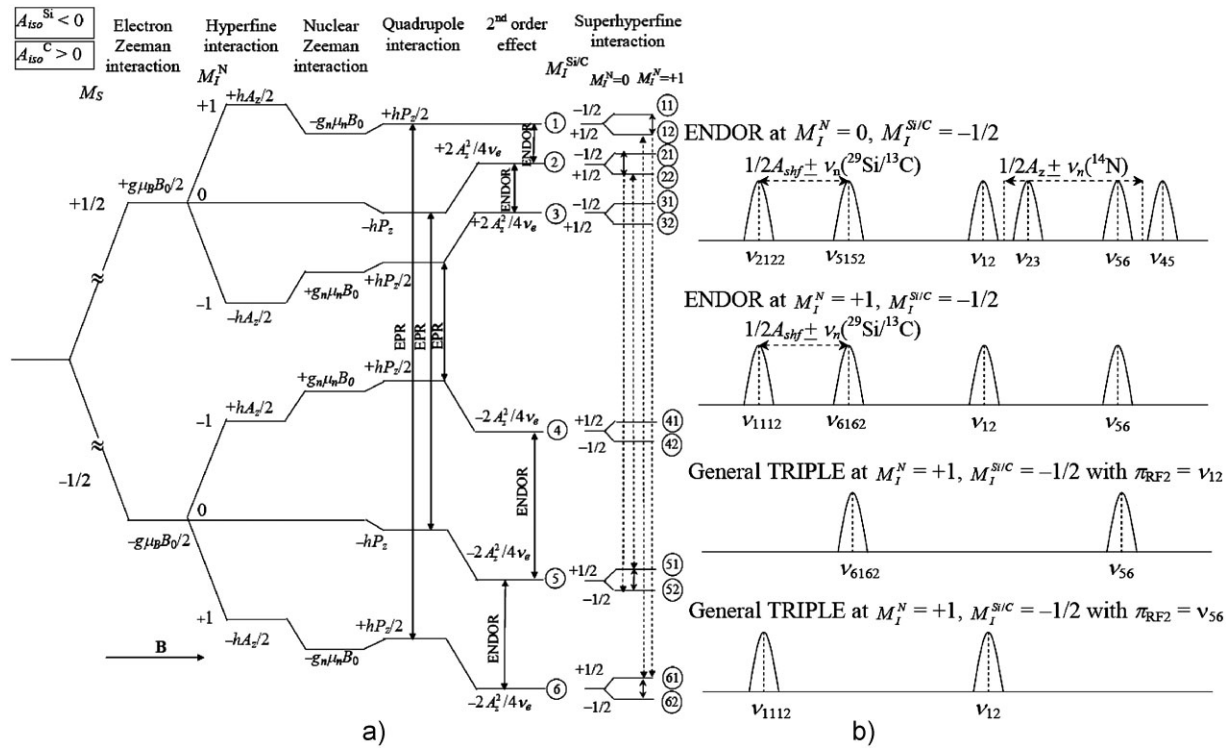


Figure 2 The energy level scheme for ^{14}N ($S=1/2, I=1$; taking into account the second order effect) and its shfi with ^{29}Si nuclei for $a_{I,\text{Si}} < 0$ (or with ^{13}C for $a_{I,\text{C}} > 0$) (a) and corresponding ENDOR and General TRIPLE spectra (b). ν_e – free electron Zeeman frequency. The scheme was drawn according to Ref. [21].

assigned to a ^{29}Si shfi by ENDOR measurements as reported in [15]. Figure 3(2) shows the X-band Davies pulsed ENDOR spectra measured in 6H SiC sample for $B \perp c$, recorded at a magnetic field position 348.36 mT of the central triplet lines of the N_{k1} and N_{k2} centers (Fig. 3(2), spectrum

(a)) and at the position of the low-field ^{29}Si shf satellite line at 346.94 mT (Fig. 3(2), spectrum (b)).

All ENDOR spectra show intense ^{14}N ENDOR signals of N_{k1} and N_{k2} centers at frequencies higher than 15 MHz [7–10]. With B_0 set at the central triplet lines of the N_{k1} and

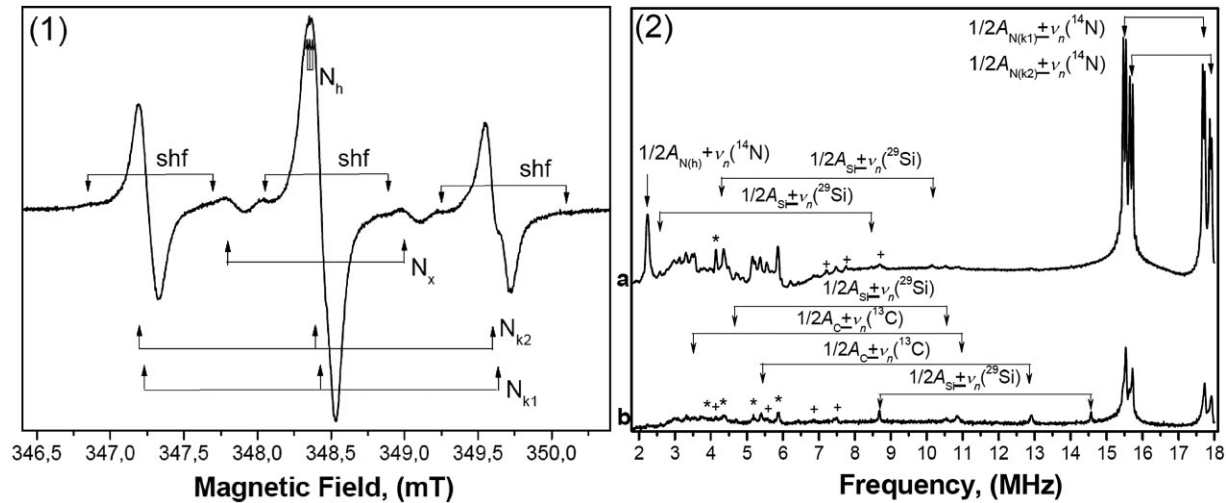


Figure 3 First derivative of the X-band FS ESE spectrum (1) and pulsed Davies ENDOR spectra (2) measured in n-type 6H SiC at $T=6$ K and $B \perp c$. The ENDOR spectra were recorded at the following FS ESE observer positions: (a) the N_h line overlapped with the central $N_{k1,k2}$ triplet lines ($B_0 = 348.36$ mT), (b) the outer shf line of the low-field $N_{k1,k2}$ triplet lines ($B_0 = 346.94$ mT). “*” – high frequency ENDOR lines of ^{29}Si shf lines, “+” – high-frequency ENDOR lines of ^{13}C shf lines.

N_{k2} (Fig. 3(2)(a)), all four lines of the quadrupole-split ENDOR spectra of N_{k1} and N_{k2} are observed. Considering the ^{14}N hfi and nuclear quadrupole constants of N_{k1} and N_{k2} according to Ref. [15], the ENDOR signals at 15.672, 15.696, 17.838, and 17.928 MHz have been assigned to N_{k1} and those at 15.528, 15.558, 17.700, and 17.778 MHz to N_{k2} . The ENDOR line at 2.41 MHz is observed only for such field settings where the spectrum of N on the “h” lattice site (N_h) is excited and was consequently attributed to the high-frequency ENDOR signals of the N_h center according to Ref. [8].

All other ENDOR signals are related to shfi with ^{29}Si and ^{13}C nuclei, which are observed mostly in the low-frequency part of ENDOR spectrum when the ENDOR spectrum is taken at the central triplet lines of the N_{k1} and N_{k2} centers, while in the case when the ENDOR spectra are recorded at the shf satellite lines of N_{k1} and N_{k2} (Fig. 3(2)(b)) additional ^{29}Si and ^{13}C signals from more strongly coupled nuclei appear at higher frequencies (8–15 MHz).

Except for the two ^{29}Si ENDOR lines at 14.564 and 8.691 MHz belonging to one strongly coupled ^{29}Si nucleus the assignment of the ENDOR signals to either ^{13}C or ^{29}Si remains still vague because of the huge number of overlapping signals at frequencies below 8 MHz. In addition, even for these clearly resolved two ENDOR lines it is not possible to distinguish if they couples with either the N_{k1} or N_{k2} donor state as their FS ESE spectra overlap severely at X band frequencies (Fig. 3(2)(a)).

However, the later question shall be answered by General TRIPLE spectroscopy, where a clear assignment of the ^{13}C and ^{29}Si ENDOR lines to one of the two N donors, N_{k1} or N_{k2} shall be feasible on the basis of their well resolved ^{14}N ENDOR spectra. Likewise, General TRIPLE experiments are expected to support the assignment of the various low-frequency ^{13}C and ^{29}Si ENDOR lines. In addition, General TRIPLE experiments will also allow for

the determination of the relative sign of the ^{13}C or ^{29}Si shfi constants. If we assume, that the isotropic ^{14}N hfi constants of the N donors to be positive we can even derive absolute signs of these coupling parameters. In the following, the results of such General TRIPLE experiments on the N_{k1} and N_{k2} donors in 6H SiC will be presented.

Figures 4 and 5 display the comparison between Davies ENDOR spectra and General TRIPLE ENDOR spectra measured when low-frequency (Figs. 4(b) and 5(b)) and high-frequency (Figs. 4(c) and 5(c)) ENDOR lines of N_{k1} and N_{k2} were “pumped.” In the ENDOR and TRIPLE ENDOR experiments, the magnetic field was set at the position of the low-field satellite shf lines observed in FS ESE spectra (Fig. 3(1)).

As it seen from Fig. 4 the ENDOR lines that “react” in intensity on the “pumping” of N_{k1} ENDOR lines at 15.653 and 17.867 MHz are the lines at 14.564 and 8.691 MHz (labeled as Si1) assigned to ^{29}Si nuclei according to Ref. [14]; the lines at 10.526 and 4.71 MHz (Si2) which belong also to ^{29}Si nuclei; the lines at 7.489 MHz (C1), 6.856 MHz (C2), and 5.571 MHz (C3), which according to Ref. [11] are due to a shfi with ^{13}C nuclei; and a line at 4.381 MHz (Si3) which according to Refs. [11, 22] belongs to a shfi with a ^{29}Si nucleus.

From Fig. 5 it is clearly seen that the ENDOR lines that “respond” in their intensity on the “pumping” of the N_{k2} ENDOR lines at 15.467 and 16.676 MHz are the lines at: 12.909 and 5.392 MHz (labeled as C1), 10.846 and 3.364 MHz (C2) which according to Ref. [15] belong to shfi with ^{13}C nuclei; 5.878 MHz (Si1), 5.187 MHz (Si2) which according to Ref. [22] belong to shfi with ^{29}Si nuclei; and a line at 4.144 MHz (C3) which according to Ref. [11] is attributed to a shfi with ^{13}C nucleus.

Recording the General TRIPLE ENDOR spectrum under condition when the high-frequency ENDOR line of N_{k1} at 17.867 MHz was “pumped” (Fig. 4(c)), one can find

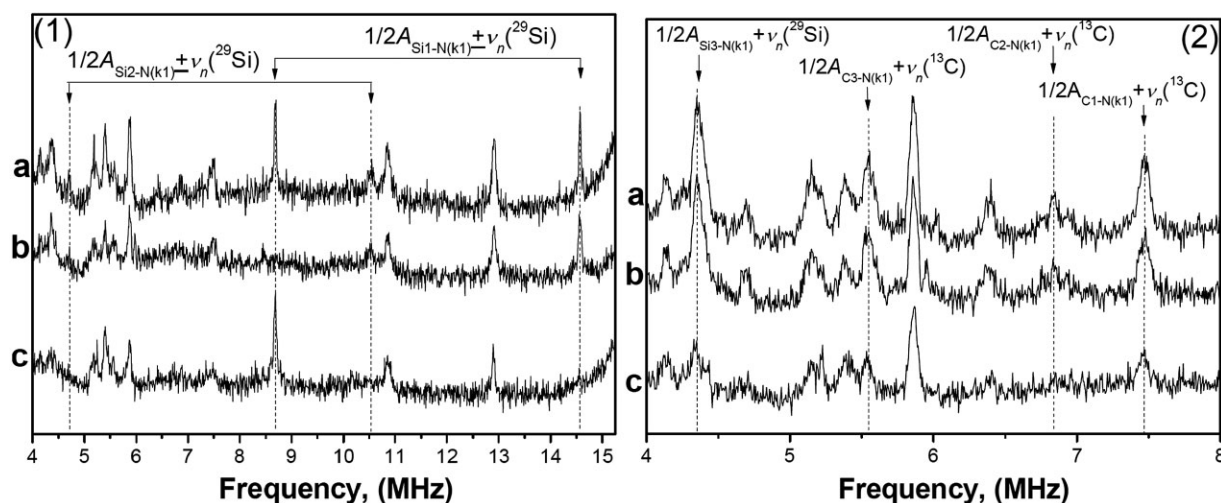


Figure 4 X-band pulsed Davies ENDOR (a) and General TRIPLE-ENDOR spectra (b,c) measured in n-type 6H SiC samples when low-frequency (b) and high-frequency (c) ENDOR lines of N_{k1} at 15.653 and 17.867 MHz were “pumped”, respectively. $B_0 = 346.94$ mT (1), $B_0 = 346.85$ mT (2). $B \perp c$, $T = 6$ K.

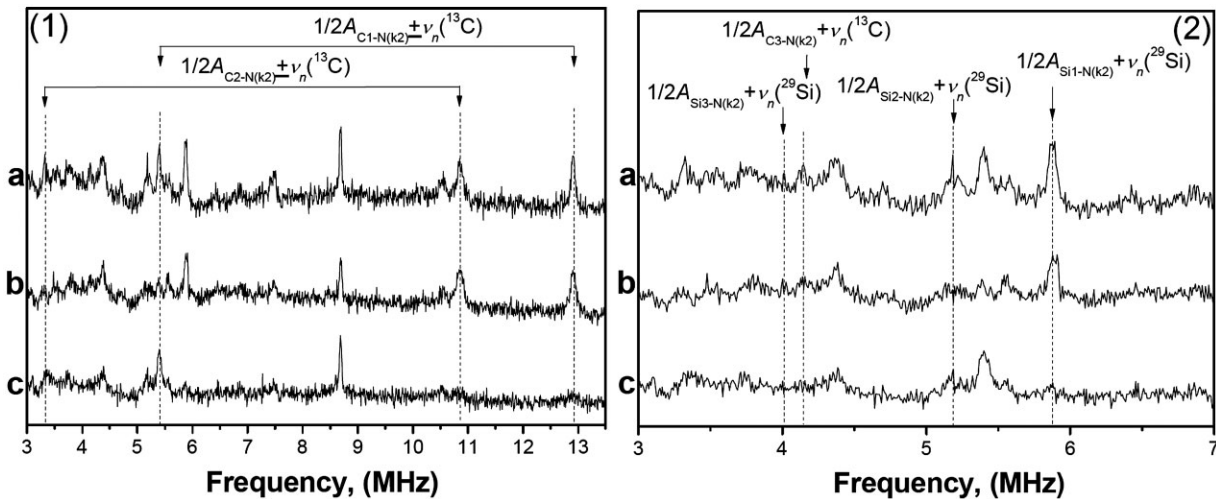


Figure 5 X-band pulsed Davies ENDOR (a) and General TRIPLE-ENDOR spectra (b,c) measured in n-type 6H SiC samples when low-frequency (b) and high-frequency (c) ENDOR lines of N_{k2} at 15.467 and 17.676 MHz were “pumped”, respectively. $B_0 = 346.94$ mT (1), $B_0 = 346.85$ mT (2). $B \perp c$, $T = 6$ K.

that the Si1, Si2, and Si3 as well as C1, C2, and C3 high-frequency ENDOR lines are de-enhanced while the Si1 and Si2 low-frequency ENDOR lines are enhanced. According to Fig. 2 the relative signs of shfi constants for Si1, Si2, and Si3 should be opposite in respect to the sign of hfi constant for N_{k1} (in our case $a_i > 0$ for N_{k1} and N_{k2}) and, thus, are negative, while the relative signs of shfi constants for C1, C2, and C3 are supposed to be positive. Recording the General TRIPLE ENDOR spectrum under condition when the high-frequency ENDOR line of N_{k2} at 17.676 MHz was “pumped” (Fig. 5(c)) one can see that the C1, C2, and C3 as well as the Si1 and Si3 high-frequency lines are de-enhanced while the C1 and C2 low-frequency ENDOR lines are enhanced. This indicates that the signs of shfi constants for C1, C2, and C3 should be the same as the sign of hfi constant for N_{k2} and, hence, are positive while the signs of shfi constants for Si1 and Si3 should be negative. Unfortunately, we were not able to determine the relative sign of shfi constant for the Si2 line.

Figure 6 shows the pulsed ENDOR spectrum measured when B_0 was set to the field position of the N_h spectrum, which coincides with the central lines of the N_{k1} and N_{k2} hf triplets. From the analysis of ENDOR spectra measured at different observer field positions (Figs. 4 and 5) it was found that the ENDOR signals at 10.146 and 8.709 MHz should be related to a ^{13}C and ^{29}Si shfi of the N_h center. The high-frequency ENDOR line at 10.146 MHz (labeled as Si1) was already observed in our previous work [15] and attributed to shfi with a ^{29}Si nucleus with its low-frequency line at 4.355 MHz, but wrongly assigned to a shfi of the $N_{k1,k2}$ centers. This mistake occurred because these ENDOR lines in Ref. [15] were measured at field positions where the spin-coupled N_x centers contribute to the ENDOR experiment, and consequently the resulting ENDOR spectra will display contributions from all three donor centers N_h , N_{k1} , and N_{k2} . As seen from Fig. 6, the low-frequency ENDOR signal

belonging to the high-frequency signal at 8.709 MHz overlaps severely with other ENDOR lines from weakly coupled ^{13}C and ^{29}Si nuclei and makes its identification in terms of either a ^{29}Si or ^{13}C shfi difficult. However, as will be shown below, the best agreement between experimental and calculated shfi constants was obtained if the ENDOR signal at 8.709 MHz was attributed to ^{29}Si . The ENDOR lines labeled as Si3, C1, C2, and C3 in Fig. 6 have been attributed to a shfi of the N_h donor with ^{29}Si and ^{13}C nuclei according to Ref. [11]. Because the spin-lattice relaxation time of the N_h center ($\sim 8 \mu\text{s}$) is shorter than that of the $N_{k1,k2}$ centers ($\sim 24 \mu\text{s}$) it was impossible to “pump” the N_h ENDOR line and thus perform the General TRIPLE ENDOR experiment for the N_h center.

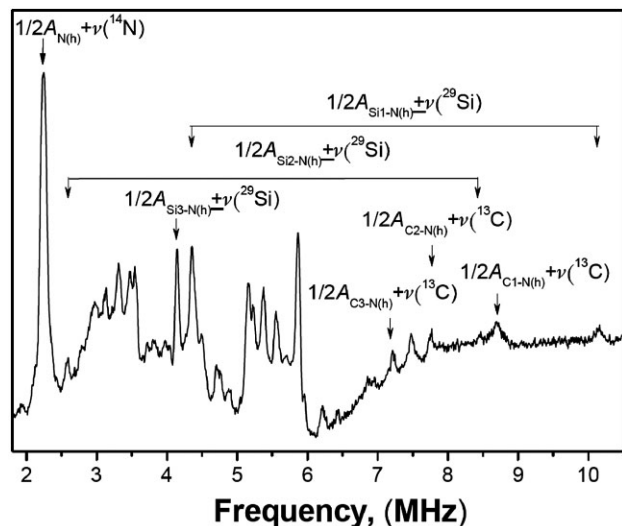


Figure 6 X-band pulsed Davies ENDOR spectra measured in n-type 6H SiC when magnetic field was set at the position of the N_h FS ESE line which coincides with the central ^{14}N hfi triplet lines of $N_{k1,k2}$. $B \perp c$, $T = 6$ K.

The experimentally obtained ^{29}Si and ^{13}C shfi parameters of the N donors are given in the Table 1. There the symbol “ \pm ” indicates that the sign of the shfi could not be determined. All other signs have been obtained from the discussed General TRIPLE experiments by assuming a positive isotropic ^{14}N hfi for the $\text{N}_{\text{k1,k2}}$ centers.

3.2 Analysis of shfi parameters for N donors in 6H SiC As was seen from Table 1 all shfi constants obtained for N donors are almost isotropic and arises from the Fermi-contact interaction term, which is described by:

$$a_l(r_l) = \frac{8\pi}{3\hbar} g_e \mu_B g_n \mu_n |\Psi(r_l)|^2. \quad (2)$$

The different signs of the isotropic shfi constants a_l for ^{29}Si and ^{13}C (see Table 1) can easily be understood by the fact that they are proportional to the nuclear g -factor g_n that has a different sign for ^{29}Si versus ^{13}C . As a result $a_{l,\text{Si}} < 0$ and $a_{l,\text{C}} > 0$ because of $g_{\text{Si}} < 0$ and $g_{\text{C}} > 0$, respectively.

For an indirect many-valley semiconductor such as 6H SiC the donor wave function $\Psi(r_l)$ at the nuclear site r_l is given as a sum of linear combination of plane waves over the conduction band minima [23]:

$$\Psi(\mathbf{r}) = F(\mathbf{r}) u_{k_0}(\mathbf{r}) \sum_{j=1}^6 \alpha_j \exp(i\mathbf{k}_0^{(j)} \cdot \mathbf{r}) = F(\mathbf{r}) u_{k_0}(\mathbf{r}) S(\mathbf{r}), \quad (3)$$

where $F(\mathbf{r})$ is the envelope function, $u_{k_0}(\mathbf{r})$ is the Bloch's factor, $\mathbf{k}_0^{(j)}$ is a k -vector at the point of the j -th conduction band minimum, α_j are the numerical coefficients of the

linear combination of the electron states for the sixfold degenerated conduction band, $S(\mathbf{r})$ is the Kohn–Luttinger interference factor.

In case of an 1s state the envelope function is given by:

$$F(r) = (\pi a_{\text{B,eff}}^3)^{-1/2} \exp\left(\frac{-r}{a_{\text{B,eff}}}\right), \quad (4)$$

where $a_{\text{B,eff}} = \epsilon_r m_0 a_B / m^*$ is an effective Bohr radius, a_B is the Bohr radius, ϵ_r is the dielectric constant, m^* is effective mass, and m_0 refers to the free-electron mass.

Usually the Bloch's factor is substituted by the dimensionless parameter [24] describing the degree of the localization of the wave function at the lattice site \mathbf{r}_l :

$$\eta = \frac{|u_{k_0}(\mathbf{r}_l)|^2}{\langle u_{k_0}(\mathbf{r}) \rangle^2}, \quad (5)$$

where the average is taken over the unit cell.

The interference factor $S(\mathbf{r})$ was calculated by taking into account the crystal symmetry of 6H SiC following Patrick [25] and can be written as a product of an axial, S_{ax} , and a planar fraction S_p :

$$S(\mathbf{r}) = S_{\text{ax}} \times S_p = 2\cos(k_z z_l) \times \sum_{j=1}^3 \alpha_j \cos(\mathbf{k}_p^{(j)} \cdot \mathbf{r}_p), \quad (6)$$

where the sum is taken over the three minima ($j = 1, 2, 3$). The quantity c in $k_z = k_0 2\pi/c$ is the lattice constant along the z axis, $k_0 = k_z/k_{z,\text{max}}$, $k_{z,\text{max}} = 2\pi/c$, and k_{max} indicates the size of the wave vector between the M and L point in the Brillouin zone; z_l is the z -coordinate of each atom l in the corresponding donor shell; \mathbf{r}_p is a planar vector;

Table 1 The ^{29}Si and ^{13}C shfi parameters of N residing quasi-cubic and hexagonal sites in 6H SiC as obtained by pulsed ENDOR and General TRIPLE spectroscopy. The last column includes the assignment of the shfi constants to N on the inequivalent positions given previously and in this work. The assignment to specific Si and C shells is given according to the theoretical calculation presented in Section 3.2.

center	shell	shf lines	A_{\parallel} , MHz	A_{\perp} , MHz	a_l , MHz	b_l , MHz	assignment and ref.
N_{h}	I	Si1	± 14.48	± 14.51	± 14.50	∓ 0.009	$\text{N}_{\text{k1,k2}}$ [15]
		Si2	± 11.06	± 11.06	± 11.06		this work
		Si3	± 2.359	± 2.359	± 2.359		N_{h} [11]
	II	C1	± 9.95	± 9.95	± 9.95		N_{h} [11]
		C2	± 8.095	± 8.095	± 8.095		N_{h} [11]
		C3	± 6.994	± 6.994	± 6.994		N_{h} [11]
N_{k1}	I	Si1	-23.124	-23.268	-23.22	0.048	$\text{N}_{\text{k1,k2}}$ [15]
	I/III	Si2	-15.18	-15.20	-15.19	0.007	this work
	III	Si3	-2.78	-2.84	-2.82	0.02	^{14}N [22], N_{k1} [11]
	II	C1	7.519	7.519	7.519	0.175	N_{k1} [11]
		C2	6.733	6.208	6.383		N_{k2} [11]
		C3	3.945	3.684	3.771		N_{k2} [11]
N_{k2}	II	Si1	-5.81	-5.81	-5.81	0.035	^{14}N [22]
	VIII	Si2	± 4.479	± 4.479	± 4.479		^{14}N [22]
	IX	Si3	-1.942	-2.047	-2.012		N_{k2} [15]
	I	C1	18.366	18.402	18.39		$\text{N}_{\text{k1,k2}}$ [15]
	III	C2	14.25	14.25	14.25		$\text{N}_{\text{k1,k2}}$ [15]
	I/IV	C3	0.753	0.753	0.753		N_{k1} [11]

$\mathbf{k}_0^{(j)}$ is the planar part of $\mathbf{k}_0^{(j)}$ which is equal to $[k_{x_0}^j, k_{y_0}^j] = [k_x^j \pi/a, k_y^j \pi/a]$, and a is the lattice constant in the hexagonal plane. By rotation of the \mathbf{k} vector in reciprocal space between the equivalent band minima one can obtain the values of k_x^j and k_y^j equal to (1; 1.366; 0.366) and (1; -0.366; -1.366) for $j = 1; 2; 3$, respectively.

Substitution of Eqs. (3)–(6) into Eq. (2) leads to:

$$a_l(r_l) = R(a_{B,eff})^{-3} C \eta \exp(-2r_l/a_{B,eff}) \times 4 \cos^2(k_z z_l) \left[\sum_{j=1}^3 \alpha_j \cos(k_x^j x_l + k_y^j y_l) \right]^2, \quad (7)$$

where x_l, y_l are coordinates of l -th atom in a coordinate frame centered at the donor site, $R = 8\pi g_e \mu_B g_n \mu_n / 3\hbar$ and C is a factor obtained by the normalization of the wave function in Eq. (3):

$$C(a_{B,eff})^{-3} \int_0^\infty \int_0^{2\pi} \int_0^{2\pi} |S(r, \theta, \phi)|^2 \times \exp(-2r_l/a_{B,eff}) r^2 dr \sin\theta d\theta d\phi = 1, \quad (8)$$

where θ and ϕ are the polar and azimuthal angles of \mathbf{r} . The numerical integration of Eq. (8) yields the value $C = 0.074$.

Using Eq. (7) the shfi constants $|a_l|$ have been calculated for the ^{29}Si and ^{13}C nuclei located at the different distances r_l from the N donors substituting “k1,” “k2,” and “h” sites and accounting for the planar part of the interference factor. The coefficients α_j of the linear combinations of the plane waves for the degenerated conduction band minima were determined from the solution of the equation system written for the planar part of the interference factor $(S_p)^2$. Here the ratio of the shfi constants to the largest value of them for the same type of the atoms was used. In the case of N_h substituting a C site ($N_{h,C}$) we obtained: $\alpha_1 = 1, \alpha_2 = -1, \alpha_3 = 1$; for N_{k1} substituting a C site ($N_{k1,C}$): $\alpha_1 = 1, \alpha_2 = -1.35, \alpha_3 = -1$ followed; and for N_{k2} substituting a Si site ($N_{k2,Si}$) the solution was $\alpha_1 = 1, \alpha_2 = -1.5, \alpha_3 = -0.224$.

The only fitting parameters that entered the theory are $a_{B,eff}$, and η . Their values can be determined by the best agreement between theoretically calculated and experimentally obtained shfi constants $|a_l|$ in an optimization procedure. For the three N donor species the best fit between experimental and theoretical values of the shfi constants $|a_l|$ was found for $a_{B,eff}$ values equal to 15, 9, and 10 Å for N_h, N_{k1} , and N_{k2} , respectively, which coincide with those evaluated in Ref. [10] as 13.2, 10.1, and 10 Å using the effective mass values 0.26 m_0 and ground-state binding energies of 81.0, 137.6, and 142.4 meV for N_h, N_{k1} , and N_{k2} , respectively.

Two different values of η were taken as fitting parameters for each of the three donor states in order to account for the difference in this dimensionless quantity at the Si and C atoms. The reason is, that unlike the mono-elemental Si, in which P forms only one donor state, SiC is a

composed of two elements, Si and C, for which R has different values: $R(\text{Si}) = 0.827 \times (10^7 \times a_{B,eff})^{-3}$ MHz and $R(\text{C}) = 1.046 \times (10^7 \times a_{B,eff})^{-3}$ MHz and the N donors constitute only a few donor states in the band gap with different electron spin density.

The best fit was obtained for the following values of η for N_h : $\eta(\text{Si}) = 78, \eta(\text{C}) = 43$; for N_{k1} : $\eta(\text{Si}) = 36, \eta(\text{C}) = 11$; and for N_{k2} : $\eta(\text{Si}) = 11.0, \eta(\text{C}) = 17$. Comparing the η values obtained at Si and C atoms for N donors, it is seen that the degree of localization of the electron density at Si and C atoms for nitrogen in 6H SiC is smaller than that at Si atoms for P donors in Si crystals ($\eta = 186$) [26]. In the case of N_h and N_{k1} , the largest part of the electron density is located at the Si sublattice, while for N_{k2} the largest part of the electron density is located at the C sublattice.

The behavior of the shfi constants $|a_l|$ described above is schematically illustrated in Fig. 7 where the theoretical values of $|a_l|$ for every Si and C atoms are plotted as function of their distances (r_l) from the N donors substituting quasi-cubic and hexagonal sites. The comparison between the theoretical and experimental data in Fig. 7 allows us to distribute the obtained experimental shfi constants $|a_l|$ over the shells surrounding the N donors. The best agreement between theory and experimental data was obtained if k_z was chosen to be 0.2.

In Fig. 7, a shell refers to a set of atoms that are equidistant from the N donors. Those C and Si atoms in the shell for which $(S_p)^2 \ll 1$ were not shown in the Fig. 7 since for these atoms the calculated shfi constants have negligible small and therefore unobservable values of $|a_l|$.

As can be seen from Fig. 7, the calculated shfi constants $|a_l|$ have the largest values for Si atoms located in the first shell of N_h and N_{k1} (14.36 and 23.6 MHz, respectively) and they are in a good agreement with those obtained experimentally. Among the shfi constants calculated for N_{k2} the largest value (18.5 MHz) was obtained for C atoms located in the first shell of N_{k2} and it coincides again with that obtained experimentally. These facts give us the confidence to consider that the N donors at “h” and “k1” lattice positions are substituting C atoms while those at “k2” position are replacing Si atoms.

No satisfactory agreement between the theory and experiment was obtained by assuming that a N donor at the “k2” lattice position occupies a C site. Indeed, in this case the value $|a_l|$ calculated from the theory for the Si atoms was found to be larger than the isotropic shfi constant for the C atoms, which contradicts with the experimental data.

The interference effects due to the $(S_p)^2$ factor in Eq. (6) causes that the wave function of the N donors does not decrease monotonically with increasing distance r_l from the donor site. Moreover, the obtained different values of $(S_p)^2$ for atoms located in the same shell give rise to different values of the shfi indicating that the distribution of the electron spin density over the atoms in one shell around the N donor is not equal.

From the analysis of the ENDOR data presented in Table 1 it follows that the isotropic and anisotropic

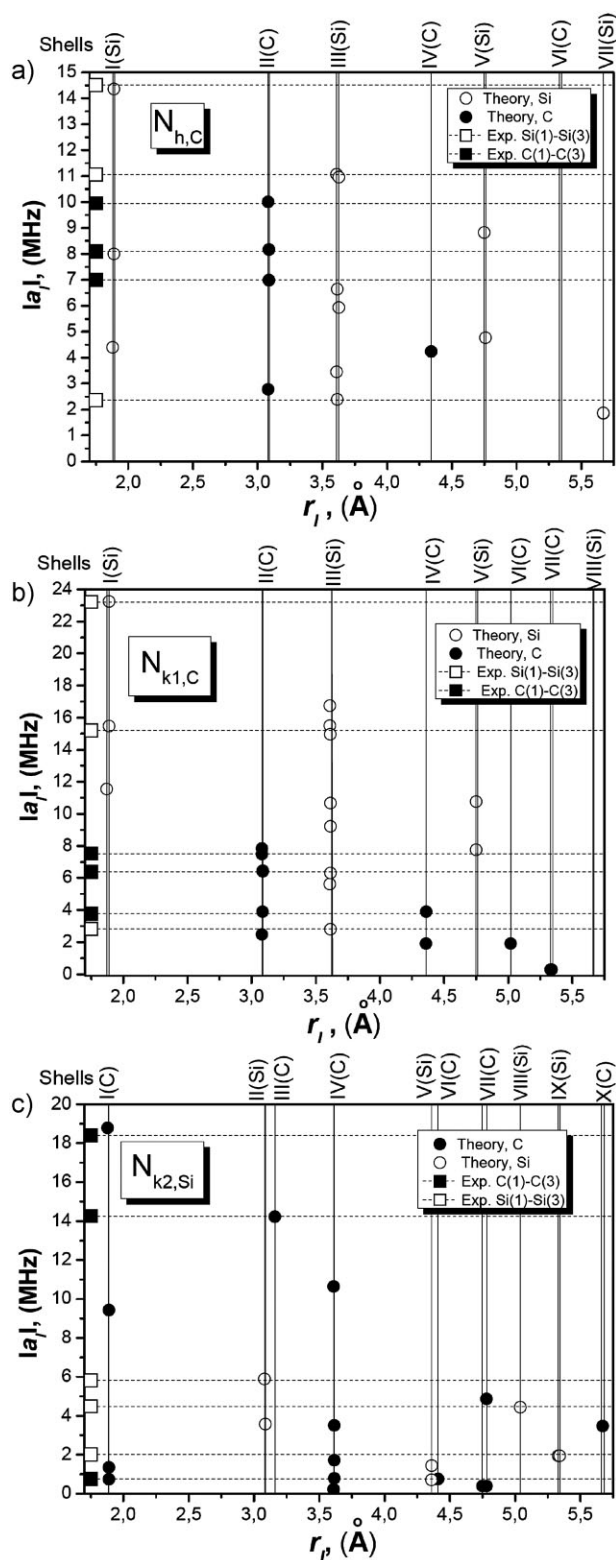


Figure 7 Calculated and experimental isotropic shfi constants $|a_I|$ as a function of the distance r_I of Si and C atoms from the central nitrogen atom of the $N_{h,C}$ (a), $N_{k1,C}$ (b), and $N_{k2,Si}$ (c) donors. Circles correspond to the theoretical values of $|a_I|$ obtained from Eq. (7); squares and dashed lines represent the experimental data. I–X are the Si and C shells.

shfi constants, a_I and b_I , have opposite signs for a number of ^{29}Si nuclei. Different signs of the isotropic and anisotropic shfi constants for ^{29}Si and ^{13}C were also previously observed in 6H SiC doped with shallow boron acceptors and explained by the rehybridization of Si and C sp -orbitals due to unpaired spin density at the boron indicating that the simple point dipole–dipole approximation is not applicable for the description of the shfi behavior of shallow impurities in SiC polytypes [27] and it is necessary to integrate the matrix elements of the dipole–dipole operator on the wave functions in Eq. (3).

In the case of shallow donors, the ^{29}Si and ^{13}C shfi constants are strongly affected by the interference factor $(S_p)^2$, which can be equal to zero at some points of \mathbf{r} . The dipole–dipole interaction is proportional to $1/|\mathbf{r}_I - \mathbf{r}|^3$ and $1/|\mathbf{r}_I - \mathbf{r}|^5$ and has a δ -function like dependence on the vector \mathbf{r} . Nevertheless, due to the specific properties of the interference factor $(S_p)^2(x, y)$ the properties of the dipole–dipole interaction cannot be modeled by a δ -function. The sharp dependence of the dipole–dipole interaction on coordinates does not allow us to replace the function $|u_k(\mathbf{r})|$ by its average value at the r_I points. Therefore, *ab initio* approaches are requested for the analysis of such detailed properties of the shfi parameters of the shallow donors, where rehybridization and spin polarization effects are hidden in real values of the product $|u_k(\mathbf{r})|^2 (S_p)^2 / |\mathbf{r}_I - \mathbf{r}|^5$. This conclusion is supported by *ab initio* calculations of the hf and shf interactions for group-V donors in Si which has been recently performed within Green's functions approach [28] and can be successfully applied for the description of the shfi constants of shallow N donors in SiC.

Having obtained the distribution of the electronic wave function over the Si and C shells located around the N donors, we are able to evaluate the position of the conduction-band minima in 6H SiC. The task is the same as that of finding the ratio k_0/k_{\max} in case of the conduction-band minima of Si crystals [24]. The Raman scattering results place the conduction-band minima of 6H SiC in Brillouin zone on the ML symmetry line, leaving the parameter k_z undetermined [29].

Since the position of the conduction band minima depends on the interference effects this parameter can be evaluated by plotting the dependence of the theoretically obtained shfi constants $|a_I|$ of N donors on k_z using Eq. (7):

$$|a_I|(k_z) = |a_I|(k_z = 0) \cos^2(2\pi\kappa_z z_I), \quad (9)$$

where $\kappa_z = k_{0z}/k_{\max}$ changes from 0 to 0.5.

The shfi constants $|a_I|$ as a function of k_{0z}/k_{\max} as calculated from Eq. (9) for N donors substituting different lattice sites in 6H SiC are presented in Fig. 8 along with the experimental data.

The best agreement between the $|a_I|$ constants, obtained from Eq. (9), and the experimental ones corresponds to the shaded area with $k_{0z}/k_{\max} = 0.2 \pm 0.05$ in Fig. 8. As a result, the conduction band minimum lies near the M-point: $(0.5k_{x,\max}; 0.5k_{y,\max}; 0.2k_{z,\max})$ with $k_{x,\max} = k_{y,\max} = 2/a$ and

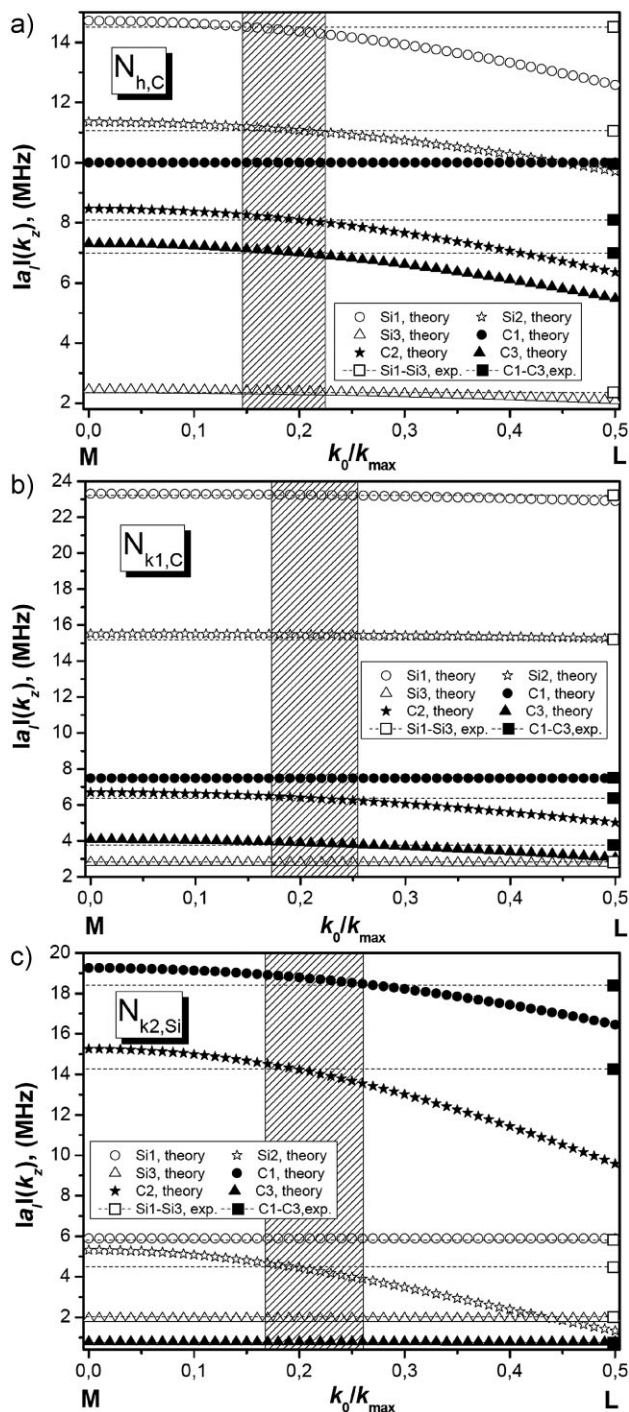


Figure 8 Shfi constants $|a_l|$ as function of the position of the conduction band minimum k_0/k_{\max} calculated from Eq. (9) for Si and C atoms located in the three nearest shells of the $N_{h,C}$ (a), $N_{k1,C}$ (b), and $N_{k2,Si}$ (c) donors in 6H SiC. The shaded area indicates the position of k_0/k_{\max} obtained from a comparison of the experimental data (squares and dashed lines) with theory (asterisks, triangles, and circles).

$k_{z,\max} = 2/c$ and in its equivalent points can be obtained by rotation about $n \times 60^\circ$ with $n = 1 \dots 5$.

3.3 Shallow and deep donor state of nitrogen substituting C and Si sites in 6H SiC An inspection of the measured ^{29}Si and ^{13}C shfi parameters of the N donors summarized in Table 1 indicates that the largest shfi constants were obtained for the ^{29}Si nuclei located in the first shell of N_h and N_{k1} , while for N_{k2} the largest shfi constants were obtained for the ^{13}C nuclei located in the first shell of N_{k2} . It should be noted that the shfi values a_l for the Si and C atoms located in the first shell of the N donors are not noticeably influenced by interference effects to make them smaller than those obtained for the Si and C atoms located in the next shells. Therefore, we can conclude that N_{k1} and N_{k2} substitute different atom sites: N_{k1} and N_h unambiguously occupy a C site in the 6H SiC lattice and the Si atoms are located in the nearest-neighbor positions of N_{k1} and N_h . At the same time, the largest value of the shfi constants with ^{13}C nuclei obtained for N_{k2} indicates that the N donor at the “k2” lattice site occupies a Si site in the 6H SiC lattice and the C1 atom locates in the nearest-neighbor positions of N_{k2} . The fact that a satisfactory agreement between the theoretical and experimental data was obtained assuming that N at “k2” position occupies a Si site, while no agreement was obtained for the case of N substituting C site, supports this conclusion.

From the infrared (IR) absorption and Hall measurements [30, 31] it is well known that N in 6H SiC produces three donor levels in the band gap with values 81, 137.6, and 142.4 meV. The donor energy levels derived from the IR absorption spectra and Hall measurements were assigned to the ^{14}N EPR spectra by employing photo-EPR experiments and samples with different degree of compensation [32]. It was found that the three distinct nitrogen EPR spectra of the N_h , N_{k1} , and N_{k2} donors were observed in samples with a low degree of compensation while only two EPR spectra from N_{k1} and N_{k2} centers were detected in the samples with a high degree of compensation. This clearly indicates that the EPR spectrum due to N_h corresponds to the most shallow donor energy level while the two others (N_{k1} , N_{k2}) are responsible for the two deeper energy levels at 137.6 and 142.4 meV.

The distribution of the occupied paramagnetic N donor state among the “k1” and “k2” positions was explored by optical recharging experiments of the N centers with interband light for compensated 6H SiC samples. It could be verified that the EPR spectrum due to N_{k1} with the larger value of the ^{14}N hfi constant corresponds to the donor energy level at 137.6 meV while the EPR spectrum due to N_{k2} with the smaller ^{14}N hfi constant corresponds to the donor energy level at 142.4 meV [32]. The results of the assignment of the ^{14}N EPR spectra to the donor energy levels are given in Table 2. Hence N_{k2} center corresponds to the deeper energy level in the band gap.

The first principle local-density functional calculations [33] for the N atom on C and Si sites indicates that due to the

Table 2 The spin-Hamiltonian parameters for N donors in 6H SiC obtained from FS ESE and ENDOR experiments [15] along with their energy characteristics [29, 30].

parameters	N_h	N_{k1}	N_{k2}
$g_{ }$	2.0048	2.0040	2.0037
g_{\perp}	2.0028	2.0026	2.0030
a_I/h , MHz	2.468	33.564	33.221
b_I/h , MHz	0.137	0.009	0.004
e^2qQ/h , MHz	0.017	0.007	0.007
energy level, meV	81.04	137.6	142.4
valley-orbit splitting, meV	12.6	60.3	62.6

different charge density distributions around the N atom on C and Si site the N_C center acts as a shallow donor while the N_{Si} center due to the strong localization of the wave function does not constitute a shallow donor state. This conclusion is consistent with the distribution of the electronic wave function around N donor found for N_{k1} and N_{k2} from ENDOR measurements. As can be seen from Table 1, the shfi constants for N_{k1} with ^{29}Si and ^{13}C nuclei have larger values than those found for N_{k2} indicating that for N_{k1} the spin density of the wave function on the nearest C and Si shells is higher and spreads over the whole 6H SiC unit cell. The wave function of the N_{k2} center is mostly localized around the N atom on the two nearest C and Si shells but with a smaller spin density (see Table 1). This means that N_{k2} center substituting silicon atoms act as deep donor center. In this case, two types of the donor energy level schemes in the band gap can be assumed for N donors substituting C and Si sites corresponding to the inequivalent positions formed by N dopants in the 6H SiC lattice. In the framework of the existence of the two types of the donor energy level schemes the N_h and N_{k1} center can be attributed to the shallow donors while N_{k2} center can be tentatively attributed to the one of the deep N donor state formed by N substituting Si sites. To get other energy levels in paramagnetic state and confirm the tentative assignment of the N_{k2} center with deep N donor state substituting Si site the further investigations of the 6H SiC samples with different degree of compensation and C/Si ratio is required.

4 Conclusions A significantly new conception about the donor states of N in 6H SiC polytype has been presented in the paper. Based on the analysis of the ligand hyperfine structure for N donors obtained from pulsed ENDOR and pulsed General TRIPLE ENDOR spectroscopy it was shown for the first time that N substitutes both, C and Si sites, in the 6H SiC lattice in contrast to the so far accepted opinion that N can only substitute at C sites.

Benefiting from the advantage of the TRIPLE ENDOR spectroscopy the shf lines observed in the EPR and ENDOR spectra of n-type 6H SiC were assigned to the specific C and Si atoms located around N donors residing at quasi-cubic lattice sites in 6H SiC. As a result, the shfi parameters for Si and C atoms, which are located in the nearest environment of

the N donors, have been obtained. It was found that the shfi parameters for Si and C atoms, which are located in the nearest environment of the N donors are almost isotropic with only very small anisotropic shfi parameters.

The theoretical analysis of the ligand shf structure of the N donors has been performed taking into account the Kohn–Luttinger interference effect. It was found that due to the interference effect the shfi values a_I for the ^{29}Si and ^{13}C atoms and hence the wave function of the N donors does not decrease monotonically with increasing distance from the N donors. But at the same time the largest values of the isotropic shfi a_I for the Si and C atoms located in the first shell of the N donors are not noticeably influenced by the interference effect to make them smaller than those obtained for the Si and C atoms located in the next shells. As a result, for N_{k1} and N_h the largest value of the shf coupling was found for ^{29}Si nuclei, while for N_{k2} the largest value of the shf coupling was obtained for ^{13}C nuclei. This gives us a strong argument to conclude that in 6H SiC nitrogen substitutes different type of sites. The N donors at “k1” and “h” positions reside at C sites, while N donors at “k2” position incorporate at Si sites.

This conclusion is also supported by the difference in the values of the shf constants obtained for N_{k1} and N_{k2} with the ^{13}C nuclei. As can be seen from Table 1 the ^{13}C shfi constants obtained for N_{k1} are ranging between 7.519 and 3.945 MHz while ^{13}C shfi constants obtained for N_{k2} are 18.366 and 14.25 MHz. Such large values of the ^{13}C shfi constants as obtained for N_{k2} in comparison with those of N_{k1} cannot be explained if we suppose that C atoms are located in the next neighbor shell of N_{k2} . Moreover, in this case the shfi constant for N_{k2} with ^{29}Si nuclei should be significantly larger than that obtained for ^{13}C nuclei, which is not a realistic scenario.

From pulsed general TRIPLE ENDOR spectra of N donors it was found that the isotropic and anisotropic shf coupling constants a_I and b_I with ^{29}Si nuclei have different signs. Since the shfi constants of N donors are strongly affected by the interference factor it was concluded that the simple point dipole–dipole approximation is not applicable for the analysis of the a_I and b_I signs and *ab initio* approaches are requested where rehybridization and spin polarization effects can be accounted for to explain the behavior of the shfi constants.

From the dependence of the isotropic shf coupling constants on k_{0z}/k_{max} the position of the conduction-band minima in 6H SiC locating in the ML direction was found to be at a distance of about $k_{0z}/k_{\text{max}} = 0.2 \pm 0.05$ from the M-point. The obtained position of the conduction band minimum compares reasonably well with the theoretically predicted position [34] at about 63% from L to M.

Thus, in spite of the established opinion available in the literature that N substitutional is most stable at C site and N_C configuration is energetically more favorable, we reserve the right to conclude that N_{k2} center can be tentatively attributed to the one of the deep donor states formed by N substituting Si sites.

Taking into account that the N doping concentration is very sensitive to Si and C content it was expected that the incorporation of N on Si sites over the three inequivalent positions can be achieved by properly varying of the C/Si ratio during crystal growth [35, 36].

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