Silicon carbide (SiC) has a variety of hexagonal polytypes, including 4H, 6H, and 15R, which are distinguished by their crystallographic structure and electronic properties. The 4H polytype, in particular, is of interest due to its high-temperature stability and wide bandgap, making it suitable for high-temperature electronics and optoelectronics.

The E15 and E16 centers are two types of carbon vacancies in 4H-SiC, which have been the subject of extensive study. These centers are important for understanding the electronic and magnetic properties of SiC, as well as for applications in semiconductor devices.

The E15 center is associated with a positively charged carbon vacancy, while the E16 center is associated with a positively charged silicon antisite (Si). Both centers have been studied experimentally using electron paramagnetic resonance (EPR) and hyperfine spectroscopy.

The EPR spectra of the E15 and E16 centers exhibit a wide variety of spectral features, which are sensitive to the local structural and electronic environment. The EPR spectra are typically obtained using microwave and radiofrequency (rf) pulses, and the hyperfine (HF) splitting is induced by the interaction of the electron spin with the nuclear spins of the surrounding atoms.

The HF satellites observed in the EPR spectra are a result of the interaction between the electron spin and the nuclear spins of the surrounding atoms. The HF splitting is determined by the natural abundance of the isotope, the distance between the electron and nuclear spins, and the orientation of the magnetic field.

Recent studies have used pulsed electron-nuclear double-resonance (ENDOR) spectroscopy to investigate the hf properties of the E15 and E16 centers in 4H-SiC. ENDOR is a technique that uses microwave and rf pulses to excite the nuclear spins and observe the resulting nuclear transitions.

The ENDOR spectra of the E15 and E16 centers are characterized by a unique pattern of hf splittings, which are sensitive to the local atomic environment. The hf properties of the E15 and E16 centers have been used to assign the hf satellites to specific nuclear spins, which are associated with the surrounding atoms.

The ENDOR spectra of the E15 and E16 centers in 4H-SiC have been measured using a Bruker E500 spectrometer equipped with a 3.5-mm electron beam and a 1.5-mm substrate. The hf properties of the E15 and E16 centers have been compared to theoretical predictions, and the results have been used to assign the hf satellites to specific nuclear spins.

The ENDOR spectra of the E15 and E16 centers in 4H-SiC have been used to determine the hf properties of the surrounding atoms, which are sensitive to the local structural and electronic environment. The hf properties of the E15 and E16 centers have been used to assign the hf satellites to specific nuclear spins, which are associated with the surrounding atoms.

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HF splittings for $\text{B}[0001]$, their four values for ID1/EI5 (labeled ID1-1–4) were close to the HF splittings for EI5 ($b$, $c$, $f$, and $g$). Also, the four values labeled ID2-1–4 for ID2/EI6 corresponded to those for EI6 ($a$, $d$, $e$, and $g$), respectively.

Comparing the HF structures of EI5 and EI6, it is immediately clear that satellites $a$ and $d$ for EI6 have the same angular patterns as those of $b$ and $c$ for EI5. Their intensity ratios are also the same, i.e., $b:c = 1:3$ for EI5 and $a:d = 1:3$ for EI6, as is estimated in Fig. 1(a). The angular dependence of $c$ and $d$ clearly revealed that these satellites consist of three HF structures with intensity ratios of 1:1:1. Furthermore, the symmetry of $a$ and $b$ coincided with that of the Si dangling bond (DB) on the Si$_1$ atom (axially symmetrical around the $c$ axis, see Fig. 2), and the three HF structures in $d$ and $c$ were also axially symmetrical around the Si DBs on three Si atoms, i.e., Si$_1$, Si$_3$, and Si$_4$. Summarizing this, both EI5 and EI6 centers revealed four $^{29}\text{Si}$ HF structures that corresponded to four Si atoms surrounding a carbon vacancy. Therefore, it is quite reasonable to identify the EI6 center as a carbon vacancy ($V_{\text{C}}^-$), similar to the EI5 center, rather than a silicon antisite ($\text{Si}^{-}\text{C}^-$). In the original Si$_c^-$ model, only the EPR spectrum for $\text{B}[1\bar{1}00]$ was measured and then satellite $d$ was assigned to a combination of two HF structures from the Si$_1$ and Si$_2$ atoms in Si$_c^+$. However, this assignment does not fit our complete angular data.

The EI6 center has another HF satellite $e$. We carried out pulsed-ENDOR measurements (10 K) on this satellite by fixing a magnetic field at its position and scanning the frequency of the rf pulse. The inset in Fig. 3 shows a typical ENDOR spectrum, where three $^{28}\text{Si}$ HF splittings can clearly be observed. The relative intensity of this satellite in the cw-EPR spectrum [Fig. 1(a)] also indicates the contribution of three Si atoms. Although the angular dependence of this satellite indicates an axial symmetry around the $c$ axis [Fig. 1(b)], looking through the higher resolution ENDOR (Fig. 3) reveals that the symmetry axis is slightly tilted from the $c$ axis. Judging from this symmetry and the number of Si atoms, satellite $e$ should originate from the Si$_3$, Si$_6$, and Si$_7$ atoms in a carbon vacancy (Fig. 2).

We determined spin-Hamiltonian parameters, $g$ and $A$ (HF) tensors, for the Si$_1$ to Si$_7$ atoms by simulating the angular dependence of corresponding HF satellites. All the $g$ and $A$ tensors were well described by axially symmetrical tensors. The solid lines in Fig. 1(b) show an excellent agreement between the experiment and simulation. The spin-Hamiltonian parameters are summarized in Table I. We also confirmed that these parameters could perfectly reproduce the angular-dependence data with respect to different rotation planes ($\text{B}$ was rotated from [0001] to $[\bar{1} 1 00]$). For EI5, the parameters remained almost unchanged with decreasing the temperature. For EI6, however, they were obviously temperature dependent above 10 K. The table also shows theoretical $A$ tensors recently calculated by Bockstedte et al. Similar theoretical results were also independently reported by Gali et al. Comparing these theoretical values with our experimental parameters, the EI5 center is in good agreement with $V_{\text{C}}^-$ at the $k$ site, and the EI6 center fits well with that at the $h$ site. Therefore, we concluded that the origins of EI5 and EI6 are both $V_{\text{C}}^-$ and their respective locations should be $k$ and $h$ sites. It should also be noted that the theoretical calculation predicted much smaller $A$ principal values for Si$_c^+$ and these were inconsistent with our experimental parameters.

The conclusion that both EI5 and EI6 centers are the same
A is the Bohr magneton, \( I \) the wave function, and EPR parameters reported by Son et al. 4

...dominant and observed in high-purity semi-insulating...2.0026 2.0052 15.48 10.61 2.11 1.39 97.7° 0.87 0.69 0.2

...was also reported by the other group.12 In fact, they were...2.00279 2.00489 14.26 9.77 2.58 1.72 101.0° 0.82 0.64 0.2

...trum resolved by pulsed ENDOR at 10 K, and a typical ENDOR spec-

...revealed that EPR intensities...1000 °C), 7 our isochronal-annealing study...2.0032 2.0046 12.29 8.45 3.21 2.20 103.6° 0.72 0.57

...have a tetrahedral structure. Using a LCAO (linear combination of atomic orbitals) approximation,...2.00322 2.00484 6.46 4.46 5.02 3.75 95° 0.72 0.57

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...for the Fermi-level pining in such semi-insulating materials.

The A tensors we determined revealed the atomic structures of two types of \( V_C^+ \), which we found to be greatly different. For EI5, the direction \( \theta_i \) of the Si2–4 DBs determined from the \( A(\text{Si}_{2,4}) \) tensor was 109.2° (Fig. 2 and Table I), which is just the tetrahedral angle (109.28°). Thus, the EI5 center appears to have a tetrahedral structure. Using a LCAO (linear combination of atomic orbitals) approximation, we could estimate the wave function for this defect in terms of the 3s- and 3p-orbital densities, \( \eta^2 \alpha^2 \) and \( \eta^2 \beta^2 \), on each Si\(_i\) atom, where \( \eta^2 \alpha^2 = A_{iso}(\text{mT})/163.93, \eta^2 \beta^2 = A_{aniso}(\text{mT})/4.08, A_{iso} = [A_{x}(\text{Si}_{1}) + 2A_{y}(\text{Si}_{1})]/3, \) and \( \alpha^2 + \beta^2 = 1.6,7,13 \) For EI5, the unpaired electron distributes nearly equally on Si1–4 atoms (see Fig. 2). For EI6, on the other hand, the direction \( \theta_i \) of the Si2–4 atoms decreased towards 90°, indicating a planar structure, and thus a nonbonding character was expected between Si1 and Si2–4 atoms. As a result, the unpaired-electron density is localized on the Si1 atom by 40% (Fig. 2). However, the sums of unpaired-electron distributions on Si1–4 atoms were kept to the same value (∼66%) for EI5 and EI6.

The structural distortion for EI6 became maximum when the temperature decreased to 10 K, as can be seen from angle \( \theta_i \) (Table I). The 10-K ENDOR data of Fig. 3 reveal distortion at Si5–7 atoms in this situation. By simulating the experimental angular pattern (solid lines in figure), the symmetry axis of the \( A(\text{Si}_{5–7}) \) tensor was found to have tilted outward by 15.5° from the c axis. This again indicates that the EI6 center (h site \( V_C^+ \)) deforms considerably towards a planar structure. With this deformation, the unpaired electron

![FIG. 3. (Color online) \(^{29}\text{Si} \) HF splitting of satellite \( \epsilon \) for EI6 resolved by pulsed ENDOR at 10 K, and a typical ENDOR spectrum (inset).](image)

TABLE I. Spin-Hamiltonian parameters of EI5 and EI6 centers. The spin Hamiltonian \( H \) is given by \( H = \mu_B \mathbf{B} \cdot \mathbf{g} \cdot \mathbf{S} + \sum \mathbf{S} \cdot \mathbf{A} \cdot \mathbf{I} \), where \( \mu_B \) is the Bohr magneton, \( \mathbf{g} \) is a \( g \) tensor (principal values are \( g_i \) and \( g_j \)). \( \mathbf{S} \) is an electron spin operator, \( \mathbf{A} \) is a HF tensor for each atom in the wave function, and \( \mathbf{I} \) is a nuclear spin operator corresponding to each \( A \) tensor. Principal values of \( A \) are expressed in mT using a conversion factor that 1 mT = 28.02 MHz. \( \theta_i \) is the angle between the \( A_i \) principal axis and the c axis (see also Fig. 2). The table also contains previous EPR parameters reported by Son et al. (Refs. 6 and 7). The \( A(\text{Si}_{2,3,4}) \) tensor in Ref. 6 was not axial symmetrical and showed a different \( \theta_i \) value (95°); however, this result was obtained using an extra fitting parameter of a misalignment angle. Since we did not use such a parameter and did check the fitting in two different orientation data, our \( A(\text{Si}_{2,3,4}) \) tensor will be more reliable. In the bottom, theoretical \( A \) tensors obtained by the \textit{ab initio} calculation (Ref. 4) are shown.

<table>
<thead>
<tr>
<th></th>
<th>EI5 ((S = \frac{1}{2}, C_{3v}))</th>
<th>EI6 ((S = \frac{1}{2}, C_{3v}))</th>
<th>Theory (Ref. 4)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( g_i )</td>
<td>2.00322 2.00484 6.49 4.47</td>
<td>2.00032 2.0046 12.29 8.45</td>
<td>7.04 4.36 4.07</td>
</tr>
<tr>
<td>( g_{\perp} )</td>
<td>2.0046 4.47</td>
<td>2.00472 13.06 8.97</td>
<td>4.36 4.07 5.54</td>
</tr>
<tr>
<td>( A_{i} )</td>
<td>5.18 3.63 109.2° 0.40 0.29</td>
<td>2.97 2.01 102.6° 0.75 0.59</td>
<td>3.32 3.11 5.75</td>
</tr>
<tr>
<td>( A_{\perp} )</td>
<td>5.02 3.75 95° 0.29</td>
<td>2.58 1.72 101.0° 0.82 0.64</td>
<td>1.39 0.87</td>
</tr>
<tr>
<td>( A_{\parallel} )</td>
<td>2.20 103.6° 0.72 0.57</td>
<td>1.23 1.97 104.4° 0.82 0.64</td>
<td>3.89 3.68</td>
</tr>
<tr>
<td>( A_{\perp} )</td>
<td>2.01 102.6° 0.75 0.59</td>
<td>2.01 1.72 101.0° 0.82 0.64</td>
<td>0.79 0.71 1.54</td>
</tr>
<tr>
<td>( A_{\parallel} )</td>
<td>1.39 0.87</td>
<td>1.39 0.87</td>
<td>1.54 0.79</td>
</tr>
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</tr>
</tbody>
</table>

V\(_C^+\) can capture an electron of the donor, carbon vacancies may play an important role for the Fermi-level pining in such semi-insulating materials.
for EI6 became more localized on the Si1 atom (47%); however, the total $\eta^2$ on the Si1–4 atoms was found to be almost unchanged (68%).

Despite being the same type of defect, the EI5 center had invariant $g$ and $A$ values, while those for EI6 were considerably temperature dependent, as plotted in Fig. 4. We think this difference is closely related to the symmetry of the distortions. The theoretical calculation for the $k$ site predicted that the pseudo Jahn-Teller effect generates a pair of Si1 and Si2–4 atoms (a Si1–Si4 pair is also formed).4 Although this distorted configuration indicated a $C_{1h}$ symmetry,4 there are three equivalent configurations ($Si_{1'}-Si_{2'}$, $Si_{1'}-Si_{3'}$, and $Si_{1'}-Si_{4'}$ pairs), because the Si2–4 atoms are $C_{3v}$ symmetry related. Thus, thermally activated reorientation between the three configurations possibly occurs, which enabled us to observe their average state with a $C_{3v}$ state.

We speculated that due to the pairing of Si1 and Si2–4 atoms, the average state of EI5 is always confined and approaches a tetrahedral structure at relevant temperatures ($\approx 50$ K), resulting in unchanging $g$ and HF parameters. However, the $h$-site $V_C^{+}$ had only one orientation for distortion (planar distortion along $c$ axis) retaining $C_{3v}$ symmetry, and hence no reorientation effect could take place. Furthermore, this type of distortion enabled the Si1 atom to move a great deal because of the nonbonding character of Si1 and Si2–4 atoms. This made it possible to observe structural change in EI6 with decreasing temperature. The theoretical calculation for EI6 also predicted the presence of a $C_{1h}$-distorted structure, in addition to the $C_{3v}$ state. However, we did not observe such a state even at 4 K, and therefore the $C_{3v}$-distorted state shown here will be energetically preferable.

The presence of reorientation in the symmetry-related configurations in EI5 and the absence of such dynamic effects in EI6 could also be inferred from the much faster spin relaxation in the former rather than the latter center. From three-pulse inversion recovery measurements of pulsed EPR,10 we found that the spin-lattice relaxation time ($T_1$) was three times shorter for EI5 ($4.8 \times 10^{-6}$ sec) than for EI6 ($13.0 \times 10^{-6}$ sec) at 80 K. This can be also confirmed by conventional EPR where the EI6 signal was much more easily saturated to microwave power, compared to the EI5 signal. Also, a similar motional effect was detected in the Ky1 and Ky2 centers in 6H-SiC which were assigned to $V_C^{+}$ at the $k_1$ and $k_2$ sites (two inequivalent quasicubic sites).9

In summary, we found a complete set of $^{29}$Si HF parameters for EI5 and EI6 centers through EPR and pulsed ENDOR techniques. Although they were originally assigned to $V_C^{+}$ (for EI5) and $Si_C^{+}$ (for EI6), our complete data demonstrated that both EI5 and EI6 were $V_C^{+}$ centers but their locations should have been $k$ and $h$ sites, as recently suggested by the theoretical calculations.4,5 This conclusion was also supported by facts obtained by experiments, such as similar $g$ values, their coexistence, and the same thermal stability. Despite being the same kind of defect, the two types of $V_C^{+}$ were found to be quite different in structural distortion and temperature dependence, which could reasonably be explained by the symmetry of distortions at $k$ and $h$ sites.