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Spatial and Hyperfine Characteristics of SiV^- and SiV^0 Color Centers in Diamond: DFT Simulation

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Abstract—One of the most promising platforms to implement quantum technologies are coupled electron-nuclear spins in diamond in which the electrons of paramagnetic color centers play a role of "fast" qubits, while nuclear spins of nearby ^{13}C atoms can store quantum information for a very long time due to their exceptionally high isolation from the environment. Essential prerequisite for a high-fidelity spin manipulation in these systems with tailored control pulse sequences is a complete knowledge of hyperfine interactions. Development of this understanding for the negatively charged "silicon-vacancy" (SiV^-) and neutral (SiV^0) color center, is a primary goal of this article, where we are presenting shortly our recent results of computer simulation of spatial and hyperfine characteristics of these SiV centers in H-terminated cluster $C_{128}[SiV]H_{98}$ along with their comparison with available experimental data.

Keywords: silicon-vacancy (SiV) color center, diamond, ^{13}C nuclear spin, hyperfine interaction, density functional theory

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INTRODUCTION

Single negatively charged and neutral silicon-vacancy (SiV^- and SiV^0) color centers in diamond exhibiting narrow zero-phonon lines at ~738 and ~947 nm with high Debye–Waller factor (~0.7) and having doublet ($S = 1/2$) and triplet ($S = 1$) ground electronic states are currently of great interest because they allow for effective optical interfacing their spin state to photons (see, e.g. [1]). By analogy with the well-known nitrogen-vacancy (NV) color center the nuclear spins ^{29}Si belonging to the SiV centers as well as nearby ^{13}C nuclear spins in a hosting diamond lattice can be used in numerous applications as additional resource for quantum memory. Recent experiments [2–4] done at low temperatures (~4 K) demonstrated simultaneous microwave control and optical readout of the SiV^- center spin, a key prerequisite for further quantum information processing tasks. However, at these temperatures the SiV^- center exhibits very short spin coherence time of 38 ns [2]. Therefore, further progress with SiV^- centers was expected at temperatures reduced to millikelvins [5], which will provide a significant (up to 10 ms) increase in the

coherence time of the electron spin of single SiV^- centers. Very recently the quantum register [6, 7] and quantum repeater [8] were demonstrated for a first time using *hfi*-coupled electron-nuclear spin systems SiV^-–^{13}C at millikelvins temperatures. In turn, the neutral color SiV^0 center [9] has much longer spin coherence time [10] at liquid-helium temperatures but can be optically bright and stable only in special boron-doped diamond samples. The SiV^0 center is associated with the KUL1 electron paramagnetic resonance center [9, 11] with zero-field splitting D = 942 MHz. Very recently optically detected magnetic resonance (ODMR) at $^{29}SiV^0$ ensemble was experimentally implemented [12] opening the way to use this spin system for interfacing to photons. Hyperfine interaction data for the center are known only for ^{29}Si and ^{13}C atoms being nearest to Si [13]. Essential point for high-fidelity spin manipulation in the above systems with tailored control pulse sequences is a complete knowledge of hyperfine interactions (*hfi*) in them. It is the aim of this report to present shortly our recent results concerning simulation of *hfi* characteristics for different hybrid electron-nuclear spin systems SiV-^{13}C in diamond and their comparison with available experimental data [4].

METHODS AND BASIC RESULTS

Here we are presenting the analysis of hyperfine interactions (*hfi*) of the SiV^0 and SiV^- centers with the ^{13}C nuclear spins differently located in the diamond lattice with respect to the electronic spins of these centers. The center properties were studied by simulating (using ORCA software package) the H-terminated carbon cluster $C_{128}[SiV]H_{98}$ hosting the SiV center in their central parts. Calculations were performed for neutral and negatively charged clusters having the triplet and doublet ground states, respectively. The structures were optimized carefully using DFT theory of DFT/UKS/PW91/RI/def2-SVP level. Then, using different levels of the theory (UKS/PW91/RI/def2-SVP, UKS/B3LYP/G/3-21G, ROKS/PW91/RI/def2-SVP), we found the total spin density distribution over the clusters and calculated the matrices A_{KL} (K, $L = X$, Y, Z) describing *hfi* of the electronic spin of the SiV centers with the nuclear spins $I = 1/2$ of ^{13}C atoms located in all possible positions within the clusters as well as for the nuclear spin $I = 1/2$ of isotopic ^{29}Si nucleus of the center.

For the neutral cluster (i.e. the cluster containing the SiV^0 center) relaxed geometry exhibited usual D_{3d} symmetry, where the Si atom located in the interstitial position between two lattice vacancies is the center of inversion. There are six equivalent nearest-neighbor (NN) carbon atoms at near-equal distances of ~2.025 Å from Si atom. Spin density was localized near-equally at these 6 carbon atoms (see Fig. 1a). *Hfi* matrices A_{KL}, calculated in the coordinate system with the Z axis directed along the (111) crystallographic direction of the diamond lattice, were nearly coinciding for couples of ^{13}C nuclear spins inversion-symmetrically located with respect to the Si atom. In turn, the matrices A_{KL} calculated for the three such equivalent pairs of NN ^{13}C were interconnected by 120° rotation matrices about the Z axis. We found [14] at UKS/B3LYP/G/3-21G theory level the values $A_\parallel \approx$ 77.5 MHz and $A_\perp \approx$ 44.5 MHz for these six C atoms (experimental values are $A_\parallel \approx$ 66.2 MHz and $A_\perp \approx$ 30.2 MHz [13]). For the ^{29}Si nucleus we got $A_\parallel \approx A_\perp =$ 81 MHz (experimental values are 76.3 and 78.9 MHz, respectively [13]). We also calculated the *hfi* matrices A_{KL} for all other possible systems SiV^0–^{13}C in the cluster $C_{128}[SiV^0]H_{98}$.

For the negatively charged clusters (SiV^- centers) inversion symmetry with respect to the Si atom also took place but nearest six C neighbors were no longer equivalent with two of them (shown in red in Fig. 1b) being located at ~0.03 Å further from Si atom then the other four (shown in blue in Fig. 1b), for which the C–Si distance was ~2.00 Å. Resulting C_{2h} symmetry group of the cluster (consisting four elements: e, $C_2^{(Z)}$, $\sigma_h^{(XY)}$, i) was different from usually considered D_{3d} symmetry which took into account the dynamical Jahn–Teller effect being essential for the center even at liquid-helium temperatures (~4 K) but which can reduce to the static Jahn–Teller effect at millikelvin temperatures. The $\sigma_h^{(XY)}$ symmetry plane was passing through the two more distant C nearest-neighbors of silicon and through the (111) diamond crystallographic direction and the $C_2^{(Z)}$ symmetry axis was perpendicular to the $\sigma_h^{(XY)}$ plane (see Fig. 1b). Spin density in this case was localized basically on the two more distant nearest C atoms resulting in $A_\parallel$ = 175 MHz and $A_\perp$ = 105 MHz, while for the other two NN ^{13}C pairs, located a little closer to the Si atom the spin density was essentially lower and respective *hfi* data were $A_\parallel =$ 37 MHz, $A_\perp$ = 21 MHz. For the ^{29}Si nucleus we got $A_\parallel \approx$ 66 MHz and $A_\perp \approx$ 78 MHz.

We also got the full *hfi* matrices for all other possible coupled SiV^-–^{13}C spin systems in the $C_{128}[SiV^-]H_{98}$ cluster. Using them we were able to identify the position of the ^{13}C nuclear spin experimentally studied in the article [4]. Experiment was done at 2 K on single SiV^- center coupled with nuclear spin ^{13}C for which the component A_{ZZ} = 720 kHz of *hfi* was measured. There was external magnetic field B = 1887 gauss directed at a small (uncontrolled) angle to the crystallographic axis (111). A diagram of the levels of the center, taking into account various interactions and experimentally found splitting of the corresponding levels, is shown in Fig. 2a.

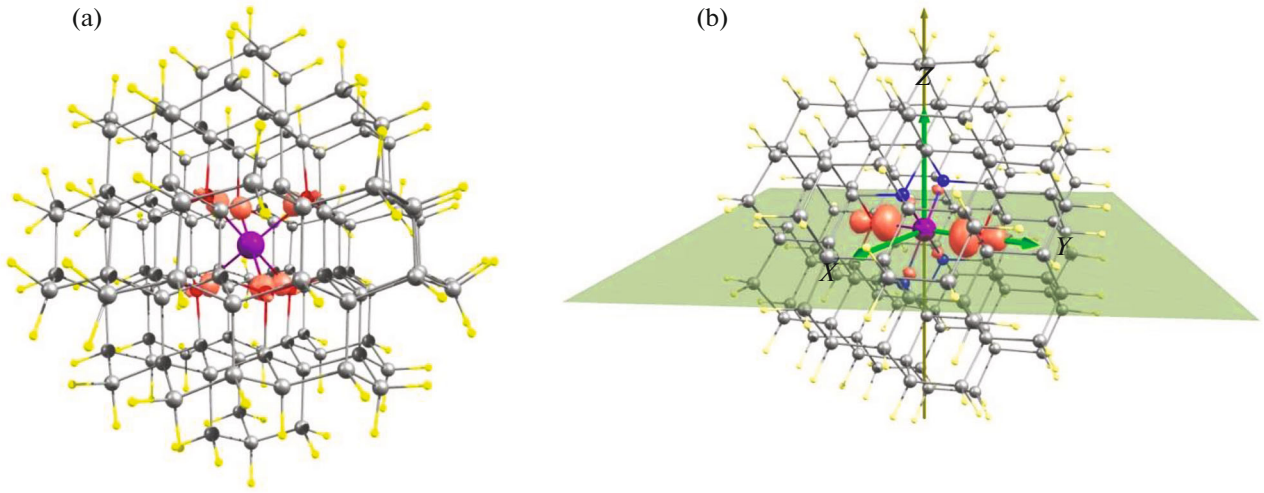

Fig. 1. Illustrations of the simulated clusters $C_{128}[SiV^0]H_{98}$ (a) and $C_{128}[SiV^-]H_{98}$ (b) with the spin density distributions shown (at isodensity value of 0.01). Si atom is shown in violet, passivating H atoms—in yellow and closest to Si carbon atoms in Fig. 1b are shown in red and blue. Additionally, the $C_2^{(Z)}$ symmetry axis and the $\sigma_h^{(XY)}$ symmetry plane (C_{2h} symmetry elements) are shown in Fig. 1b.

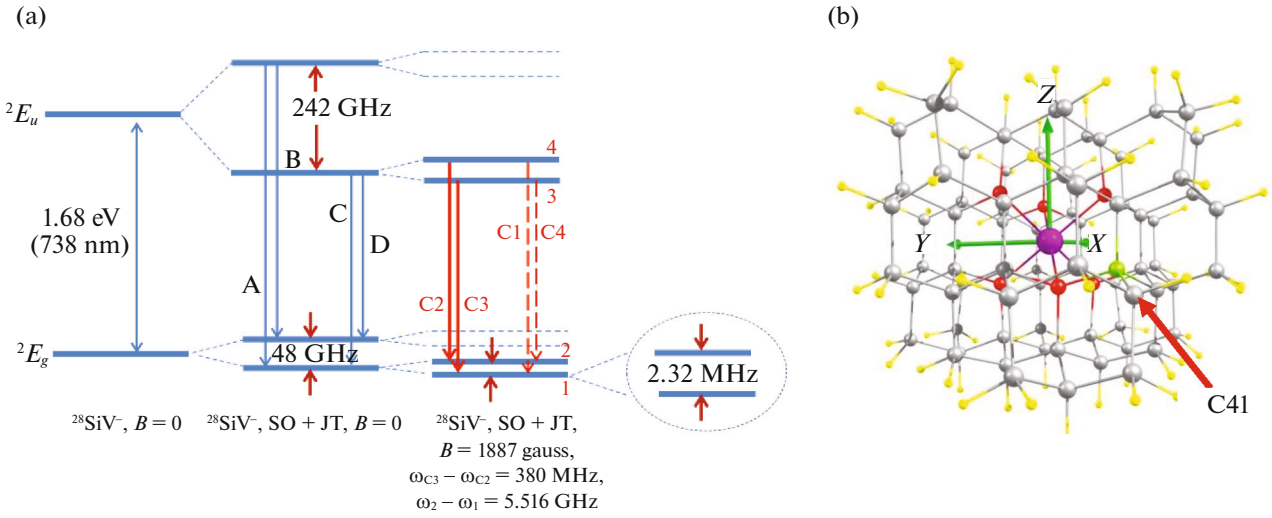

Fig. 2. (a) Energy levels and measured splitting of the coupled SiV^-—^{13}C spin system studied experimentally in [4]. (b) Position C41 of the studied nuclear spin ^{13}C in the cluster.

The optical transition giving the characteristic line of the SiV^- center at 1.68 eV ($\lambda = 738$ nm) and shown in the left part of Fig. 2a has the fine structure (A–D transitions) due to spin-orbit (SO) interaction and the Jahn–Teller (JT) effect, leading to the splitting of the ground and excited states of the center at 48 and 242 GHz, respectively, in the absence of an external magnetic field. In the presence of an external magnetic field $B = 1887$ gauss, the low-energy doublet states of the center were split due to the Zeeman effect so that the frequencies of the C3 and C2 transitions differed by 380 MHz, and the splitting of the states 1 and 2 due to the Zeeman effect for the electron spin of the SiV center was 5.516 GHz. Finally, the experimentally measured splitting of state 1 due to both the Zeeman effect for the nuclear ^{13}C spin and the hyperfine interaction was 2.32 MHz.

To describe these observations we have used standard spin-Hamiltonians (see, e.g. [14, 15]) of the ground ^2E_g and the excited ^2E_u doublet states of the SiV^- center $H_{g,e} = H_{SOg,e} + H_{JTg,e} + H_Z + H_{hfi}$, where the first term describes spin-orbit (SO) interaction

$H_{SOg,e} = \lambda_{SOg,e}\mathbf{L}\cdot\mathbf{S}$ ($\mathbf{L}$ and $\mathbf{S}$ are the orbital and electronic spin operators of the center, $\lambda_{SOg,e}$ are the SO coupling constants in the ground and excited states), second term is the Jahn–Teller interaction (see [15, 16] for details), the third term $H_Z = q\gamma_L\mathbf{L}\cdot\mathbf{B} + \gamma_S\mathbf{S}\cdot\mathbf{B}$ takes into account the Zeeman interaction of $\mathbf{L}$ and $\mathbf{S}$ with external magnetic field $\mathbf{B}$ ($\gamma_L = \mu_B/\hbar$, $\gamma_S = 2\mu_B/\hbar$ are orbital and electron gyromagnetic ratios, μ_B is the Bohr magneton, q is the Ham quenching factor) and the last term $H_{hfi} = \mathbf{S}\cdot A\cdot\mathbf{I}$ which was absent in [15, 16] we added to describe *hfi* of electronic spin $S = 1/2$ of the SiV^- center with the nuclear spin $I = 1/2$ of the ^{13}C atom located somewhere in the diamond lattice (here A_{KL} is the *hfi* matrix which was calculated for the all possible positions of the nuclear ^{13}C spin in the $C_{128}[SiV^-]H_{98}$ cluster).

We have used in the above spin-Hamiltonians the previously determined experimental values of the parameters (see [15, 16]): $\lambda_{SOg} = 48$ GHz, $\lambda_{SOe} = 257$ GHz, $JT_{xg} = 7$ GHz, $JT_{yg} = 2$ GHz, $JT_{xe} = 20$ GHz, $JT_{ye} = 0$ GHz, $q = 0.1$. The g-factors for the ground and excited states were taken equal to 2.28 and 2.43 in order to obtain correspondence of the theoretical calculated data with the experimental results. Further, since in the experiment the magnetic field was deflected by a small angle from the axis of symmetry $\langle 111\rangle$ of the SiV^- center, we took this angle equal to 3^0 and found that in the magnetic field $B = 1887$ gauss the frequency difference of the C2 and C3 lines in Fig. 2a was 387.7 MHz which is close to the experimentally measured value of 380 MHz. The splitting of the states 2 and 1 in Fig. 2a calculated at the indicated parameter values was 5.5093 GHz, which again is close to the experimental value of 5.516 GHz. Finally, among the array of *hfi* matrices calculated for the $C_{128}[SiV^-]H_{98}$ cluster we found only one matrix for which the value of the A_{ZZ} element was close to the experimentally determined value of 720 kHz. This was the matrix calculated for the position of C41 in this cluster, indicated by the red arrow in Fig. 2b. Using this matrix we diagonalized numerically the spin Hamiltonians to find the energy levels of this two-spin system, and to calculate the splitting of the state 1 (Fig. 2a, right), which is defined by the *hfi* of the ^{13}C nuclear spin with the electronic spin of the center, as well as by nuclear Zeeman interaction with an external magnetic field $B = 1887$ gauss. This splitting was found to be 2.404 MHz, which again was very close to the experimentally measured value 2.32 MHz of this splitting. Thus, taking into account the coincidence of the calculated values with the corresponding experimentally determined values, we can conclude that the SiV-^{13}C two-spin system studied in [4] is a system that includes the nuclear spin ^{13}C located at position C41, shown in Fig. 2b.

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CONFLICT OF INTEREST

The authors declare that they have no conflicts of interest.

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