An \textit{ab initio} study on split silicon-vacancy defect in diamond: electronic structure and related properties

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The split silicon-vacancy defect (SiV\textsuperscript{4−}) in diamond is an electrically and optically active color center. Recently, it has been observed close to 1.68 eV, and this can be divided into three similar groups each containing four components. The relative strengths of the optical absorption for the three groups of lines are found to be the same as the ratio of the abundancies of the natural isotopes of silicon, \textsuperscript{28}Si, \textsuperscript{29}Si, and \textsuperscript{30}Si. The 4-line fine structure for an individual Si-isotope is assigned to doublet levels both in the ground and excited states which split by about 48 and 242 GHz, respectively. It has been assumed that this small splitting might be explained by dynamic Jahn-Teller effect and/or by spin-orbit effect.

Recently, single photon-emission from a 1.68-eV PL center has been demonstrated. Its zero-phonon-line (ZPL) with 5 nm width even at room temperature and the near infrared emission makes this PL center very attractive candidate for quantum optics and biomarker applications.

Spin-polarized local density approximation (LDA) within density functional theory (DFT) calculations in a very small nanodiamond model (with ~70 carbon atoms) concluded that the negatively charged split-vacancy form (see Fig. 1) of SiV defect (SiV\textsuperscript{4−}) is responsible for the 1.68-eV PL center. They exclude the neutral SiV defect (SiV\textsuperscript{0}) as a good candidate as its ground state is orbitally singlet. This model was later disputed based on a semiempirical restricted open-shell Hartree-Fock cyclic cluster model calculation where they claimed that tunneling of Si-atom along the symmetry axis may occur for SiV\textsuperscript{0} defect that can explain the doublet line in the ground state.

The fingerprint of SiV\textsuperscript{0} was found by electron paramagnetic resonance (EPR) studies. The KUL1 center with $S = 1$ high spin ground state and D\textsubscript{3d} symmetry was recently associated with SiV\textsuperscript{0} defect where 216-atom LDA supercell calculations produces relatively good agreement with the measured \textsuperscript{13}C and \textsuperscript{28}Si hyperfine couplings (see Tab. 1).

While the recent measurements are very plausible still no \textit{ab initio} theory was able to conclusively support the assignment of 1.68-eV center with the negatively charged SiV defect. LDA or any semilocal generalized gradient approximation (GGA) functionals suffer from the band gap error which inhibits to directly compare the calculated and experimental ZPL energies. Recent advances in DFT functionals made possible to accurately calculate ZPL energies and charge transition level of defects in diamond and other semiconductors. In this paper, we apply this theory to study the charge transition levels and the ZPL energies of SiV defect in diamond. These calculations yield the position and nature of defect states in host diamond and are able to reveal the nature of the shelving state in 1.68-eV PL center.

Our paper is organized as follows. In Section II we describe briefly the \textit{ab initio} method that we applied to study the electronic structure and excitations of the SiV defect. In Section III we describe the structure and the basic defect level scheme of SiV defect by group theory. Here, we combine the results from \textit{ab initio} calculations with group theory considerations in order to identify the order of important defect states and the charge state relevant for the most important 1.68-eV PL center. We discuss the results then we conclude and summarize the results in Section IV.
FIG. 1. (Color online) The split-vacancy structure of the SiV defect and the calculated spin density in neutral charge state. The isosurface of spin density is 0.05. The defect has $D_{3d}$ symmetry with the symmetry axis of [111] direction. The lattice sites of the missing carbon atoms are depicted by the smallest (pink) balls.

II. METHOD

The present calculations have been carried out in the framework of the generalized Kohn-Sham theory by using the screened hybrid functional HSE06 of Heyd, Ernzerhof and Scuseria with the original parameters (0.2 Å$^{-1}$ for screening and 25% mixing) in HSE06 in diamond happens to be nearly free of the electron self-interaction error, and is capable of providing defect-levels and defect-related electronic transitions with $\sim$0.1 eV to experiment.

We have used the Vienna Ab Initio Simulation Package VASP 5.3.2 with the projector augmented wave method (applying projectors originally supplied to the 5.2 version) in bulk calculations on the primitive cell with a $8\times8\times8$ Monkhorst-Pack (MP) set for Brillouin-zone sampling. (Increasing the MP set to $12\times12\times12$ has changed the total energy by $<0.002$ eV.) Constant volume relaxations using a cutoff of 370(740) eV in the plane-wave expansion for the wave function (charge density) resulted in an equilibrium lattice parameter of $a_{\text{PBE}}=3.570$ Å. Increasing the cutoff to 420 (840) eV has changed the lattice constant by only 0.003 Å. Therefore, considering the demands of the supercell calculations, the lower cutoff was selected. The HSE06 calculation with the $8\times8\times8$ MP set and 370(740) eV cutoff resulted in the lattice constant $a_{\text{HSE}}=3.545$ Å, indirect band gap of $E_g=5.34$ eV, in good agreement with the experimental values of $a=3.567$ Å and $E_g=5.48$ eV (see, e.g., Ref. [29]). Due to the different choice of the basis, the HSE06 values presented here differ somewhat from those in Refs. [16,20] and [29], but tests on the negatively charge nitrogen-vacancy center (NV) have shown that the higher cutoff would cause only negligible difference in the equilibrium geometry of that defect too. Defects in the supercell were allowed to relax in constant volume till the forces were below 0.01 eV/Å.

We calculated the hyperfine tensors of $^{13}$C and $^{28}$Si isotopes within PAW formalism as implemented in VASP 5.3.2 package. Here, we applied a larger 500(1000) eV cutoff for the plane wave (charge density) expansion. The hyperfine tensor ($A_{ij}^{(J)}$) between the electron spin density $\sigma(r)$ of an electron spin $S$, and the non-zero nuclear spin $I$ of nucleus $J$ may be written as

$$A_{ij}^{(J)} = \frac{1}{2S} \mu_e \mu_J \left[ \frac{8\pi}{3} \int \delta(r-R_J)\sigma(r)dr + W_{ij}(R_J) \right]$$

where the first term within the square brackets is the so-called (isotropic) Fermi-contact term, and

$$W_{ij}(R) = \int \left( \frac{3(r-R)_i(r-R)_j}{|r-R|^5} - \frac{\delta_{ij}}{|r-R|^3} \right) \sigma(r)dr$$

represents the (anisotropic) magnetic dipole-dipole contribution to the hyperfine tensor. $\mu_J$ is the nuclear Bohr magneton of nucleus $J$ and $\mu_e$ the electron Bohr-magneton. The Fermi contact term is proportional to the magnitude of the electron spin density at the center of the nucleus which is equal to one third of the trace of the hyperfine tensor, $\frac{1}{3} \sum_i A_{ii}$. The Fermi contact term arises from the spin density of unpaired electrons with $s$-character, and can be quite sizable. The spin density built up from unpaired electrons of $p$-character yields the dipole-dipole hyperfine coupling. The fraction of Fermi-contact and dipole-dipole term implicitly provides information about the character of the wave function of the unpaired electron as well as the corresponding nuclei (via $\gamma_j$). According to our recent study, the contribution of the spin polarization of core electrons to the Fermi-contact hyperfine interaction is significant for $^{13}$C isotopes, thus, we include this term in the calculation of hyperfine tensors.

The excitation energies were calculated within constrained DFT method that was successfully applied to NV center in diamond. In this method one can calculate the relaxation energy of the nuclei due to optical excitation.

The formation energy of the defect with defect charge state $q$ is defined as

$$E_{\text{form}}^q = E_{\text{tot}}^q - n_c \mu_C - n_Si + qE_F + \Delta V(q)$$

by ignoring the entropy contributions, where $E_{\text{tot}}^q$ is the total energy of the defect in the supercell, $E_{\text{VBM}}$ is the calculated energy of VBM in the perfect supercell, $\mu_C$ and $\mu_{Si}$ are the chemical potentials of C and Si atoms in diamond with $n_C$ number of C atoms in the supercell, $E_F$ is the chemical potential of the electron, i.e., the Fermi-level, and $\Delta V(q)$ is the correction needed for charged supercells. The thermal charge transition level between the defect charge states of $q$ and $q+1$ is the position of the Fermi-level ($E_F$) in the fundamental band gap of diamond where the formation energies are equal in these charge states. This condition simplifies to a difference in the total energies in their respective charge states as follows,

$$E_F = E_{\text{tot}}^q - E_{\text{tot}}^{q+1} + \Delta V(q) - \Delta V(q+1),$$

where $E_F$ is referenced to the calculated $E_{\text{VBM}}$. For comparison of different defect configurations and charge states, the electrostatic potential alignment and the charge correction...
scheme of Lany and Zunger was applied for $\Delta V(q)$. Recently, this scheme was found to work best for defects with medium localization.

### III. RESULTS

We first study the structure and the obtained defect levels by HSE06 calculation. Then, we apply group theory in order to explain the symmetry of the defect states. We use the calculated thermal ionization energies, excitation energies and hyperfine couplings to identify the 1.31-eV and 1.68-eV PL centers. We also discuss the results with comparing them to the experiments.

#### A. *Ab initio* results and group theory analyses of the defect states for neutral SiV defect in diamond

We first calculated the neutral defect SiV by substituting the C-atom by a Si-atom adjacent to a nearby vacancy. The Si automatically left the substitutional site creating a split-vacancy configuration which may be described as a Si-atom placed in a divacancy where the position of the Si-atom is equidistant from the two vacant sites (see Fig. 1). The position of Si-atom is a bond center position which is an inversion center of perfect diamond lattice. In our special coordinate frame the two vacant sites reside along the [111] direction of the lattice which has a $C_3$ rotation axis. The symmetry of the defect may be described as $C_{3v} \times i$ or $D_{3d}$, where $i$ is the inversion. We note that NV center has $C_{3v}$ symmetry with no inversion. The defect has $S=1$ high-spin ground state. This finding agrees with the LDA calculations. After establishing the symmetry of the defect one can apply group theory analysis for this defect. One can build the defect states of this defect as an interaction between the divacancy orbitals and the Si-impurity states. The Si impurity has 6 immediate neighbor C-atoms in divacancy. The calculated distance between Si- and C-atoms is about 1.97 Å in the neutral charge state, which is longer than the usual Si-C covalent bond (1.88 Å). Since C-atoms are more electronegative than Si-atom the charge transfer from the Si-atom toward the C-atoms can be relatively large leaving positively charged Si ion behind. The divacancy has $D_{3d}$ symmetry with six C dangling bonds. These dangling bonds form $a_{1g}$, $a_{2u}$, $e_u$ and $e_g$ orbitals while the Si-related four $sp^3$ states should form $a_{1g}$, $e_u$, and $a_{2u}$ orbitals in $D_{3d}$ crystal field (the explicit form of these orbitals as a function of $sp^3$ states can be seen in Ref. 36). Please, note that the $a_{1g}$, $a_{2u}$ and $e_u$ states may be combined but $e_g$ orbitals should be pure C dangling bonds state (see Fig. 1). The bonding and anti-bonding combinations of these states form the defect states of SiV defect. According to HSE06 calculation the occupation of the defect states may be described as $a_{1g}^2a_{2u}^2e_u^4e_g^2$ which agrees again with previous LDA calculations. Here, the ten electrons are coming from the six electrons of C dangling bonds and the 4 $sp^3$ electrons of the Si impurity. As two electrons occupy the double degenerate $e_g$ state, the high-spin $S=1$ ground state naturally forms by following Hund’s rules. It is important to determine the position of the defect levels. Interestingly, HSE06 predicts that only $e_g$ appears in the band gap. In the spin-polarized calculation the occupied $e_g$ state in the spin-up channel is at $E_{VBM}+0.3$ eV. The $e_u$ state is resonant with the valence band and can be found just 0.64 eV below VBM. The occupied $a_{1g}$ state lies very deep in the valence band and may play no important role in the excitation or ionization processes. Our estimations indicate that the $a_{2u}$ level in the deep VB to be excited by red excitation. However, higher energetic lasers (in the green and blue spectrum) can excite this state and other states within the VB with $a_{2u}$ symmetry. The empty anti-bonding orbitals fall in the conduction band, and will not be considered any more. The most important $e_u$ and $e_g$ states are depicted in Fig. 1. Despite the $e_u$ state lies in the valence band it is still localized around the defect site. The valence band states are strongly perturbed by the presence of the defect. The VBM is triple degenerate in perfect lattice that splits to an upper $a_{1g}$ level and a lower $e_g$ level in the presence of the defect. Since this $e_g(VBM)$ state has the same symmetry as the low-lying $e_g$ defect state, that $e_g(VBM)$ state becomes a defect resonance state. Similar phenomena occurs for the deep $e_u$ defect state as well. The shallow $e_g(VBM)$ state may play an important role in the excitation/de-excitation process of the defect.

We conclude that the neutral SiV defect (i) has $^3A_{2g}$ ground state, (ii) can be theoretically ionized as $2^+$, $1^+$, as well as $1^-$ and $2^-$ by emptying or filling the double degenerate $e_g$ state in the gap. In order to establish the relevant charge states,
FIG. 3. (Color online) The electron wave function of $e_u$ and $e_g$ defect states in the neutral SiV defect. Both states are double degenerate, so both $x$ and $y$ components are depicted. Note that $e_u$ states are changing sign upon inversion while $e_g$ states do not as their irreducible representation indicates. Furthermore, Si orbitals have little contribution in $e_u$ state but no contribution to $e_g$ state. The $e_u$ state is resonant with the valence band, thus less localized, whereas the localized $e_g$ state lies in the band gap.

one has to calculate the adiabatic charge transition levels of SiV defect.

B. Charge transition levels of SiV defect in diamond

We found that the neutral, negatively charged and double negatively charged states can be found in diamond (see Fig. 4). The single positive charged state might be only found in very highly p-type doped diamond samples. The calculated $(-|0)$ level at $E_{VBM} + 1.43$ eV is very close to the level that is associated with the acceptor ionization energy of the defect from photo-conductivity measurements at $\sim E_{VBM} + 1.5$ eV. Interestingly, the calculated $(2|-)$ level at $\sim E_{VBM} + 2.14$ eV is well below the midgap. Since the $e_g$ level is fully occupied at $E_{VBM} + 1.5$ eV in $(2|-)$ charge state intra-level optical transition cannot take place, and ultra-violet excitation ($\sim 4.0$ eV) is needed to excite or ionize the defect optically to the conduction band edge. Another important note that the calculated acceptor level of NV lies at $\sim E_{VBM} + 2.6$ eV. This means that if both NV and SiV defects are present in the diamond sample then most of the NV defects should be neutral in order to detect SiV$^-$ defect. Another important point that the luminescence from SiV$^-$ defect can be more stable than that of NV$^-$ defect in nanodiamonds as a function of surface termination because the corresponding $(2|-)$ charge transition level lies deeper in the band gap than the $(-|0)$ level of NV defect. All in all, the neutral and negatively charged SiV defects are relevant for intra-level optical transitions.

![FIG. 4. The calculated formation energy of SiV defect as a function of the Fermi-level in the gap. The crossing points represent the charge transition levels. The chemical potential of Si is taken from cubic silicon carbide in the carbon-rich limit.](image)

C. Negatively charged SiV defect in diamond: analysis of the ground and excited states, and the zero-phonon-line energy

In the negatively charge SiV defect the ground state electron configuration is $e_u^4e_g^3$. This is principally a Jahn-Teller unstable system as the double degenerate $e_g$ level is partially filled (in the spin-down channel in our calculation). This has $^2E_g$ symmetry in $D_{3d}$ symmetry. In HSE06 geometry opti-
mization we allowed the systems to relax to lower symmetries. Indeed, HSE06 showed a $C_{2h}$ distortion where two C-atoms have 0.03 Å longer distance from Si-atom than the other two atoms. In this particular case the $B_2g$ state was formed in $C_{2h}$ symmetry. However, we have to note that the dynamic coupling between vibrations and electronic states cannot be taken into account in our calculation. Thus, dynamic Jahn-Teller system cannot be directly described by our method. For instance, static Jahn-Teller effect occurs for NV$^0$ in Ref. 38 while it is known from experiments that it is a dynamic Jahn-Teller system. Since the distortion from $D_{3d}$ symmetry obtained by HSE06 calculation is small the defect may well have $D_{3d}$ symmetry with dynamic Jahn-Teller effect. We note that no such an electron paramagnetic resonance center with $S = 1/2$ spin was found that could be associated with SiV$^-$ defect. This also hints that the ground state of SiV$^-$ is a dynamic Jahn-Teller system which prohibits the electron spin resonance signal similar to NV$^0$ defect.

Now, we discuss the possible excited states of this system. Again, the fully occupied $e_g$ state is resonant with the valence band. Still, one can promote one electron from this level to the $e_u$ level in the band gap. The resulted $2E_u$ excited state is again Jahn-Teller unstable. Interestingly, when the electron from the minority spin-down $e_u$ level in the valence band was promoted to the $e_g$ state in the gap then the resulted hole state pops up clearly above the valence band edge at about $E_{VBM} + 0.12$ eV [see Fig. 5(a)]. The $2E_u \rightarrow 2E_g$ optical transition is allowed. In HSE06 calculation the excited state has also $C_{2h}$ distortion but the effect is again small, and can be a dynamic Jahn-Teller system. The calculated ZPL energy is about 1.72 eV which agrees well with that of a 1.68-eV PL center. The calculated relaxation energy due to optical excitation is about 0.03 eV which is much smaller than that of NV center (about 0.21 eV), and explains the small contribution of the vibration sideband in the emission spectrum. Thus, the assignment of 1.68-eV PL center with SiV$^-$ defect is well-supported by our calculation.

We argue that the sharp zero-phonon line of SiV$^-$ as well as the relative strength of the fine-structure splittings in the ground and excited states can be well-understood by our findings. The $2E_g$ ground and $2E_u$ excited states have very similar electron charge densities, where mostly just the phase differs between the two states. As a result, the ions will be subject to similar potentials in their ground and excited states leading to only small change in the geometry due to optical excitation. This is in stark contrast to the case of NV$^-$ defect where the electron charge density strongly redistributes upon optical excitation leading to a large Stokes-shift. Another observation is that $2E_g$ state virtually is not localized at all on Si-atom due to symmetry reasons, however, our projected density of states analysis shows that there is a small contribution from the orbitals of the Si-atom in the $2E_u$ excited state, allowed by symmetry. This may explain the larger splitting in the fine-structure of the excited state than that in the ground state, the $2E_u$ state has expected to have larger spin-orbit splitting due to the small contribution of the orbitals of Si-atom than that in $2E_g$ state where this contribution is missing, as the spin-orbit strength increases with the atomic number to the fourth power.

Furthermore, our HSE06 calculations reveal that the heavily perturbed valence band edges can play important role in understanding the defect properties as those states lie closer to the $e_g$ state in the band gap than the $e_u$ resonant defect state. Therefore, we calculate the excitation from the split VBM states. A $2E_g$ and a $2A_{1g}$ excited states are built from the hole left on the $e_g$ and $A_{1g}$ states respectively [c.f., Fig. 5(b)]. We find that the $2E_g$ excited state is ~0.1 eV lower in energy than the bright $2E_u$ excited state where the calculated Stokes-shift of this transition is again small. The $2A_{1g}$ excited state is ~1.59 eV above the $2E_g$ ground state.

These results can explain the nature of the shelving state in
1.68-eV PL center. Unlike NV-center the SiV defect has inversion symmetry that plays a crucial role in the de-excitation process. Due to the inversion symmetry the $^2E_g$ and $^2A_{1g}$ excited states are shelving states because they are optically forbidden due to the same parity of their wave function with that of the ground state. Thus, the shelving states have the same spin state as the ground and the bright excited states. Since $^2E_g$ shelving state has a level very close to that of the bright $^2E_u$ state the non-radiative coupling between these states can be efficient. We further note that a new and weak near-infrared (NIR) transition at $\sim$823 nm (1.52 eV) has been found associated with the negatively charged SiV-defect.\textsuperscript{29} The measurements implied that this transition belongs to the same charge states when strain was present in the sample. This NIR transition was particularly found in ensemble measurements of nanodiamond samples when strain was present in the sample.\textsuperscript{16} Our calculations imply [Fig. 5c] that this weak radiative transition can be explained by the slightly distorted $^2A_{1g}$ excited state. Any distortion of the diamond lattice will break the inversion symmetry of the SiV defect, so the parity of the corresponding wave functions. Therefore, transitions between $^2A_1$ and $^2E$ (originally $^2A_{1g}$ and $^2E_g$) will be allowed. The calculated transition energy (1.59 eV) is very close to the detected one which further supports our assignment. Our calculations highlight the importance of the valence band edge states in understanding the optical properties of 1.68-eV center in diamond.

We note again that the $e_u$ state is resonant with the valence band. Thus, unlike the case of NV center with well-separated atomic-like states in the gap, it is probable that ionization of the defect can occur during optical excitation. In this process, a hole is created that might (temporarily) leave the defect with creating an optically inactive (2$\rightarrow)$ charge state, particularly, in the presence of external perturbations that create an effective electric field. This (2$\rightarrow$) charge state can be optically converted back to (--) state only by ultra-violet excitation.

D. Neutral SiV defect: hyperfine tensors and zero-phonon-line energy

The (2$\rightarrow$) charge state is a closed-shell singlet while the neutral and negatively charged SiV defects have $S=1$ and $S=1/2$ spin states, respectively. The SiV$^0$ defect was assigned to KUL1 EPR center with $S=1$ state and $D_{4h}$ symmetry.\textsuperscript{15,35} Our calculations supports this assignment (see Table I). The spin density is localized on four C dangling bonds in the $e_g$ orbital of divacancy. While the $e_g$ state is not localized on Si impurity but the spin density from these C dangling bonds can overlap with the Si atom which promotes a well measurable Fermi-contact term on the $^{29}$Si nuclei. The hyperfine interaction with $^{29}$Si is almost isotropic unlike the case of $^{13}$C isopces which show typical anisotropic signal due to sp$^3$ dangling bonds. The calculated and measured $^{13}$C hyperfine tensor agree very well. We note that the contribution of the spin-polarization of core electrons to the Fermi-contact term is very significant which compensates the hyperfine interaction due to valence electrons. We found this effect also for NV and other related defects.\textsuperscript{21}

| Interaction | $A_{||}$ (MHz) | $A_\perp$ (MHz) | $\Theta$ (°) |
|-------------|----------------|----------------|--------------|
| $^{13}$C (experiment)$^a$ | 66.2 | 30.2 | 35.3 |
| $^{13}$C (LDA-nocp)$^b$ | 51 | 12 | 33.3 |
| $^{13}$C (HSE06-cp) | 68 | 28 | 34.6 |
| $^{29}$Si (experiment)$^a$ | 76.3 | 78.9 | 0 |
| $^{29}$Si (LDA-nocp)$^b$ | 78 | 82 | 0 |
| $^{29}$Si (HSE06-cp) | 92 | 97 | 0 |

$^a$ Ref. 15 $^b$ Ref. 15

Next, we discuss the optical transitions for SiV$^0$. Intra-level transition may occur between the fully occupied $e_u$ state and the empty $e_g$ state in the spin-down channel. While the fully occupied $e_u$ state lies in the valence band a strong resonant excitation may occur from this state. In hole picture the excited state may be described as $e_{u}^{1}e_{g}^{1}$ while the ground state is $e_{g}^{2}$. The electron configuration of $e_{g}^{2}$ results in $^3A_{2g}$ triplet state and $^3E_g$, $^1A_{1g}$ singlet states. The ground state is $^3A_{2g}$. The electron configurations of $e_{u}^{1}e_{g}^{1}$ results in $^3A_{1u}$, $^3A_{1u}$, $^3A_{2u}$, $^3A_{2u}$, $^3E_u$, and $^1E_u$ multiplets. Among these states $^3A_{1u}$ and $^3E_u$ states are optically allowed from the $^3A_{2g}$ ground state. Polarization studies of the 1.31-eV center indicates that $^3A_{1u} \rightarrow ^3A_{2g}$ transition occurs in the PL process.\textsuperscript{31} The $^3A_{1u}$ state can be described as linear combination of Slater-determinants that cannot be treated within constraint DFT. However, the $M_S=1$ substate of $^3E_u$ multiplet can be described by a single Slater-determinant. The calculated excitation energy is about 1.63 eV which is significantly larger than 1.31 eV. Thus, we may conclude that $^3E_u \rightarrow ^3A_{2g}$ transition is not responsible for the 1.31-eV PL line. As the only other feasible transition is $^3A_{1u} \rightarrow ^3A_{2g}$, our result indirectly confirms the experimental finding.

We also study the role of the valence band resonant states similar to the case of the negatively charged defect. When the electron is promoted from $e_{1g}(VB)$ state to the $e_g$ state in the gap then $^3E_g$ state is created. The calculated excitation energy of this shelving state is $\sim$1.27 eV. This coincides with the small peak found in Ref. 16 simultaneously with the peak of 1.31-eV. This transition is optically allowed only when the inversion symmetry of the defect is broken. This might happen due to strain in the diamond sample. Nevertheless, our calculation implies that this $^3E_g$ state can play an important role in the de-excitation process as a shelving or metastable state.

We note that the experiments indicate\textsuperscript{16} that the ground
state of the neutral SiV defect resides at \( \sim 0.2 \) eV above the valence band edge. According to HSE06 calculations the occupied single particle \( e_g \) level lies at \( E_{\text{VBM}} + 0.3 \) eV that agrees nicely with the implications from the experiments. In addition, we found a metastable state of the defect which may explain the temperature dependence of the 1.31-eV PL spectrum\(^{16}\). We also propose that strain may induce a weak PL transition from this shelving state because this shelving state has the same spin as that of the ground state, and the parity selection rule may be relaxed in slightly distorted geometry of the SiV defect. We further note that a very similar conclusion can be drawn for the optical excitation of the neutral SiV defect as was hinted for the negatively charged defect: a hole is created in the valence band in the excitation process that may leave defect temporarily or permanently which leads to a charge conversion from neutral to negatively charged SiV defect.

IV. SUMMARY AND CONCLUSION

We carried out \textit{ab initio} supercell calculations on SiV defect in diamond. The calculations could positively confirm the assignment of 1.68-eV and 1.31-eV PL centers to the negatively charged and neutral SiV defect, respectively. The calculations reveal the high importance of the inversion symmetry of the center as well as the role of resonant valence band states in understanding the optical properties of the defect. We show that the shelving states of 1.68-eV PL center are from valence band excitations where the lowest-energy shelving state may have NIR emission to the ground state in strain diamond samples. We show that holes are created in the excitation of the negatively charged and neutral SiV defects that may lead to charge conversion of these centers. In addition, we show that the acceptor level of SiV defect lies very deep in the band gap. As a consequence, the 1.68-eV PL center can be photo-stable when it is close to the surface of hydrogenated diamond surface. On the other hand, SiV defect is double negatively charged in such diamond samples where the NV-defect is negatively charged. Thus, the Fermi-level should be set lower than the midgap of diamond, in order to conserve its negative charge state.

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