

Electronic properties and hyperfine fields of nickel-related complexes in diamond

R. Larico,¹ J. F. Justo,² W. V. M. Machado,¹ and L. V. C. Assali¹

¹*Instituto de Física, Universidade de São Paulo, CP 66318, CEP 05314-970 São Paulo, São Paulo, Brazil*

²*Escola Politécnica, Universidade de São Paulo, CP 61548, CEP 05424-970 São Paulo, São Paulo, Brazil*

(Received 2 December 2008; revised manuscript received 28 January 2009; published 5 March 2009)

We carried out a first-principles investigation on the microscopic properties of nickel-related defect centers in diamond. Several configurations, involving substitutional and interstitial nickel impurities, have been considered either in isolated configurations or forming complexes with other defects, such as vacancies and boron and nitrogen dopants. The results, in terms of spin, symmetry, and hyperfine fields, were compared with the available experimental data on electrically active centers in synthetic diamond. Several microscopic models, previously proposed to explain those data, have been confirmed by this investigation, while some models could be discarded. We also provided insights into the microscopic structure of several of those centers.

DOI: [10.1103/PhysRevB.79.115202](https://doi.org/10.1103/PhysRevB.79.115202)

PACS number(s): 61.72.Bb, 71.55.Cn

I. INTRODUCTION

Diamond is a material which stands alone in nature, carrying a unique combination of electronic, mechanical, thermal, and optical properties. Diamond is the hardest known natural material, having a large bulk modulus, high thermal conductivity, and a large electronic band gap. Those properties make it a prototypical material to a number of applications, ranging from drilling and cutting tools to electronic devices used to operate under extreme conditions.¹ More recently, new potential applications for doped diamond have been proposed, such as superconducting materials² and quantum computing.^{3,4}

There are two major methods with widespread use for growing macroscopic samples of synthetic diamond. Chemical-vapor deposition (CVD) methods produce high-quality diamond thin films grown over large areas. On the other hand, the high-pressure high-temperature (HPHT) processes produce bulk diamond at relatively high growth rates and low costs. In those processes, samples are grown out of graphite, using $3d$ transition-metal (TM) alloys (involving nickel, cobalt, and iron) as solvent-catalysts. Nickel is the major impurity that has been unambiguously identified in the resulting diamond, but some cobalt-related centers have also been identified.⁵ Such residual nickel impurities, either isolated or forming complexes with other defects, can generate several electrically and optically active centers.⁶ Understanding the nature and microscopic structure of those centers is crucial in developing diamond-related technologies. Recently, nickel-related centers have been considered for optical applications, as single-photon sources that could be used in quantum computing or waveguide optical communications.^{7,8} Following the experimental identification of nickel-related centers, several microscopic models have been proposed to explain such data. However, there is still considerable controversy over a unified model which could explain most of those active centers in diamond. Here, we used first-principles calculations to address this question.

Over the last decade, nickel-related impurities in diamond have been investigated by several theoretical approaches.⁹⁻¹² However, no investigation has provided a comprehensive picture of most of the nickel-related active centers identified

in diamond so far using the same methodology. We used first-principles, total-energy calculations, based on the full-potential linearized augmented plane-wave (FP-LAPW) methodology,¹³ to investigate the structural and electronic properties of those centers in terms of the spin, symmetry, ground-state multiplet, formation and transition energies, and hyperfine parameters. We focused our investigation on centers involving isolated nickel, in either interstitial or substitutional configurations, and complexes involving nickel and vacancies or dopants (boron and nitrogen).

This paper is organized as follows. In Sec. II we discuss the available electron-paramagnetic-resonance (EPR) experimental data of nickel-related defects in diamond. In Sec. III, we present the methodology used in this investigation. Sections IV and V present and discuss the results in the context of experimental data.

II. SURVEY ON THE EXPERIMENTAL DATA

Electron-paramagnetic-resonance and optical-absorption measurements have been used to identify a number of nickel-related active centers in diamond, and have been recently reviewed.⁶ The electronic properties of those centers have been analyzed in terms of either the Ludwig-Woodbury (LW) (Ref. 14) or the vacancy¹⁵ model. According to the LW model, when a $3d^n 4s^2$ ion ($1 \leq n < 9$) occupies an interstitial site in a type-IV semiconductor, its $4s$ electrons are transferred to the $3d$ orbitals, resulting in a $3d^{n+2}$ configuration. In the tetrahedral crystal field, the $3d$ states are split into $e+t_2$ irreducible representations. The threefold t_2 states lie lower in energy than the twofold e states. This level ordering is the result of the octahedral crystal field, created by the next-nearest neighbors of the impurity, which is stronger than the tetrahedral crystal field from the nearest neighbors. The same ion in a substitutional site would present a $3d^{n-2}$ configuration, since four electrons are needed to bind with the four nearest-neighboring host atoms. However, in this case the crystal field has tetrahedral symmetry, driving the e states to lie lower in energy than the t_2 ones. Additionally, in the LW model, the gap levels are filled according to Hund's rule. The LW model is schematically presented in Fig. 1.

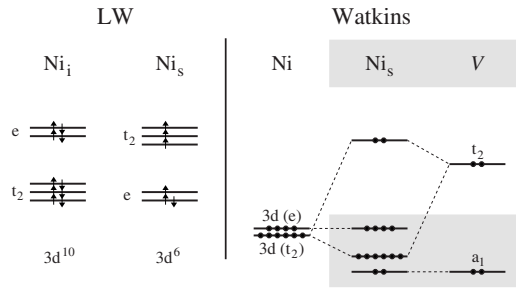


FIG. 1. Schematic representation of the gap states for an isolated interstitial (Ni_i) or substitutional (Ni_s) nickel in neutral charge state, according to models of Ludwig and Woodbury (Ref. 14) and Watkins (Ref. 15) (vacancy) models. The \uparrow and \downarrow arrows represent the spins up and down, respectively. Gray regions represent the valence and conduction host bands. For simplicity, the system is considered in a tetrahedral symmetry, neglecting distortions.

For substitutional impurities, there is an alternative model, called the vacancy model, proposed by Watkins¹⁵ for TM elements near the end of the $3d$, $4d$, and $5d$ series. This model proposed that the electronic structure of the impurity resulted from a weak interaction between the impurity-related $d-t_2$ states and the t_2 vacancy-related ones, as represented in Fig. 1. The vacancy-related states came from the dangling bonds on the host atoms surrounding the vacant site into which the transition metal was inserted. As a result, the impurity band-gap states would have a vacancy-like behavior. Although those two models were developed to describe the properties of $3d$ transition-metal impurities in silicon, they have been extensively used to explain the microscopic properties of those impurities in other semiconductors,¹⁶ such as nickel-related impurity centers in diamond.

Nickel in diamond has been detected in a tetrahedral symmetry with a spin $S=3/2$ by EPR (Ref. 17) and optical measurements,¹⁸ and has been labeled W8 center. The microscopic model suggested for this center, based on either the LW or vacancy models, is an isolated substitutional nickel in the negative charge state (Ni_s^-) in a $3d^7$ configuration.¹⁷

Two major active centers have been found in synthetic diamond, which have been associated to interstitial nickel, labeled NIRIM-1 and NIRIM-2 centers.¹⁹ The NIRIM-1 has been identified with a spin $S=1/2$ in a trigonal symmetry at low temperatures ($T < 25$ K), which switches to a tetrahedral symmetry at higher temperatures. This center was discussed in the context of the LW model, and interpreted as resulting from an isolated interstitial nickel in the positive charge state (Ni_i^+).¹⁹ Since substitutional nickel in a positive charge state would give a spin $S=5/2$ according to the LW model, it was ruled out as a possible microscopic configuration for the NIRIM-1 center. More recently, independent investigations suggested that this center could, in fact, be formed by Ni_s^+ , giving a spin $S=1/2$,^{11,20} indicating that the vacancy model is more suitable to describe this center.

The NIRIM-2 center has been identified with a spin $S=1/2$ with a strong trigonal distortion.^{19,21,22} The microscopic structure of this center is still the subject of controversy. It was initially associated to an interstitial nickel with an impurity or vacancy nearby.¹⁹ More recently, this center has been proposed to be formed by a complex of nickel and

boron²⁰ or even by an isolated interstitial Ni.¹¹

Post-growth annealing treatments introduce new active centers in the as-grown samples, which have been labeled NE centers.²³ It has been suggested that those NE centers involve nickel, nitrogen, and vacancies. The NE4 center, which displays a D_{3d} symmetry and a spin $S=1/2$, has been tentatively associated to an interstitial Ni sitting in the middle position of a divacancy. This vacancy-nickel-vacancy unit (VNiV), also called nickel in a double semivacancy,²³ would be aligned along a $\langle 111 \rangle$ direction. This configuration has also been labeled as NiC_6 in the literature, which represents, besides the impurity, the six nearest-neighbor carbon atoms. The LW model¹⁴ was invoked to describe this configuration, in which the Ni impurity would donate six of its ten d electrons to form bonds to the six neighboring carbon atoms. The remaining four $3d$ electrons should occupy the lower triplet d orbital, according to Hund's rule. Since the center has a spin $S=1/2$, then this center was assumed to be in the negative charge state (VNiV^-), associated to a t_2^5 electronic configuration. The NE4 center is the precursor to several other NE centers, which are formed by replacing nearest-neighbor carbon atoms with nitrogen ones,²³ in a $\text{NiC}_{6-m}\text{N}_m$ ($1 \leq m \leq 6$) configuration. Recently, a center with rhombohedral symmetry and spin $S=1$, has been observed in diamond.²⁴ A (VNiV) configuration was suggested for this center, similar to that of NE4, but here in the neutral charge state. The NE1 center has a monoclinic symmetry and spin $S=1/2$, and has been suggested to be formed by a (VNiV) configuration plus two nearest-neighbor nitrogen atoms (NVNiVN).²³ The NE8 center has a monoclinic symmetry and spin $S=1/2$, and has been suggested to be formed by a (VNiV) configuration plus four nearest-neighbor nitrogen atoms (N_2VNiVN_2).²³

EPR data have unambiguously shown that nickel can pair with boron and nitrogen impurities in diamond, forming new active centers. A center, labeled NOL1, has been identified with spin $S=1$ and trigonal symmetry.²⁵ It has been suggested that this center is formed by an interstitial $\text{Ni}_i^{2+}(3d^8)$ impurity axially distorted by a boron (B_s^-) along a $\langle 111 \rangle$ direction, with an unspecified interatomic distance between the impurities. A more recent examination of the trigonal boron-related NOL1 center suggested a different model, which would involve substitutional nickel and boron, $\text{Ni}_s^+\text{B}_s^0$, with the acceptor boron in a next-nearest-neighbor site, with no covalent bonding between the impurities.²⁰

In samples with high concentrations of both nickel and nitrogen, other active centers have been identified. In addition to the NE centers, the AB5 center, with a spin $S=1$ and trigonal symmetry, has been identified.²⁶ The microscopic model proposed for this center is a substitutional nickel (Ni_s^{2-}) with a nearby substitutional nitrogen atom (N_s^+). Table I summarizes the properties of nickel-related EPR active centers in diamond, as well as the respective proposed microscopic models.

Most of the microscopic models proposed in the previous paragraphs have been built based on an ionic model,²⁸ which has been proposed to describe the $3d$ transition metal-acceptor pairs $\text{TM}_i^+-\text{A}_s^-$ in silicon¹⁴ (TM in a tetrahedral interstitial site in a positive charge state plus an acceptor A in

TABLE I. Experimental data on the electrically active centers of Ni-related defects in diamond. The table presents the symmetry, spin, and proposed microscopic model. X represents an unknown specie (a vacancy or impurity), and V represents a vacancy. A list of additional relevant active centers in diamond can be found in Ref. 27.

Label	Symmetry	S	Model
W8	Tetrahedral	3/2	Ni_s^- ^a
NIRIM-1	Trigonal ($T < 25$ K)	1/2	$\text{Ni}_i^+, \text{Ni}_s^+$ ^{c,d}
NIRIM-2	Trigonal	1/2	$\text{Ni}_i^+X, \text{Ni}_i^+\text{CB}_s^-$ ^d
NE4	Trigonal	1/2	$(\text{VNiV})^-$ ^e
NE4*	Rhombohedral	1	$(\text{VNiV})^0$ ^f
NE1	Monoclinic	1/2	$(\text{NVNiVN})^-$ ^e
NE8	Monoclinic	1/2	$(\text{N}_2\text{VNiVN}_2)^+$ ^e
NOL1	Trigonal	1	$\text{Ni}_s^+\text{B}_s^0, \text{Ni}_i^{2+}\text{B}_s^-$ ^g
AB5	Trigonal	1	$\text{Ni}_s^{2-}\text{N}_s^+$ ^h

^aReference 17.

^bReference 19.

^cReference 11.

^dReference 20.

^eReference 23.

^fReference 24.

^gReference 25.

^hReference 26.

a negative charge state). According to that model, the pair stable configuration corresponds to a classical system consisting of a TM_i^+ electrostatically bound to a nearest-neighbor A_s^- embedded in a dielectric medium.²⁹ Since the negatively charged acceptor has a closed shell, the electronic properties of the pair can be directly related to the positive TM ion placed in a screened Coulomb field.

III. METHODOLOGY

We used the all-electron spin-polarized FP-LAPW method,¹³ implemented in the WIEN2K package.³⁰ The calculations were performed within the framework of the density-functional theory, using the Perdew-Burke-Ernzerhof exchange-correlation potential.³¹ All the calculations were performed considering a 54-atom reference supercell. The methodology separates the crystalline space into two distinct regions: the atomic and interstitial ones. The electronic wave functions were expanded in terms of spherical harmonics in the atomic regions and of plane waves in the interstitial ones. We chose all atomic spheres with a radius of $R=0.64$ Å. Therefore, $2R$ was much smaller than the crystalline interatomic distance of 1.54 Å, such that atomic sphere overlap was avoided even in the case of large atomic relaxations. We used a $2 \times 2 \times 2$ grid to sample the irreducible Brillouin zone as well as the Γ point. The number of atoms in the reference simulation cell and k points were sufficient to provide converged results, which has been confirmed by testing some systems with larger supercells and k -point sampling.

Convergence in the total energy was tested by varying the number of plane waves describing the electronic wave functions in the interstitial region; a $7.0/R$ value provided converged results. Self-consistent iterations were performed until total energy and the total charge in the atomic spheres changed by less than 10^{-4} eV/atom and 10^{-5} electronic

charges/atom between two iterations, respectively. Additionally, the atomic positions were relaxed, without any symmetry constraints, until the forces were smaller than 0.02 eV/Å. All those approximations and convergence criteria have been shown to provide an accurate description of several defect centers in semiconductors.^{32,33}

The formation energy of a complex in a q charge state (E_f^q) was computed by

$$E_f^q = E_{\text{tot}}^q(N - n_C, n_X, n_Y) - (N - n_C)\mu_C - n_X\mu_X - n_Y\mu_Y + q(\epsilon_v + \epsilon_F + \delta_q), \quad (1)$$

where $E_{\text{tot}}^q(N - n_C, n_X, n_Y)$ is the total energy of the defect supercell with $N - n_C$ carbon atoms ($N=54$ is the number of carbon atoms in the perfect supercell), and n_X and n_Y are the numbers of X and Y impurities, respectively. The μ_C , μ_X , and μ_Y are the computed chemical potentials of carbon, X , and Y elements, respectively. Here, depending on the complex, X and Y could be nickel, nitrogen, or boron. Those chemical potentials, computed within the same methodology described in the previous paragraphs, were obtained from the total energy of carbon in a diamond lattice, nickel in a fcc lattice, nitrogen in a N_2 molecule, and boron in a trigonal lattice. Also, ϵ_F is the Fermi energy ($0 \leq \epsilon_F \leq E_g$), where E_g is the diamond band gap. ϵ_v is the valence-band top and δ_q lines up the band structures of the bulk material with and without the impurities, for each q charge state. This correction in the valence-band top is necessary due to inhomogeneities in the charge density in the finite primitive cell, which causes a Coulomb multipole interaction with its images, as discussed in Ref. 34. Additionally, a uniform jellium background was implicitly considered to cancel out the long-range multipole interactions of charged supercells.³²

The transition energy (E_t) of a center can be obtained from the formation energy of the center at different charge states. For example, for the transition energy $q/(q+1)$ we should have

$$q/(q+1) \equiv E_{\text{tot}}^q - E_{\text{tot}}^{q+1} + q\delta_q - (q+1)\delta_{q+1}. \quad (2)$$

In order to compute the hyperfine tensors, spin-orbit coupling was included in a second-variational procedure. Additional information concerning the calculation of hyperfine tensors is presented in the Appendix.

IV. RESULTS

We considered all of the proposed microscopic models for the electrically active centers described in Table I, as well as other possible models which would lead to symmetries and spin consistent with EPR data. Figure 2 represents the diamond lattice in the $(1\bar{1}0)$ plane, showing the possible sites in which the impurities could be placed in the beginning of each simulation. All atomic positions were later relaxed, according to convergence criteria discussed in Sec. III.

A. Isolated nickel

Substitutional nickel in diamond was considered in several charge states, with the results summarized in Table II. In

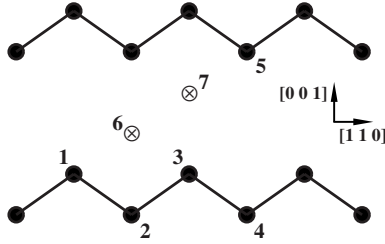


FIG. 2. Representation of the diamond lattice in the $(\bar{1}\bar{1}0)$ plane. Carbon atoms are represented by black circles. Labels from 1 to 5 indicate the crystal site positions where the impurities could be placed. The figure also shows two tetrahedral interstitial sites (6 and 7), represented by the \otimes symbol, in the $[111]$ direction.

the case of the neutral charge state (Ni_s^0), the center has no point symmetry (C_1), and presents a spin $S=1$. This configuration is only 0.1 eV more stable than the center in a constrained C_{3v} symmetry (Ni_s^{0*}). Figure 3 displays the induced energy eigenvalues in the gap region for substitutional nickel impurity. The gap states of Ni_s are vacancy-like orbitals, consistent with the vacancy model.¹⁵

Table II also presents the results for interstitial nickel. In the positively charged state (Ni_i^+), the center was initially simulated in a trigonal (C_{3v}) symmetry, in order to check if that configuration could explain the properties of the NIRIM-2 center.¹¹ In that symmetry, it presented an effective spin $S=1/2$ and an 2E multiplet ground state. By releasing the symmetry constraint, there was an energy gain of about 0.2 eV, and the center distorted to a C_{1h} symmetry. This symmetry lowering was very small, corresponding to a distortion on the nickel atom of only 0.06 Å toward one of its second-nearest neighbors, breaking the trigonal symmetry. Figure 4 compares the electronic structures of the Ni_i^+ center in both symmetries, showing that although the symmetry

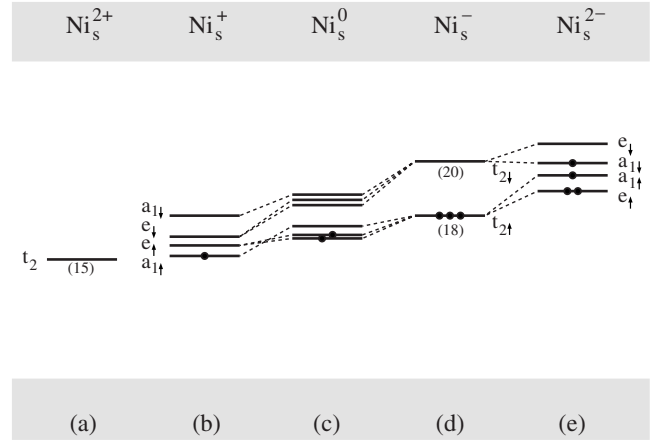


FIG. 3. The Kohn-Sham spin-polarized energy eigenvalues (around the Γ point) representing the 3d-related Ni levels in the gap region for isolated substitutional nickel in different charge states: (a) Ni_s^{2+} , (b) Ni_s^+ , (c) Ni_s^0 , (d) Ni_s^- , and (e) Ni_s^{2-} . Levels with spins up and down are represented by \uparrow and \downarrow arrows, respectively. The occupation of the gap levels is given by the number of filled circles. Numbers in parentheses represent the d -character percentage of charge inside the Ni atomic sphere.

lowering was small, there were strong effects in the electronic structure of the center. These results show that the electronic structure of interstitial nickel cannot be described by the LW model¹⁴ since the 3d nickel-related states remain resonant in the valence band, leaving a hole in the perturbed valence-band top. In trigonal symmetry, the valence-band top of the diamond crystal splits into an a_1 state, resonant in the valence band, and an e state, occupied by three electrons, inside the gap. In the C_{1h} symmetry, the e gap states split further in an a' and an a'' irreducible representation.

TABLE II. Results for isolated Ni and Ni-divacancy complexes in diamond: symmetry, spin (S), multiplet ground state (${}^{2S+1}\Gamma$), formation energies (E_F), and transition energies (E_t , with relation to the valence-band top ϵ_v). Here ϵ_F is the Fermi energy. The table also presents the calculated hyperfine parameters (A_i , where $i=1,2,3$) in the ${}^{61}\text{Ni}$ nucleus. Energies and hyperfine parameters are given in eV and MHz, respectively.

Center	Symmetry	S	${}^{2S+1}\Gamma$	E_F	E_t	A_1	A_2	A_3
Ni_s^{2+}	T_d	0	1A_1	$3.9+2\epsilon_F$	2.0(2+/+)			
Ni_s^+	C_{3v}	1/2	2A_1	$5.9+\epsilon_F$	2.6 (+/0)	123	-36	-36
Ni_s^{0*}	C_{3v}	1	3E	8.6		52	9	9
Ni_s^0	C_1	1	3A	8.5		45	18	4
Ni_s^-	T_d	3/2	4A_2	$11.5-\epsilon_F$	3.0 (0/-)	18	18	18
Ni_s^{2-}	C_{3v}	1	3A	$15.5-2\epsilon_F$	4.0 (-/2-)	-99	21	21
Ni_i^{2+}	C_{3v}	1	3A	$15.5+2\epsilon_F$	0.6(2+/+)	32	2	2
Ni_i^{+*}	C_{3v}	1/2	2E	$16.3+\epsilon_F$		29	15	15
Ni_i^+	C_{1h}	1/2	2A	$16.1+\epsilon_F$	1.1 (+/0)	66	19	17
Ni_i^0	T_d	0	1A_1	17.2				
$(\text{VNiV})^+$	C_{2h}	1/2	2A	$5.2+\epsilon_F$	0.2 (+/0)	51	17	14
$(\text{VNiV})^0$	D_{3d}	1	${}^3A_{2u}$	5.4		6	33	33
$(\text{VNiV})^-$	C_{2h}	1/2	2A	$6.2-\epsilon_F$	0.8 (0/-)	18	-52	-22
$(\text{VNiV})^{2-}$	D_{3d}	0	1A	$7.3-2\epsilon_F$	1.1 (-/2-)			

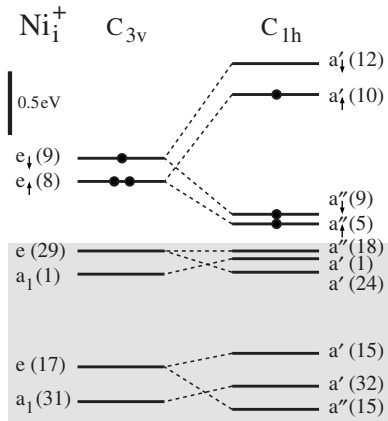


FIG. 4. The energy eigenvalues representing the $3d$ -related Ni levels for isolated interstitial nickel in the positive charge state in C_{3v} and C_{1h} symmetries. Levels with spins up and down are represented by \uparrow and \downarrow arrows, respectively. The occupation of the gap levels is given by the number of filled circles. The numbers in parentheses represent the d -character percentage of charge inside the Ni atomic sphere.

B. Ni-vacancy complexes

We initially considered an interstitial nickel paired with a nearest-neighboring vacancy (Ni_iV), as suggested as a stable configuration in several experiments.¹⁹ However, this configuration was unstable and the impurity moved toward the vacant site, forming a substitutional nickel.¹¹ We additionally considered a substitutional nickel paired with a nearest-neighboring vacancy (Ni_sV), but in the final relaxed structure, the nickel remained in the middle position between two vacancies (VNiV). Figure 5 presents the induced energy eigenvalues of this last complex, and Table II presents the respective properties.

The electronic structure of the VNiV complex cannot be described by the LW model, as it has been recently

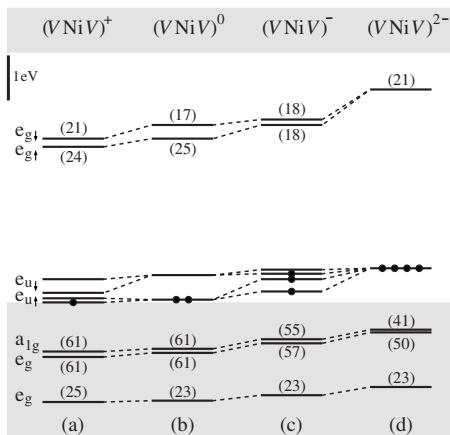


FIG. 5. The energy eigenvalues representing the $3d$ -related Ni levels in the gap region for the Ni-divacancy complexes: (a) $(\text{VNiV})^+$, (b) $(\text{VNiV})^0$, (c) $(\text{VNiV})^-$, and (d) $(\text{VNiV})^{2-}$ centers. The occupation of the gap levels is given by the number of filled circles. The numbers in parentheses represent the d -character percentage of charge inside the nickel atomic sphere. Levels with spins up and down are represented by \uparrow and \downarrow arrows, respectively.

suggested.²³ Our results indicate that the relevant electronic properties of this center should be associated to divacancy-like orbitals, which appeared in the gap, while the Ni-related orbitals remained resonant and inert inside the valence band. On the other hand, the electronic structure is well described by the crystal-field theory, in which the electronic states can be interpreted as resulting from an interaction between the divacancy states and those of the Ni atom. The one-electron ground-state structure of a diamond divacancy in D_{3d} symmetry has the $a_{2u}^2 a_{1g}^2 e_u^2 e_g^0$ configuration. In that symmetry, the Ni $3d$ energy levels are split into $2e_g + a_{1g}$. When a Ni atom is placed in the middle position of a divacancy, its e_g energy level interacts with the carbon dangling bonds, leaving a fully occupied nonbonding t_{2g} -like ($e_g + a_{1g}$) orbital inside the valence band. On the other hand, the Ni e_g state interacts with the divacancy e_g gap level, leaving the e_g -bonding level in the valence band and the e_g -antibonding one unoccupied in the gap. The relevant electronic properties of this center are related to the e_u divacancy-like orbital, which remained in the gap bottom. In the positive and negative charge states, the symmetry lowering ($D_{3d} \rightarrow C_{2h}$) is very weak and the splitting in the e_u -related states is smaller than 0.1 eV.

C. Ni-B complexes

We now consider complexes involving nickel and substitutional boron, which could potentially lead to a trigonal symmetry, to be consistent with proposed models for Ni-B centers presented in Table I. For interstitial nickel-substitutional boron pairs, we considered three microscopic configurations, according to Fig. 2: Ni_iB_s pair, with Ni and B, respectively, in sites 6 and 1; Ni_iCB_s pair, with Ni and B, respectively, in sites 6 and 4; and $\text{Ni}_i \otimes \text{B}_s$ with Ni and B, respectively, in sites 7 and 1. Table III presents the properties of those centers in several charge states. The $(\text{Ni}_i\text{B}_s)^{0*}$ complex has a degenerate configuration in C_{3v} symmetry, coming from the partially occupied e state, favoring a symmetry lowering to C_1 . The distance between the Ni and B in the pairs is crucial for the final properties of those centers, as evidenced by the electronic structure of those three centers, in the same charge state, shown in Fig. 6. The major difference emerges on the character of the highest occupied level in the center. While for the Ni_iB_s and Ni_iCB_s pairs, this level has a localized Ni $3d$ -related character, for the $\text{Ni}_i \otimes \text{B}_s$, this level is essentially delocalized. For this last center, the distance between the impurities is so large that the center can be well described by an ionic model, in which the role of boron is only to accept an electron from the nickel impurity. Therefore, the electronic structure of this complex can be well described as an isolated interstitial nickel in $2+$ charge state (Ni^{2+}).

For substitutional nickel-substitutional boron, we considered two structural configurations, according to Fig. 2: Ni_sB_s pair, with Ni and B, respectively, in sites 3 and 4; and $\text{Ni}_s \otimes \text{B}_s$ pair, with Ni and B, respectively, in sites 1 and 5. Figure 7 presents the energy eigenvalues of those pairs and Table III summarizes their properties. In the $\text{Ni}_s \otimes \text{B}_s$ centers, boron is far from the nickel impurity, working as just an acceptor, such that the electronic configuration resembles

TABLE III. Results for nickel-boron complexes in diamond: symmetry, spin (S), multiplet ground state ($^{2S+1}\Gamma$), and formation (E_F) and transition energies (E_t , with relation to ϵ_v). The table also presents the calculated hyperfine parameters (A_i) in the ^{61}Ni nucleus.

Center	Symmetry	S	$^{2S+1}\Gamma$	E_F	E_t	A_1	A_2	A_3
$(\text{Ni}_i\text{B}_s)^+$	C_{3v}	1	3A	$14.8 + \epsilon_F$	1.1 (+/0)	7	35	35
$(\text{Ni}_i\text{B}_s)^{0*}$	C_{3v}	1/2	2E	16.1		76	-62	-62
$(\text{Ni}_i\text{B}_s)^0$	C_1	1/2	2A	15.9		40	-56	-27
$(\text{Ni}_i\text{B}_s)^-$	C_{3v}	0	1A_1	$17.3 - \epsilon_F$	1.4 (0/-)			
$(\text{Ni}_i\text{CB}_s)^+$	C_{3v}	0	1A_1	$15.4 + \epsilon_F$	1.8 (+/0)			
$(\text{Ni}_i\text{CB}_s)^0$	C_{3v}	1/2	2A_1	17.2		21	-14	-14
$(\text{Ni}_i\text{CB}_s)^-$	C_{3v}	0	1A_1	$18.2 - \epsilon_F$	1.4 (+/-)			
$(\text{Ni}_i \otimes \text{B}_s)^+$	C_{3v}	1	3A	$15.9 + \epsilon_F$	0.5 (+/0)	7	-17	-17
$(\text{Ni}_i \otimes \text{B}_s)^0$	C_1	1/2	2A	16.4		-5	50	46
$(\text{Ni}_i \otimes \text{B}_s)^-$	C_{3v}	0	1A_1	$17.9 - \epsilon_F$	1.5 (0/-)			
$(\text{Ni}_s\text{B}_s)^+$	C_{3v}	0	1A_1	$3.5 + \epsilon_F$	2.6 (+/0)			
$(\text{Ni}_s\text{B}_s)^0$	C_1	1/2	2A	6.1		-99	55	-32
$(\text{Ni}_s\text{B}_s)^-$	C_{3v}	1	3A_1	$9.0 - \epsilon_F$	2.9 (0/-)	85	1	1
$(\text{Ni}_s \otimes \text{B}_s)^+$	C_{3v}	0	1A_1	$4.7 + \epsilon_F$	2.1 (+/0)			
$(\text{Ni}_s \otimes \text{B}_s)^0$	C_{3v}	1/2	2A_1	6.8		-120	48	48
$(\text{Ni}_s \otimes \text{B}_s)^-$	C_1	1	3A	$9.2 - \epsilon_F$	2.4 (0/-)	42	18	8

that of isolated substitutional Ni impurity, shown in Fig. 3. For the Ni_sB_s pair, boron plays a more important role, affecting the electronic structure of the center, although the magnetic properties of this center are associated with partially occupied energy levels with prevailing nickel character.

D. Ni-N complexes

The nickel and nitrogen complexes in diamond are generally formed as result of high-temperature thermal annealing, in which nitrogen impurities become highly mobile and end up pairing with the less mobile nickel ones. We considered centers with nickel in interstitial, substitutional, and divacancy sites complexing with nitrogen. According to Fig. 2, the Ni_iN_s center has Ni and N atoms in sites 6 and 1, respectively, and the Ni_sN_s center has Ni and N atoms in sites 3 and 4, respectively. Table IV presents the results for Ni-N pairs.

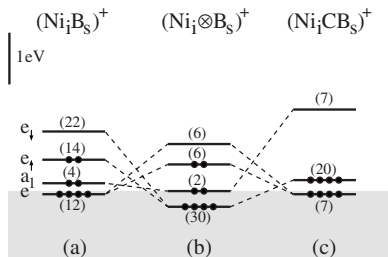


FIG. 6. The energy eigenvalues in the gap region for three configurations involving interstitial nickel-substitutional boron complexes in the positive charge state: (a) $(\text{Ni}_i\text{B}_s)^+$, (b) $(\text{Ni}_i \otimes \text{B}_s)^+$, and (c) $(\text{Ni}_i\text{CB}_s)^+$. The occupation of the levels is given by the number of filled circles. The numbers in parentheses represent the d -character percentage of charge inside the nickel atomic sphere.

Figure 8 describes the electronic structure of Ni-N complexes as resulting from an interaction of the energy eigenvalues of the impurities in isolated configurations. For the $(\text{Ni}_s\text{N}_s)^0$ complex, there is a hybridization between $3d$ -related gap states of Ni_s with those $2p$ -related ones of N_s . This indicates a typical covalent interaction between those two impurities.³⁵ Despite this hybridization, the highest occupied energy level in the $(\text{Ni}_s\text{N}_s)^0$ complex has an e representation, with a prevailing $3d$ character. On the other hand, for the $(\text{Ni}_i\text{N}_s)^0$ complex, the electronic structure results from a weaker interaction between the states of the isolated impurities, more consistent with an ionic model.²⁸ In this last case, the highest occupied level has both $3d$ -related Ni and $2p$ -related N characters.

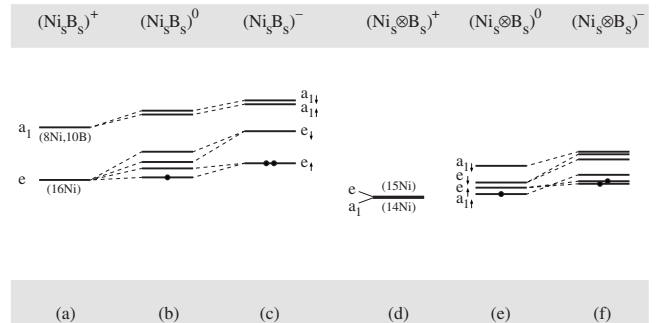


FIG. 7. The energy eigenvalues for the substitutional nickel-substitutional boron complexes in two configurations: [(a)–(c)] for the Ni_sB_s complex and [(d)–(f)] for the $\text{Ni}_s \otimes \text{B}_s$ complex. The occupation of the gap levels is given by the number of filled circles. The numbers in parentheses represent the d -character (p -character) percentage of charge inside the nickel (boron) atomic sphere. Levels with spins up and down are represented by \uparrow and \downarrow arrows, respectively.

TABLE IV. Results for nickel-nitrogen complexes in diamond: symmetry, spin (S), multiplet ground state ($^{2S+1}\Gamma$), formation (E_F) and transition energies (E_t with relation to ϵ_v). The table also presents the calculated hyperfine parameters (A_i) in the ^{61}Ni nucleus.

Center	Symmetry	S	$^{2S+1}\Gamma$	E_F	E_t	A_1	A_2	A_3
$(\text{Ni}_i\text{N}_s)^+$	C_{3v}	0	1A_1	$15.8 + \epsilon_F$	3.2 (+/0)			
$(\text{Ni}_i\text{N}_s)^0$	C_{3v}	1/2	2A_1	19.0		82	14	14
$(\text{Ni}_i\text{N}_s)^-$	C_{3v}	0	1A_1	$22.5 - \epsilon_F$	3.5 (0/-)			
$(\text{Ni}_s\text{N}_s)^+$	C_{3v}	0	1A_1	$6.0 + \epsilon_F$	3.1 (+/0)			
$(\text{Ni}_s\text{N}_s)^0$	C_1	1/2	2A	9.1		-110	70	-30
$(\text{Ni}_s\text{N}_s)^-$	C_{3v}	1	3A_1	$12.6 - \epsilon_F$	3.5 (0/-)	-58	2	2
$(\text{NVNiVN})^+$	C_{2h}	1/2	2A	$3.2 + \epsilon_F$	1.3 (+/0)	28	-20	-24
$(\text{NVNiVN})^0$	C_{2h}	0	1A	4.5				
$(\text{NVNiVN})^-$	C_{2h}	1/2	2A	$7.5 - \epsilon_F$	3.0 (0/-)	177	58	43
$(\text{N}_2\text{VNiVN}_2)^+$	C_{2h}	1/2	2A	$2.7 + \epsilon_F$	3.7 (+/0)	-167	-18	-15
$(\text{N}_2\text{VNiVN}_2)^0$	C_{2h}	0	1A	6.4				
$(\text{N}_2\text{VNiVN}_2)^-$	C_{2h}	1/2	2A	$10.7 - \epsilon_F$	4.3 (0/-)	1	-5	-4

Table IV presents the results for complexes involving nickel and nitrogen impurities in a divacancy site. We considered two possible configurations, according to the proposed models for the NE1 and NE8 active centers described in Table I. The NVNiVN complex involves the precursor VNiV plus two nitrogen atoms in diametrically opposed positions, replacing two of the nickel six nearest-neighbor carbon atoms. The N_2VNiVN_2 complex has four substitutional nitrogen atoms, replacing four of those nearest-neighbor carbon atoms. The electronic structure of those two centers shows a strong covalent interaction between the divacancy-related orbitals and the nitrogen-related ones, which is similar to what is observed for complexes involving cobalt-nitrogen complexes in diamond.³⁶ Nitrogen incorporation into the precursor substantially alters the electronic structure of that center. This shows that the current interpretation, in which nitrogen atoms play a role of only donating electrons to the precursor, is not valid.

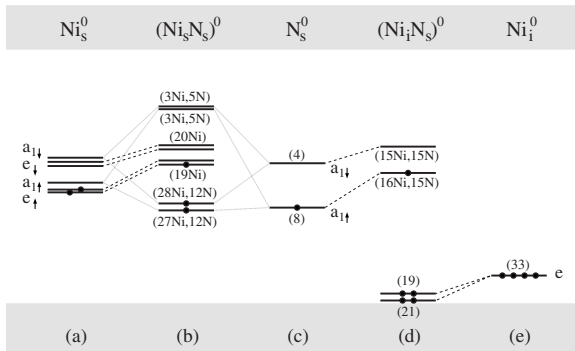


FIG. 8. The energy eigenvalues for the (Ni_iN_s) and (Ni_sN_s) complexes in the neutral charge state. The figure shows that the electronic structure of those centers results from hybridization between the $2p$ nitrogen with $3d$ nickel levels coming from its precursors in isolated configurations.

V. DISCUSSIONS AND CONCLUSIONS

The results are now discussed in the context of the experimentally identified active centers observed in synthetic diamond. In a previous investigation, we have shown that the microscopic configuration of a substitutional nickel in the negative charge state (Ni_s^-) was consistent with the properties of the W8 center,¹¹ including symmetry, spin, acceptor transition energy, and hyperfine parameters. Additionally, we have shown that the previously proposed microscopic models for the NIRIM centers, described in Table I, based on interstitial nickel impurities, were not consistent. For example, the NIRIM-1 center could be better explained by an isolated substitutional nickel in the positive charge state (Ni_i^+).^{11,20} The Ni_i^+ configuration has a very small trigonal C_{3v} distortion away from the T_d symmetry, with the Ni atom moving only 0.02 Å away from its tetrahedral site, resulting in a small energy gain of 0.15 eV.¹¹ This small energy difference could explain the experimental result for the low-temperature $C_{3v} \rightarrow T_d$ transition observed in the NIRIM-1 center. Additionally, the W8 and NIRIM-1 centers have been observed to coexist in the same samples,¹⁹ which could only occur if their respective transition energies lie close to each other in the band gap. According to Table II, the Ni_s^- donor and acceptor transition energies are only 0.4 eV apart. All these elements provide strong evidence that the Ni_i^+ is the microscopic structure of the NIRIM-1 center.

For the NIRIM-2 center, a direct comparison between theory and experiment was more complicated. One of the proposed microscopic models for the NIRIM-2 center was an interstitial nickel with a nearby vacancy.¹⁹ Theoretical investigations showed that this configuration is unstable,¹¹ such that the interstitial nickel migrates toward the vacant site, becoming a substitutional impurity. This would be fully expected considering defect energetics, since the formation energy of substitutional nickel is considerably lower than that of an interstitial one. We have previously suggested that isolated interstitial nickel in the positive charge state (Ni_i^+)

could explain some of the properties of the NIRIM-2 center.¹¹ This investigation shows that Ni_i^+ is unstable in trigonal symmetry, lowering to a C_1 one. However, the energy gain from this symmetry lowering is only 0.2 eV, and the final configuration is not far from a trigonal symmetry. Recently, it has been proposed that NIRIM-2 should involve interstitial nickel with a next-nearest-neighbor boron atom.²⁰ The results for this proposed configuration, $(\text{Ni}_i\text{CB}_s)^0$, are fully consistent with the experimental data for NIRIM-2 in terms of symmetry and spin. Our results indicated that another center, involving boron and substitutional nickel, $(\text{Ni}_s\otimes\text{B}_s)^0$, also provides results consistent with experimental data of NIRIM-2. This last configuration would be a strong candidate to explain the NIRIM-2 center since it involves substitutional nickel, and formation energy is considerably smaller than that for a pair involving interstitial nickel. A definite answer on the NIRIM-2 microscopic model could be achieved if future experiments could resolve the Ni hyperfine parameters, since according to Table III, those parameters are considerably different for those two last configurations.

Another center has been associated to nickel-boron pairs. The NOL1 center, probably the same as the NIRIM-5 center, has been found in heavily boron-doped diamond.^{20,25} The center has trigonal symmetry and $S=1$. By inspection of our results, the $(\text{Ni}_i\text{B}_s)^+$ complex, suggested by Nadolinny *et al.*²⁵ as the microscopic structure of this active center, is fully consistent with the experimental data. Our results indicated that another complex involving interstitial nickel, $(\text{Ni}_i\otimes\text{B}_s)^+$, is also consistent with experimental data. Complexes involving substitutional nickel could also describe the properties of the NOL1 center. The $(\text{Ni}_s\text{B}_s)^+$ complex, suggested in Ref. 20, was found to be diamagnetic and could not explain the NOL1 results. However, the same complex in a negative charge state, $(\text{Ni}_s\text{B}_s)^-$, is fully consistent with the experimental data. Although this center has been only observed in heavily boron-doped diamond, our results indicated that nickel in isolated configurations, Ni_s^{2-} or Ni_i^{2+} , are also consistent with the experimental data. In the case of the Ni_i^{2+} , the high concentration of boron would only be required to place the Fermi level near the valence-band top to access the 2+ charge state, and not necessarily participating into the complex. In order to clarify this, EPR experiments should be performed to observe the hyperfine parameters in nickel and boron nuclei.

For the NE4 centers, experiments²³ have suggested a microscopic structure given by a nickel impurity in a double semivacancy site in the negative charge state $(\text{VNiV})^-$. Our results for this configuration give a trigonal symmetry and a spin $S=1/2$, both results consistent with the experimental findings. The NE4* center,²⁴ from Table I, has been suggested to be formed by $(\text{VNiV})^0$. Our results corroborate that suggestion, although they indicate a trigonal symmetry, while experiments suggested a rhombohedral one. Moreover, our calculations found a hyperfine parameter (A_\perp) of 60 MHz in the nearest-neighbor carbon atoms, very close to the experimental value of 79 MHz.²⁴

The NE1 and NE8 centers have been suggested to be formed by nickel-nitrogen complexes associated to a double semivacancy site.²³ Our results, in terms of spin and symme-

try, for the $(\text{NVNiVN})^-$ and $(\text{N}_2\text{VNiVN}_2)^+$ complexes are fully consistent with the experimental data and the proposed microscopic configurations. However, according to Table IV, the $(\text{NVNiVN})^+$ and $(\text{N}_2\text{VNiVN}_2)^-$ complexes also provide results consistent with those data. However, experiments²³ could not resolve the Ni-related hyperfine fields, in order to compare with the values presented in Table IV. On the other hand, those experiments have identified hyperfine fields in the nitrogen and the nearest-neighbor carbon nuclei. For the NE1 center, the experimental values for those fields are $A_\parallel(\text{N})=59$ MHz, $A_\perp(\text{N})=40$ MHz, $A_\parallel(\text{C})=49$ MHz, and $A_\perp(\text{C})=31$ MHz. For the $(\text{NVNiVN})^-$ complex, our results provide $A_\parallel(\text{N})=42$ MHz and $A_\perp(\text{N})=17$ MHz and negligible values in the carbon nuclei. For the $(\text{NVNiVN})^+$ complex, our results provide $A_\parallel(\text{C})=92$ MHz and $A_\perp(\text{C})=40$ MHz and negligible values in the nitrogen nuclei. Therefore, it was not possible to make a final remark on the microscopic structure of the NE1 center. For the $(\text{N}_2\text{VNiVN}_2)^+$ complex, hyperfine fields in the nitrogen and carbon nuclei are fully consistent with experimental values of the NE8 center. Finally, the $(\text{Ni}_s\text{N}_s)^-$ complex has been proposed as the microscopic structure of the AB5 center.²⁶ From all the complexes involving nickel and nitrogen considered here, that configuration was the only one consistent with the experimental results of the AB5 center.

The results show that one cannot decide, *a priori*, which model, the vacancy or Ludwig-Woodbury one, is better suited to describe the electronic structure of a certain defect system. While the vacancy model is generally suited for substitutional and double semivacancy Ni-related complexes, the LW one is better suited for interstitial Ni-related complexes. Although for complexes involving interstitial Ni, the LW would be favored, a low spin configuration is often observed. Therefore, the electronic structures of transition-metal active centers in diamond are more complex than initially conceived by either the vacancy or LW models. Building microscopic configurations for active centers in diamond, by using EPR data, should take into account the limitations of those two models.

In all centers investigated here, we found that the electronic spin densities were very localized, which resulted in very small relaxations beyond the second-nearest-neighbor atoms of the defect constituents. Additionally, large hyperfine parameters in the nickel nuclei were generally observed. In those complexes in which nickel had small hyperfine parameters, those parameters were large in the carbon or dopant nearest-neighbor atoms, confirming that those centers have a very localized magnetization.

In summary, we have performed a theoretical investigation on nickel-related complexes in diamond, in terms of electronic structure and hyperfine fields. We have explored several microscopic configurations that could explain the experimental data on EPR active centers in synthetic diamond, confirming or discarding some of the previously proposed microscopic models and suggesting different ones. These results provide a comprehensive picture on Ni-related active centers in diamond using a single theoretical methodology.

ACKNOWLEDGMENTS

The authors acknowledge partial support from Brazilian agency CNPq. The calculations were performed using the computational facilities of the CENAPAD and the LCCA-CCE (Universidade de São Paulo).

APPENDIX: CALCULATION OF THE HYPERFINE TENSORS

The EPR data can provide important information related to electrically active centers in semiconductors, such as symmetry, spin, and gyromagnetic factor, and in some stances the atomic composition of those centers. The hyperfine spectrum of a center results from an interaction between nuclear magnetic moments ($\vec{\mu}_I$) and the moments of unpaired electrons. The crystalline field, in which the impurity (or other defects) is immersed, is generally strong enough to quench the respective orbital moment. However, it has been shown that in the case of transition-metal impurities, the orbital moment is not fully quenched by the crystal field, generating, in some cases, a large energy anisotropy. Most of the theoretical investigations have neglected this anisotropic contribution, but it is very important for systems such as those investigated here.

The hyperfine fields were computed using the implementation from the WIEN2K package³⁰ that uses a scalar-relativistic approximation.³⁷ According to that approach, the hyperfine magnetic field (\vec{B}_{hf}) is computed considering three components: the Fermi contact (\vec{B}_c), the dipolar (\vec{B}_{dip}), and the orbital (\vec{B}_{orb}) terms.

$$\vec{B}_{\text{hf}} = \vec{B}_c + \vec{B}_{\text{dip}} + \vec{B}_{\text{orb}}. \quad (\text{A1})$$

These three components are given in terms of the angular (\vec{L}) and spin (\vec{S}) electronic moments (in \hbar unities) and the Bohr magneton ($\beta_e = e\hbar/2m$):

$$\vec{B}_c = \frac{8\pi}{3} \beta_e \vec{m}_{\text{av}}, \quad (\text{A2})$$

$$\vec{B}_{\text{dip}} = -g_e \beta_e \langle \Phi | \frac{S(r)}{r^3} \left[\vec{S} - 3(\vec{S} \cdot \vec{r}) \frac{\vec{r}}{r^2} \right] | \Phi \rangle, \quad (\text{A3})$$

$$\vec{B}_{\text{orb}} = 2\beta_e \langle \Phi | \frac{S(r)}{r^3} \vec{L} | \Phi \rangle, \quad (\text{A4})$$

where Φ is the relativistic large component of the wave function and $S(r)$ is the reciprocal relativistic mass enhancement:

$$S(r) = \left[1 + \frac{\varepsilon - V(r)}{2mc^2} \right]^{-1}, \quad (\text{A5})$$

where ε and $V(r)$ are the kinetic energy and the Coulomb potential, respectively.

\vec{m}_{av} is the average nuclear magnetization,

$$\vec{m}_{\text{av}} = \int \delta_T(\vec{r}') \vec{m}(\vec{r}') d\vec{r}' = \int \delta_T(\vec{r}') \langle \Phi | \vec{\sigma} \delta(\vec{r} - \vec{r}') | \Phi \rangle d\vec{r}', \quad (\text{A6})$$

where $\delta_T(\vec{r}')$ is given in terms of the Thomas radius ($r_T = Ze^2/mc^2$):

$$\delta_T(\vec{r}') = \frac{1}{4\pi r'^2} \frac{r_T}{[2r(1 + \varepsilon/2mc^2) + r_T]} \quad (\text{A7})$$

and $\vec{\sigma}$ are the Pauli matrices.

The splitting in energy resulting from the interaction between the hyperfine magnetic fields (\vec{B}_{hf}) and $\vec{\mu}_I$ is described by

$$E = -\vec{\mu}_I \cdot \vec{B}_{\text{hf}}. \quad (\text{A8})$$

This splitting in energy may be described in terms of a spin Hamiltonian (H). The eigenvalues of this Hamiltonian provide information on the separation between absorption lines in the magnetic spectra,

$$H = \vec{J} \cdot \vec{A} \cdot \vec{I} = (\vec{L} + \vec{S}) \cdot \vec{A} \cdot \vec{I}, \quad (\text{A9})$$

where \vec{I} is the nuclear spin and \vec{A} is a (3×3) hyperfine interaction tensor.

The hyperfine interaction tensor has the following components A_{ij} :

$$A_{ij} = a_{ij}^c \delta_{ij} + a_{ij}^{\text{dip}} + a_{ij}^{\text{orb}}, \quad (\text{A10})$$

with

$$\sum_i a_{ii}^{\text{dip}} = 0 \quad \text{and} \quad \sum_i a_{ii}^{\text{orb}} \neq 0.$$

In an experiment, when the direction of the external static magnetic field ($\hat{n} = \sin \theta \cos \varphi \hat{i} + \sin \theta \sin \varphi \hat{j} + \cos \theta \hat{k}$) is varied with respect to the sample axis, the relevant quantity is the projection of the hyperfine interaction tensor in that direction:

$$\begin{aligned} A(\theta, \varphi) &= \hat{n} \cdot \vec{A} \cdot \hat{n} \\ &= A_{11} \sin^2 \theta \cos^2 \varphi + (A_{12} + A_{21}) \sin \theta \cos \varphi \sin \varphi \\ &\quad + A_{22} \sin^2 \theta \sin^2 \varphi + (A_{23} + A_{32}) \cos \theta \sin \theta \sin \varphi \\ &\quad + A_{33} \cos^2 \theta + (A_{13} + A_{31}) \cos \theta \sin \theta \cos \varphi. \end{aligned} \quad (\text{A11})$$

By choosing a convenient set of six directions, i.e., six sets of (θ, φ) , the values of $A(\theta, \varphi)$ in those directions allows building of the hyperfine interaction tensor. It can be later diagonalized to obtain the three principal values, also called hyperfine parameters (A_1 , A_2 , and A_3), and their respective eigenvectors.

The hyperfine tensor \vec{A} is given in terms of

$$\vec{A} = a^c \mathbb{1} + \vec{B} + \vec{C}, \quad (\text{A12})$$

where $\mathbb{1}$ is the unitary tensor, a^c is the contact term, \vec{B} is a traceless anisotropic tensor related to the dipolar interaction,

and \vec{C} is an anisotropic tensor related to the orbital interaction.

If the angular magnetic moment is quenched, the isotropic part of the hyperfine tensor is exactly the Fermi contact interaction and the anisotropic part is the dipolar interaction. However, if the angular moment is not quenched, there

should be a contribution from this interaction to the hyperfine tensor changing both the isotropic and anisotropic terms. In this investigation, we observed that the hyperfine orbital field is generally relevant and cannot be neglected. This was result of the spin-orbit coupling in the $3d$ localized orbitals, which are deformed due to the crystalline field.

-
- ¹J. Isberg, J. Hammersberg, E. Johansson, T. Wikström, D. J. Twitchen, A. J. Whitehead, S. E. Coe, and G. A. Scarsbrook, *Science* **297**, 1670 (2002).
- ²K. W. Lee and W. E. Pickett, *Phys. Rev. Lett.* **93**, 237003 (2004).
- ³J. J. L. Morton, *Nat. Phys.* **2**, 365 (2006).
- ⁴A. Gali, M. Fyta, and E. Kaxiras, *Phys. Rev. B* **77**, 155206 (2008).
- ⁵D. J. Twitchen, J. M. Baker, M. E. Newton, and K. Johnston, *Phys. Rev. B* **61**, 9 (2000).
- ⁶A. Yelisseyev and H. Kanda, *New Diamond Front. Carbon Technol.* **17**, 127 (2007).
- ⁷J. R. Rabeau, Y. L. Chin, S. Praver, F. Jelezko, T. Gaebel, and J. Wrachtrup, *Appl. Phys. Lett.* **86**, 131926 (2005).
- ⁸E. Wu, J. R. Rabeau, G. Roger, F. Treussart, H. Zeng, P. Grangier, S. Praver, and J.-F. Roch, *New J. Phys.* **9**, 434 (2007).
- ⁹U. Gerstmann, M. Amkreutz, and H. Overhof, *Phys. Status Solidi B* **217**, 665 (2000).
- ¹⁰K. Johnston and A. Mainwood, *Diamond Relat. Mater.* **12**, 516 (2003).
- ¹¹R. Larico, L. V. C. Assali, W. V. M. Machado, and J. F. Justo, *Appl. Phys. Lett.* **84**, 720 (2004).
- ¹²J. P. Goss, P. R. Briddon, R. Jones, and S. Öberg, *J. Phys.: Condens. Matter* **16**, 4567 (2004).
- ¹³D. J. Singh, *Planewaves, Pseudopotentials and the LAPW Method* (Kluwer Academic, Norwell, 1994).
- ¹⁴G. W. Ludwig and H. H. Woodbury, *Solid State Phys.* **13**, 223 (1962).
- ¹⁵G. D. Watkins, *Physica B & C* **117-118**, 9 (1983).
- ¹⁶A. Zunger, *Solid State Phys.* **39**, 275 (1986).
- ¹⁷J. Isoya, H. Kanda, J. R. Norris, J. Tang, and M. K. Bowman, *Phys. Rev. B* **41**, 3905 (1990).
- ¹⁸G. Davies, A. J. Neves, and M. H. Nazaré, *Europhys. Lett.* **9**, 47 (1989).
- ¹⁹J. Isoya, H. Kanda, and Y. Uchida, *Phys. Rev. B* **42**, 9843 (1990).
- ²⁰J. M. Baker, *J. Phys.: Condens. Matter* **15**, S2929 (2003).
- ²¹M. H. Nazaré, A. J. Neves, and G. Davies, *Phys. Rev. B* **43**, 14196 (1991).
- ²²P. W. Mason, F. S. Ham, and G. D. Watkins, *Phys. Rev. B* **60**, 5417 (1999).
- ²³V. A. Nadolinny, A. P. Yelisseyev, J. M. Baker, M. E. Newton, D. J. Twitchen, S. C. Lawson, O. P. Yuryeva, and B. N. Feigelson, *J. Phys.: Condens. Matter* **11**, 7357 (1999).
- ²⁴K. Iakoubovskii, A. Stesmans, B. Nouwen, and G. J. Adriaenssens, *Phys. Rev. B* **62**, 16587 (2000).
- ²⁵V. A. Nadolinny, J. M. Baker, M. E. Newton, and H. Kanda, *Diamond Relat. Mater.* **11**, 627 (2002).
- ²⁶A. J. Neves, R. Pereira, N. A. Sobolev, M. H. Nazaré, W. Gehlhoff, A. Näser, and H. Kanda, *Diamond Relat. Mater.* **9**, 1057 (2000).
- ²⁷<http://www.kc.tsukuba.ac.jp/div-media/epr>
- ²⁸S. Zhao, L. V. C. Assali, J. F. Justo, G. H. Gilmer, and L. C. Kimerling, *J. Appl. Phys.* **90**, 2744 (2001).
- ²⁹L. V. C. Assali and J. R. Leite, *Phys. Rev. B* **36**, 1296 (1987).
- ³⁰P. Blaha, K. Schwarz, G. Madsen, D. Kvaniscka, and J. Luitz, in *WIEN2k, An Augmented Plane Wave Plus Local Orbitals Program for Calculating Crystal Properties*, edited by K. Schwarz (Technical Universität Wien, Vienna, Austria, 2001).
- ³¹J. P. Perdew, K. Burke, and M. Ernzerhof, *Phys. Rev. Lett.* **77**, 3865 (1996).
- ³²L. V. C. Assali, W. V. M. Machado, and J. F. Justo, *Phys. Rev. B* **69**, 155212 (2004).
- ³³L. V. C. Assali, W. V. M. Machado, and J. F. Justo, *Appl. Phys. Lett.* **89**, 072102 (2006).
- ³⁴T. Mattila and A. Zunger, *Phys. Rev. B* **58**, 1367 (1998).
- ³⁵L. V. C. Assali and J. F. Justo, *Phys. Rev. B* **58**, 3870 (1998).
- ³⁶R. Larico, L. V. C. Assali, W. V. M. Machado, and J. F. Justo, *J. Phys.: Condens. Matter* **20**, 415220 (2008).
- ³⁷S. Blügel, H. Akai, R. Zeller, and P. H. Dederichs, *Phys. Rev. B* **35**, 3271 (1987).