

The Twelve-Line 1.682 eV Luminescence Center in Diamond and the Vacancy-Silicon Complex

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Ab initio cluster methods are used to investigate vacancy-impurity complexes in diamond. We assign the 1.682 eV, twelve-line optical band to a vacancy-Si complex which has a very unusual, possibly unique structure with a Si atom at the center of a split vacancy. The method also successfully accounts for the 1.945, 2.156, and 2.985 eV optical transitions in trigonal vacancy-N defects and estimates of radiative lifetimes are given. [S0031-9007(96)01232-X]

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The optical properties of diamond, well known to antiquity, continue to surprise and stimulate theoretical and experimental investigations. There are several reasons for this. Optical properties are invariably related to defects within the diamond and the extremely localized states of many centers amplify the importance of many-body corrections. These defects are then a severe proving ground for theoretical techniques. In addition, the small carbon mass generates substantial electron-phonon coupling, which together with the high degeneracy associated with symmetric defects, often leads to important and subtle Jahn-Teller (JT) effects. The high purity and large band gap of diamond facilitate experimental studies of isolated centers in great detail. Among some of the most important optical centers, vacancy-impurity complexes are particularly prominent. Positron annihilation studies [1] show that vacancies are common defects in chemical vapor deposited diamond. They can occur in aggregates with concentrations up to 50 ppm which persist up to 1100 °C. At a temperature around 600 °C neutral vacancies begin to migrate [2], and readily complex with impurities creating further optically active defects. The best studied of these complexes is the vacancy-nitrogen, [V-N]⁻, complex. This trigonal center gives an emission peak at 1.945 eV which has been correlated with an $S = 1$ electron paramagnetic resonance (EPR) active center [3]. In samples with increasing neutron dose, and lower Fermi levels [4], the 1.945 eV line decreases in intensity while a new line at 2.156 eV grows. It is then suggested that the neutral [V-N] defect is responsible for the 2.156 eV optical transition. Other [V-N_n] defects also exist: the *H*3 center for $n = 2$, the *N*3 center for $n = 3$, and the *B* center for $n = 4$. All are known to be optically active [7,8], with the assignment for the *B* center being tentative.

In contrast to the single or double luminescence lines due to these centers, the [V-Si] defect shows a resolved

set of *twelve* photoluminescent lines around 1.682 eV [9]. Each of the three naturally occurring Si isotopes account for a set of four lines, representing a transition from an orbitally twofold degenerate ground state, split by 0.02 meV, to a doublet excited state split by 1.07 meV. We show here that the origin of these doublets lies in the extraordinary structure of the [V-Si] defect which makes it unique among vacancy-impurity complexes so far investigated.

To deduce the structure and properties of these complexes, we employ spin-polarized local density functional cluster theory, incorporating norm-conserving pseudopotentials using the AIMPRO program [10]. The method calculates the energy and relaxed structures of large H-terminated clusters (~70 atoms for the present study). These clusters are large enough to model the geometrical structure of the defect. The N, Si, and C atoms are treated using first principles pseudopotentials [11], and the hydrogen atoms with a bare Coulomb potential. The wave functions are expanded in s , p_x , p_y , and p_z Gaussian orbitals and the charge density expanded in s Gaussian functions. The basis for N and Si used in all of the calculations consists of four independent atom-sited s and p Gaussian orbitals with different exponents for the expansion of the electronic wave function, and a linear combination of five s Gaussian functions for the fit to the charge density. Four independent s and p Gaussian orbitals are sited on all C atoms, and the charge density fitted by four s Gaussians. To improve the description of the wave functions, a single s and a set of p orbitals are placed at bond-centered locations, and a single s orbital was added to the charge density fit.

More precise estimates of the optical transition energies are made by using the Slater transition method, which predicts the band gap for the "pure diamond" cluster to be 5.8 eV, in good agreement with experiment (5.5 eV).

This value is relatively insensitive to cluster size being 5.7 eV in a 131 atom cluster. The underestimate in the gap size implicit in density functional theory is offset by the confining effect of the H termination which elevates the antibonding states of the conduction band. The effect is similar to the use of a “scissor” operator. Similar shifts are expected for the defect levels and make estimates of the transition energies at best semiquantitative. The radiative transition rates are evaluated from the transition dipole moments using the pseudo-wave-functions of the relevant states.

These methods have previously been used to explore the structures, energy levels, vibrational modes, and reorientation or migration energies of a large number of defects in diamond with conspicuous success: for example, the single substitutional N atom, the *A* and *B* centers [12], the *H3* and *H4* centers [13], and the vacancy and interstitial [15].

To illustrate the use of the method, we consider first the well-studied case of $[V-N]^-$ (see, for example, Refs. [3, 16–18]). The energy levels of this trigonal defect can be understood from those of a vacancy [14,15]. The latter introduces a filled a_1 and partially filled t_2 level into the band gap. For neutral $[V-N]$, where an N atom replaces one of the neighbors of the vacancy, the t_2 level is now occupied by three electrons and lies above the occupied a_1 level. In fact, we found that this a_1 level was pushed downwards towards the valence band leaving a t_2 level deep within the band gap. The trigonal symmetry of $[V-N]$ splits t_2 into a filled a_1 state lying below an e level containing one electron. Thus we expect $[V-N]$ to possess an $S = 1/2$ ground state. In the negative charge state, the e level contains two electrons and thus the system can possess an effective spin of either $S = 1$ or $S = 0$ resulting in 3A_2 , 1A_1 , and 1E ground states. If the orthonormal e orbitals are denoted by x and y , then the many-body states constructed from the pair of electrons occupying these orbitals are

$$\Psi(^3A_2) = \frac{1}{\sqrt{2}}(x_1y_2 - x_2y_1) \times \begin{cases} \alpha_1\alpha_2, \\ (\alpha_1\beta_2 + \alpha_2\beta_1)/\sqrt{2}, \\ \beta_1\beta_2, \end{cases}$$

$$\Psi(^1A_1) = (x_1x_2 + y_2y_1)(\alpha_1\beta_2 - \alpha_2\beta_1)/2,$$

$$\Psi(^1E) = \begin{cases} (x_1y_2 + x_2y_1) \\ (x_1x_2 - y_1y_2) \end{cases} \times (\alpha_1\beta_2 - \alpha_2\beta_1)/2.$$

The energies of these states can be evaluated by assuming that the spin-polarized density functional expression for the energy corresponds to a single Slater determinant [19]. Thus the determinantal configuration wave functions $|x_1 \uparrow y_2 \uparrow\rangle$, $|x_1 \uparrow x_2 \downarrow\rangle$, and $|x_1 \uparrow y_2 \downarrow\rangle$ give the energies of 3A_2 , $\frac{1}{2}(^1E + ^1A_1)$, and $\frac{1}{2}(^1E + ^3A_2)$, and hence each multiplet.

We now describe the results of the calculation. The relaxed $[V-N]^-$ ($S = 1$) defect has trigonal symmetry and the three N-C bond lengths are 1.44 Å. The bond lengths of the three C radicals are 1.45 Å. The Kohn-Sham energy levels revealed the t_2 -derived a_1^\uparrow and a_1^\downarrow levels (occupied) to lie 1.08 and 1.32 eV below the e^\uparrow and e^\downarrow levels. The Kohn-Sham levels in the region of the band gap are plotted in Fig. 1. The wave functions of the e levels have little amplitude on N in agreement with EPR studies [3] and are derived from the three radicals of the vacancy, as indicated in Fig. 2. The total energies of the electronic configurations gave the 3A_2 , 1E , 1A_1 ordering of the multiplets, with energies of 0.00, 0.44, and 1.67 eV, respectively. Thus, in agreement with experiment, Hund’s rule is satisfied.

We now consider the optically excited state found by promoting an electron from a_1^\downarrow to the e^\downarrow level. This leaves a single hole in the e level and corresponds to a 3E term. The vertical excitation energy is the energy difference of these configurations and differs from the zero-phonon line by the relaxation energy of the excited state. A transition state calculation gave an optical energy of 1.77 eV in fair agreement with the 1.945 eV experimentally observed for $^3A_2 \rightarrow ^3E$. The radiative lifetime of ~ 20 ns, compared to the experimental value of 13 ± 0.5 ns [5] is found using the expression [6] $\frac{1}{\tau_{ij}} = 4nE_{ij}^3|\mathbf{x}_{ij}|^2/3$, where n is the refractive index of diamond, and $\mathbf{x}_{ij} = \langle \psi_i | \mathbf{x} | \psi_j \rangle$ and E_{ij} are the dipole matrix element and transition energy, respectively, in a.u. Estimates of the radiative lifetime are sensitive to the transition energy and spatial extent of the wave function. If the experimental transition energy is used in this expression, the estimated lifetime is reduced to 15 ns.

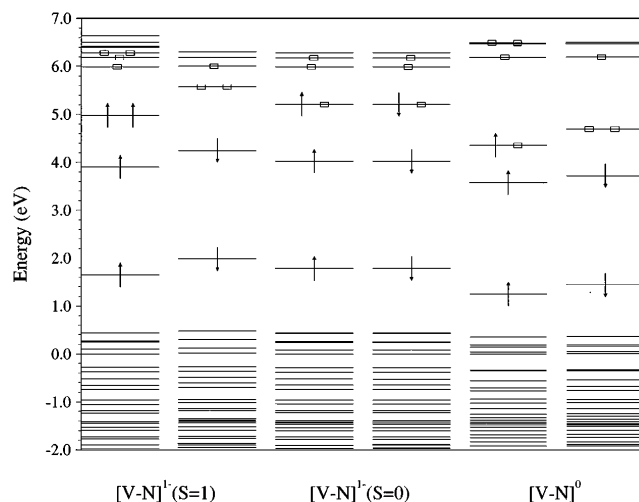


FIG. 1. The spin-polarized Kohn-Sham eigenvalues for the $[V-N]$ complex in diamond. Only the states in the region of the gap are plotted. Arrows indicate occupation and spin, and the empty boxes show empty states. The “valence band tops” have been aligned to facilitate comparison.

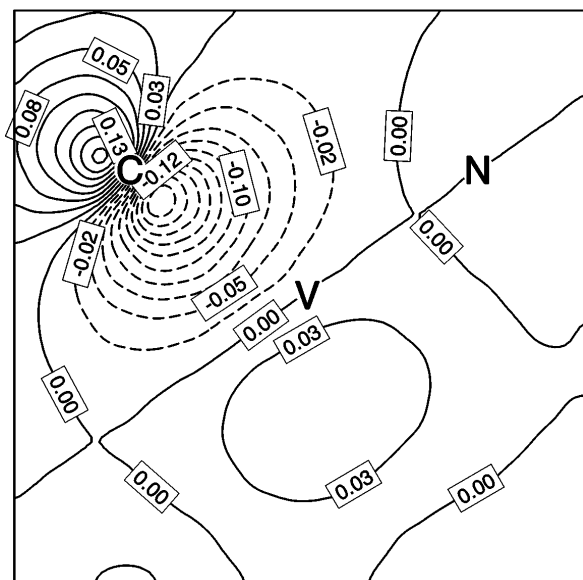


FIG. 2. A contour plot for one of the e -level wave functions (a.u.). The plane passes through the vacancy site which is at the center of the plot, and also through the N and one C atom. Note that the level is nodal at the N atom. The second e level is qualitatively similar.

For neutral [V-N], the e level contains one electron and hence the ground state has 2E symmetry. A transition from the lower a_1 level (Fig. 1) is allowed and we estimate this energy and radiative lifetime to be ~ 1.57 eV and 20 ns, respectively, broadly in agreement with the 2.156 eV observed ${}^2E \rightarrow {}^2A_1$ transition [20] which has an ~ 29 ns lifetime [23]. This estimate is reduced to ~ 10 ns if the experimental transition energy is used. The ground state permits a dynamic JT effect and an A_2 level is then expected to lie close to the 2E ground state [22]. The additional ${}^2A_2 \rightarrow {}^2A_1$ optical transition has been detected about 100 cm^{-1} below the 2.156 eV line.

In both charge states of [V-N], there is a filled a_1 level just above the valence band top, and a transition from this level to the e level has an energy of 3–3.5 eV, and a radiative lifetime of the order of 1 ns. Now, this extremely fast transition has an energy in the nitrogen absorption band, and as a consequence may not be observed. In any case it is not likely to be responsible for either the 1.945 or 2.156 eV spectra.

For the [V-N₃] defect, the ordering of levels in the band gap is reversed with the a_1 level now lying above the e . The upper a_1 level contains just one electron in the neutral charge state. No JT effects are then expected for the ground state of this defect. The excited state possesses 2E symmetry, and might undergo such a distortion, but none are observed [21]. The N-C bond lengths are 1.43–1.44 Å and the C-C bond lengths of the unique C atom are 1.46 Å. The $e \rightarrow a_1$ transition energy at 2.8 eV is in good agreement with the observed value of 2.985 eV for the ${}^2A_1 \rightarrow {}^2E$ transition. The calculated radiative life-

times are 10 and 8 ns using the calculated and experimental transition energies, respectively (cf. experimental estimates of 40 ns [23]). The theory then is able to account for the ground state electronic structure, the symmetries of the principal optical transitions with semiquantitative estimates of their energies and rates.

Fortified by the agreement of these results with experiment, we then considered the [V-Si] complex. We find in contrast to [V-N] defects that the Si atom is unstable at its lattice site and spontaneously moves to the split-vacancy site yielding a defect of D_{3d} symmetry as illustrated in Fig. 3. The six dangling bonds form two gap e levels (Fig. 4) whose states are made up of bonding and antibonding combinations. The lower level is filled and possesses odd parity (e''), whilst the upper is half-filled and has even parity (e'). This configuration produces ${}^3A'_2$, ${}^1E'$, and ${}^1A'_1$ multiplets, and our calculations show that the $S = 1$ spin configuration is around 0.25 eV more stable than $S = 0$, thus agreeing with Hund's rule. The orbitally nondegenerate ${}^3A'_2$ ground state rules out this charge state as a candidate for the 1.682 eV band. However, the position of the deep e levels shown in Fig. 4 suggests that the defect can readily act as an acceptor in synthetic or type Ib diamonds and in the negative ionized case, the upper e' level has a single hole leading to a ${}^2E'$ ground state. An internal optical transition can then occur between the e levels leading to a ${}^2E' \rightarrow {}^2E''$ optical line at 1.86 eV in good agreement with the observed line at 1.682 eV. The doublets are likely to be split by spin orbit or more likely a JT effect. The radiative lifetimes of the transition are estimated to be 3 ns using the calculated transition energy, and 2 ns using the experimental value, which is in excellent agreement with experimental values of 1–4 ns [24].

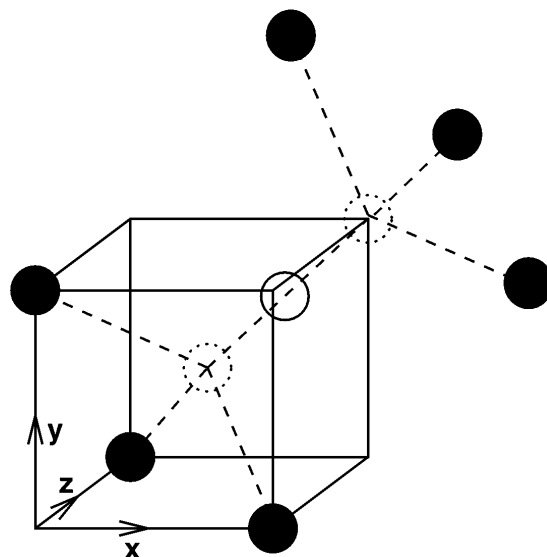


FIG. 3. A schematic representation of the relaxed split-vacancy geometry of the V-Si complex. The solid circles represent C atoms, the empty circle the relaxed Si site, and the dashed circles the diamond lattice sites.

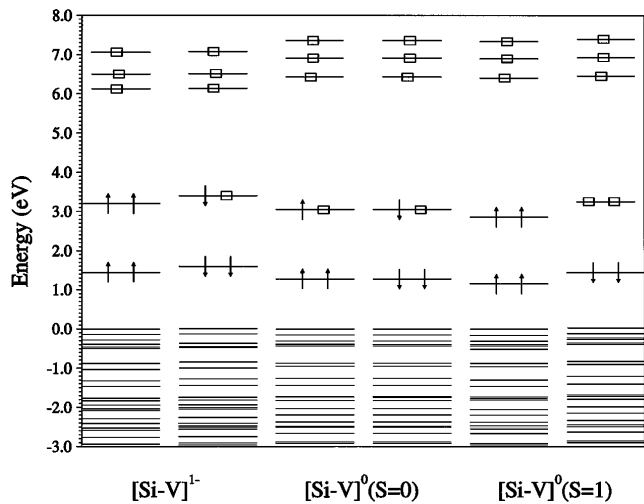


FIG. 4. The spin-polarized Kohn-Sham eigenvalues for the V-Si complex in diamond in the region of the band gap. The notation is as in Fig. 1, and the valence band tops aligned.

The split-vacancy site for Si may well be unique. Preliminary calculations show that in [V-Ge], the impurity does not prefer this site but remains at a C site pushing away its three C neighbors, although a metastable configuration exists in the split-vacancy configuration.

In conclusion, the calculations give a good account of the optical properties of trigonal [V- N_n] defects and point to the [V-Si] $^-$ defect, where Si occupies a split-vacancy site, as being responsible for the twelve optical lines seen around 1.682 eV. This spectrum results from an internal transition between two doubly-degenerate e levels. The ground state is paramagnetic but there is little wavefunction amplitude at the Si nucleus.

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