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Acceptor level of nitrogen in diamond and the 270-nm absorption band

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The 270-nm optical-absorption band is seen in a wide variety of diamonds but there are conflicting opinions about its relationship with the common substitutional nitrogen center. Here we use density-functional theory to show that in addition to a deep donor level, substitutional nitrogen has an *acceptor* level lying in the gap, which is involved in the 270 nm transition. Specifically we show that the calculated level and its stress response are consistent with those of the 270 nm defect. This indicates that substitutional nitrogen in diamond has three charge states and not two as has been commonly assumed. We also show that N_s^+ has an absorption band with a peak around 270 nm and hence can account for the lack of correlation between the 270-nm band and N_s^0 in those diamonds containing centers which compensate nitrogen. Finally, we discuss the origin of the 271-nm absorption feature and suggest that the nitrogen-hydrogen center is a strong candidate.

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Fifty years ago the first report appeared of electron paramagnetic resonance (EPR) of neutral substitutional nitrogen (N_s^0) in diamond: the P1 center.[1] N_s^0 is trigonal with spin density associated primarily with a unique carbon neighbor. The distortion was originally thought to be Jahn-Teller in origin but calculations showed the highest gap level is derived from an a_1 orbital, and the distortion could be understood as either a pseudo-Jahn-Teller effect, with a close-by unoccupied t_2 level, or a chemical rebonding favoring threefold-coordinated N and C atoms.[2–4] N_s^0 is clearly a donor as electron irradiation, lowering the Fermi level, leads to the formation of N_s^+ and the disappearance of the P1 signal.[5] Electrical conductivity and Seebeck measurements demonstrate that it behaves as a donor, with an ionization energy of 1.7 eV.[6] Optically, the threshold for the ionization to the conduction band is about 2.2 eV; the larger value is attributed to a very small intensity of the zero phonon line (ZPL) consequent upon a large structural change when N_s^0 ionizes. Thus N_s behaves as a deep donor, possessing two thermodynamically stable charge states: N_s^0 and N_s^+.

Recently, we used density-functional theory to investigate the energy levels of a range of defects in diamond.[7] The donor level of N_s could be located reasonably accurately by evaluating the difference in ionization energies $\Delta[E(0)-E(+)]$ of a 64-atom supercell containing N from that of a reference cell containing a marker whose donor level was known from experiment. The donor level of N is then found by shifting the experimental donor level of the marker by $\Delta[E(0)-E(+)]$. Using bulk diamond as a marker, located the (0/+) level of N_s at $E_c-1.5$ eV, in good agreement with experiment. Notably similar calculations suggest N_s also possesses an *acceptor level*, lying at $E_c-1.1$ eV, although we were unaware at that time of any experimental evidence for this level.

In addition to the EPR, a broad optical-absorption (OA) band centered at 270 nm (4.6 eV) has been linked[8] with N_s^0. The main evidence for the identification is that in natural Ia diamonds[9] the intensity of the 270-nm band is linearly related to the concentration of N_s^0 measured by EPR or by the strength of infrared absorption bands around 1130 and 1344 cm^{-1} which have been identified with N_s^0.[10,11] Indeed, the 270-nm band is quite sensitive to the nitrogen concentration and can be used to assay N_s^0. However, this correlation does not appear to extend to all diamonds. In chemical-vapor deposition (CVD) diamonds or type-Ia synthetic diamonds grown at high temperatures, a pronounced OA band with a peak around 4.6 eV was found in material containing little N_s^0.[12] Instead, it was suggested that the 270-nm band was due to a nitrogen-boron center although this would require boron to be present in natural Ia diamonds which seems unlikely. Further, a recent study of high-quality single-crystal CVD diamonds showed that the intensity of the 270-nm band exceeds that expected from the concentration of N_s^0 measured by EPR.[13] These results imply that the 270-nm OA is not solely due to N_s^0.

In type-Ia diamonds, the 270-nm band is broad and composed of several defects with sharp ZPLs together with some phonon replicas. The band is dominated by a center having a ZPL at 4.506 eV and a weaker component has a ZPL at 4.567 eV.[11] These lines are sufficiently sharp enabling their splittings to be studied under uniaxial stress.[11] Such studies showed that these two defects were trigonal, possessed a similar stress response, and the optical lines arise from a dipole transition between a_1 orbitals.

In this Brief Report we investigate using density-functional theory the stress splittings of the lines to determine whether an assignment to nitrogen is justified, especially with reference to the theoretical potential for N_s to act as an acceptor.

We also comment on the trigonal 4.567 eV center and the optical properties of N_s^+. The 4.567 eV center is seen in a wide variety of diamonds: CVD, natural IaA[9] and diamonds grown at high pressure.[11,13,14] Its presence in both natural and single-crystal high-quality CVD diamonds limits possible assignments. For example, we can exclude the trigonal Si-vacancy defect[15,16] as Si is very rarely found in natural diamonds. Also nitrogen dimers can be excluded as these are not found in as-grown CVD diamond. One possibility, is that the center is an N-H defect. Hydrogen is known to occur in a wide range of diamonds and previous studies have shown

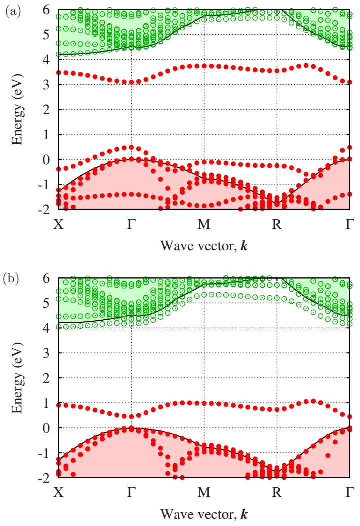

FIG. 1. (Color online) Band structures in the vicinity of the band gap of 64-atom supercell containing (a) N_s^- and (b) $(N\text{-}H)^0$. Full (red) and empty (green) circles show occupied and empty bands, respectively. Localized levels lies near to E_c and E_v in (a) and (b), respectively. The shaded areas show the valence and conduction bands of the defect-free supercell.

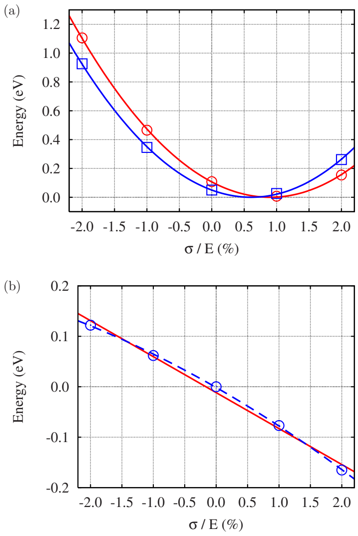

FIG. 2. (Color online) (a) Calculated energy profiles for [111] stress for [111]-oriented N_s defects in diamond. Squares and circles represent N_s^0 and N_s^-, respectively. (b) shows the variation in the electron affinity of N_s as a function of stress. Circles show the calculated data and the two lines show quadratic and linear fits. The zero in energy is defined by the electron affinity in the absence of any applied stress.

that the defect has a large binding energy (4 eV) (Ref. 17) and a donor level at $E_v+1.3$ eV.[7] Such a level suggests an ultraviolet absorption band around 4.2 eV and close to the 4.506 eV ZPL.

We use a spin-density-functional package, as implemented in AIMPRO (Ref. 18 and 19) with the local-density approximation.[20] The wave-function basis consists of atom-centered Gaussians.[21] The charge density is Fourier transformed using plane waves with a cutoff of 350 Ry, yielding well-converged total energies. Core electrons are eliminated by using norm-conserving pseudopotentials.[22] The lattice constant and bulk modulus of bulk diamond are, respectively, reproduced to within ~1% (an overestimate) and 2% (underestimate) of experiment. The calculated direct and indirect band gaps agree with published plane-wave values[23] and the methodology has been tested on many defects in diamond and other materials.[7] We use 64-atom simple cubic supercells of side length $2a_0$ to simulate the nitrogen defects, together with other cells as described below. In all cases we sample the Brillouin zone using the Monkhorst-Pack scheme,[24] using a sampling density of 0.64×10^{-3} Å^{-3} per point. We estimate an error in the relative energies of different structures due to Brillouin-zone sampling of <10 meV.

We are interested in the variation in the acceptor level of N_s^0 with uniaxial stress of magnitude σ in direction defined by n_i (i labels the Cartesian axis). This leads to a displacement of the lattice vectors of a supercell containing the defect by $\delta a_i=\epsilon_{ij}a_j$ (where a sum is taken over the repeated index). Here ϵ_{ij} is the strain tensor arising from the stress tensor $\sigma_{ij}=\sigma n_i n_j$. We use elasticity theory to relate the strain and stress tensors. Test calculations showed that Poisson's constant and Young's E modulus to be 0.1 and 1223 GPa, respectively,[25] in agreement with previous theory and experiment.[26]

The absorption threshold of the $N_s^0+\nu\rightarrow N_s^-+h^+$ optical transition is the sum of the electron affinity $E(-)-E(0)$ of the defect and the energy of the bound hole. Here $E(-)$ and $E(0)$ refer to the energies of the cell containing the defect in the negative and neutral charge states. We shall see that the hole is only weakly bound and hence the effect of stress on this partner is similar to the shift of the valence-band top. This shift is the same for all $\langle 111\rangle$ directions and this implies that the major contribution to the splitting of the optical line under $\langle 111\rangle$ stress comes from the effect of stress on the acceptor level and not on the hole state.

The shift of the acceptor level can be found as follows. In each charge state the equilibrium lattice constant was first obtained by allowing an isotropic variation in the lattice constant to minimize the total energy. Implicit in this approach is the notion that within the real material the dilated N-C interactions are randomly oriented, so that the material *on average* remains cubic. For each direction of stress that we have examined in the case of the defect cell, the lattice vectors have been strained as described above and the location of all atoms allowed to move to minimize the total energy.

In the absence of strain, we find N_s^0 and N_s^- are trigonal, each with a unique and broken N-C bond of length 1.99 and 2.15 Å, respectively. The remaining three N-C bonds are of length 1.46(1.43) Å for $N_s^0(N_s^-)$. The C-C bonds of the unique neighbor are compressed to 1.47(1.45) Å. These short C-C bonds suggest that both charge states would give a local vibrational mode lying above the Raman frequency. Such a mode has been found and detected for N_s^0.[3,27] N_s^+ in contrast is tetrahedral with four N-C bonds of length 1.54 Å.

Figure 1(a) shows the band structure of N_s^-. A localized fully occupied gap level lies near E_c with a_1 symmetry. The top of the valence band is split by the trigonal strain field of the defect into a_1 and e states, the former of which could be

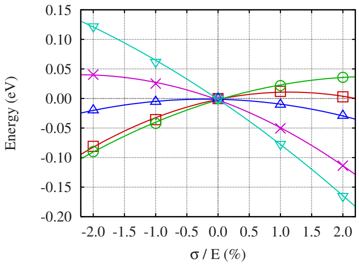

FIG. 3. (Color online) Plot of the variation in the electron affinity of N_s, aligned along [111], as a function of strain σ/E for $[1\bar{1}0]$ (○), [110] (×), [100] (△), [111] (▽), and $[1\bar{1}\bar{1}]$ (□).

involved in the 4.056 eV transition.[11] Figure 2(a) shows the variation in total energy for the neutral and negative charge states of nitrogen as a function of σ/E for stress along the [111] axis parallel to the unique N-C "bond." As one would expect, applying a compressive strain parallel to the bond dilation leads to an increase in energy, with the minima for both charge states lying in the tensile region.

The variation in the electron affinity, $E(-)-E(0)$, is plotted in Fig. 2(b). We find this varies approximately linearly with σ/E, yielding a coefficient of -71 meV/% compressive strain. Thus, under compression of the bond direction characterized by the electrons in an antibonding combination, the acceptor level moves upward in energy. This is precisely as one would expect, with the increase in proximity of the N lone pair and the carbon radical or lone pair, depending upon charge state, destabilizing the defect.

Figure 3 shows the variation in the electron affinity with σ/E in all directions we analyzed. The linear term in the variation is -21.6, -31.5, 2.3, 38.4, and 71.3 in the $[1\bar{1}\bar{1}]$, $[1\bar{1}0]$, [100], [110], and [111] directions, respectively, in units of meV per % strain. These values may be converted into a stress coefficient using Young's modulus, $E = 1223$ GPa,[25] yielding stress coefficients of -1.77, -2.58, 0.19, 3.15, and 5.84 in the $[1\bar{1}\bar{1}]$, $[1\bar{1}0]$, [100], [110], and [111] directions, respectively, in units of meV/GPa.

Now, if N_s are randomly oriented, on an average there will be 25% aligned along [111] and 75% aligned along $[1\bar{1}\bar{1}]$, $[\bar{1}1\bar{1}]$, or $[\bar{1}\bar{1}1]$. Applying uniaxial compressive stress along [111] will result in 25% moving up in energy and 75% moving down. The acceptor level will differ for the two families of defects and the splitting between them is then around 7.6 meV/GPa. Similarly, [110] stress would split the defects into two equal populations with a stress splitting in the acceptor levels of 5.7 meV/GPa whereas under [100] stress, the line would not split.

The splitting of the acceptor level is summarized in Table I along with experimental values for the 4.507 eV transition.[11] Our estimates are about 1 meV/GPa, too large but certainly consistent with an assignment of the optical center to N_s^-.

TABLE I. Experimental values (Ref. 11).

Stress	⟨111⟩	⟨110⟩
N_s	7.6(6.2)	5.7(4.4)
N-H	6.7(5.0)	5.0(4.2)

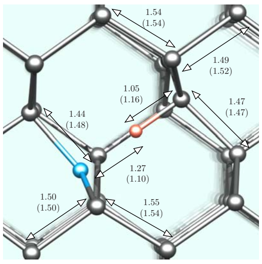

FIG. 4. (Color online) Schematic of the structure of N-H complex. Horizontal and vertical directions are approximately [110] and [001], respectively, with gray, blue, and orange atoms being C, N, and H, respectively. Distances are in Å for the neutral (positive) charge state.

We now turn to the effect of stress on the donor level of (N-H). In this trigonal defect H lies near the center of one N-C bond,[17] as shown in Fig. 4. The calculated donor level lies at $E_v+1.3$ eV,[7] consistent with the band structure [Fig. 1(b)] which shows a fully occupied level close to E_v. We expect then an OA band arising from the ionization of N-H as in $(\text{N-H})^0+\nu \rightarrow (\text{N-H})^+ + e^-$, where the electron is only weakly bonded to the defect. The splitting of the ZPL under stress is then approximately given by the splitting of the donor level found from $E(0)-E(+)$.

The stress-splitting parameters, found in the same way as for N_s^-, are given in Table I and compared with experimental data for the 4.567 eV OA center. Once again we overestimate the experimental splitting by about 1 meV/GPa, and the calculated values are consistent with an assignment of the 4.567 eV ZPL to N-H.

The calculated stretch and bend modes of N-H lie at 3325 and 1404 cm^{-1}, respectively. The downward shifts of the former with ^{13}C and ^{2}H are 6 and 907 cm^{-1}, whereas the shift with ^{15}N is $\ll 1$ cm^{-1}. Experimentally, a number of C-H modes have been reported in CVD diamond[28] and prominent ones lie around 3323 and 3123 cm^{-1} and close to the predicted frequency of N-H. These shifts by 6 and 9 cm^{-1} with ^{13}C and appear to be independent of N isotope. However, these modes are not seen in natural diamond,[29] unlike the 4.567 eV OA line. Thus we believe that the vibrational modes of NH have not yet been reported.

Our calculations suggest that part of the 270-nm band is due to charge-state changes in N_s^0 and N-H. However, in diamonds without nitrogen aggregates, and with low concentrations of N_s^0, the lack of a correlation between its intensity and EPR requires a different explanation. We suppose that in these diamonds, there are compensating centers causing nitrogen to be present as N_s^+. For example, it is known that CVD diamond contains vacancy defects with low-lying levels which can trap electrons in nitrogen donors resulting in the formation of N_s^+.[30,31] This explains why secondary-ion-mass spectroscopy measurements can show a greater concentration of nitrogen than expected from EPR measurements of N_s^0. We suggest that the 270-nm band has a component which is due to the transition $N_s^+ + \nu \rightarrow h^+ + N_s^0$. The ZPL for this transition is the position of the donor level relative to the valence-band top, i.e., 5.5–1.7 or 3.8 eV but the large lattice

TABLE II. Calculated and experimental values in eV for ZPL and absorption peaks for N_s in diamond. Experimental values are given in parenthesis.

Transition	ZPL	Absorption peak
$N_s^0+\nu\rightarrow e^-+N_s^+$	1.5(1.7)	2.9 (?)
$N_s^0+\nu\rightarrow h^++N_s^-$	4.4(4.0)	4.7(4.6)
$N_s^-+\nu\rightarrow e^-+N_s^0$	1.1 (?)	1.4 (?)
$N_s^++\nu\rightarrow h^++N_s^0$	4.0 (?)	4.6(4.6)

relaxation of N_s^0 suggests that the ZPL has weak intensity and that pronounced absorption occurs at the vertical excitation energy.[32,33] Constraining the structure of N_s^0 to be the same as N_s^+, i.e., tetrahedral, gives the vertical transition energy of 4.6 eV and hence we expect that the absorption should peak in the 270-nm band as indeed observed in CVD diamonds with low concentrations of N_s^0.[13] Table II shows the calculated and experimental minimum energy and vertical transition energies. As expected, the greatest differences between the minimum-energy transitions (ZPL) and the vertical transitions (absorption peaks), occur between the neutral and positive charge states.

In conclusion we have used density-functional theory to investigate defects potentially responsible for the 270-nm OA band observed in synthetic, CVD, and natural Ia diamonds. There are at least three defects which possess absorption bands in this region. The dominant one in material where nitrogen is present as a neutral defect is due to the a charge-state change involving the *acceptor level of* N_s. The calculated transition energy, defect symmetry, and stress response agree well with observations.

In material where nitrogen is present as N_s^+, the strong lattice relaxation consequent on a change in charge state from the tetrahedral defect results in a structureless absorption peak at 270 nm. In material containing H, it is proposed that N-H defects possess donor levels around $E_v+1.3$ eV and ionization of these could explain the ZPL at 4.567 eV. Thus nitrogen has a complex and rich role in optical transitions.

Also investigated were the effects of stress on the acceptor level of substitution nitrogen and the donor level of the nitrogen-hydrogen defect. It has been shown that the 4.057 eV ZPL, seen in a wide variety of diamonds, is probably due to a transition where a valence-band electron is trapped by N_s^0. The symmetry, position of the acceptor level near $E_c-1.1$ eV, and the stress response of the transition are consistent with the assignment. This implies that substitutional nitrogen has three charge states and the position of the acceptor level shows that nitrogen would compensate phosphorus which has a donor level of 0.6 eV. Moreover, neutral nitrogen would trap photogenerated or radiation-generated electrons with an impact on diamond radiation detectors. The acceptor level would lead to a photoconductivity threshold around 4.6 eV and which has indeed been observed.[34,35] It will lead to a thermoluminescence trap and several traps with activation energies around 1.2–1.4 eV have been reported in as-grown CVD diamond.[36] It has also been shown that the symmetry, position of the donor, and the stress response of the N-H defect support an assignment to the 4.567 eV ZPL, also seen in a wide variety of diamonds. Finally, we suggest that the 270-nm band seen in CVD diamond with low concentrations of N_s has a component coming from N_s^+ and shows that there have to be deep acceptors present in the diamond.

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