Substitutional oxygen-nitrogen pair in diamond

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Nitrogen is the most important defect in diamond forming a series of aggregates that are used to characterize different types of diamond. Aggregation of substitutional N and O are investigated using detailed *ab initio* plane-wave calculational procedures. Different charge states of the N-N substitutional pair (the *A* center) are considered as well as states of an adjacent O-N substitutional pair. Both are suggested to be stable defects, and in charged negative form the [N-O] defect can lead to shallow defect levels. There is substantial local lattice distortion due to a strong repulsion between ions and this leads to shortened C-N bonds, on which there is a related buildup of charge relative to that on a normal C-C bond, and this is responsible for the shallow levels. Possibly such a defect could even lead to efficient electron emission in a very highly nitrogen doped diamond.

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I. INTRODUCTION

Nitrogen is the most important defect in diamond. As a simple substitutional defect N_C, it forms a deep level at ~ 1.9 eV below the conduction-band edge with a well-defined magnetic-resonance signal that is often labeled as the $P1$ center.[1] These levels are not conveniently located near the conduction-band edges to make diamond an efficient electronic semiconductor, and for this reason a variety of other chemical defects are now being investigated.[2–6] Nitrogen can also pair with other N defects,[7,8] the simplest form being a nearest-neighbor N pair, [N-N] labeled as the *A* center.[9] This is one of the most common defects in diamond and it can also be observed in the positively charged form.[10] In fact, aggregation of N in diamond is quite common and this feature leads to a convenient way of classifying diamond into different types depending upon the nature of the N aggregation. Simple substitutional N_C classifies diamond as type Ib, the presence of *A* centers classifies the diamond as being type Ia*A*. It has also been suggested from electron-spin-resonance (ESR) measurements on powdered diamond that the overall behavior of the *A* center depends on the properties of other defects close to or even on the surface of diamond.[1,10] This follows the observation by Loubser[11] that the intensity of the *A* center ESR signal varied with average particle size.

Oxygen on the other hand has been suggested to lead to *n* type conductivity in diamond,[5] although recent electronic structure calculations[3,12] have shown that such an observation cannot be associated with a simple substitutional neutral oxygen center O_C. Calculations indicate that the defect levels are quite deep and exhibit features similar those of a simple carbon vacancy. The theoretical work did also suggest that in the negatively charged form, occupied shallow levels may arise and the defect could give rise to *n*-type conductivity. Within the supercell calculational procedure employed, the defect levels associated with O_C are found to exhibit both shallow and deep characters in as far as they show significant dispersion with supercell *K*-space vectors over the supercell Brillouin zone. The nature of how such a center acquires charge needs further investigation and especially how O interacts with N. After all, the main source of any *n*-type character in diamond would probably relate to the presence of N which in itself is responsible for raising the effective Fermi energy in the material and characterizing different types of diamond.

There could also be some other applications related to strongly *n*-type diamond that could be associated with electron field emission or even a negative electron affinity in the material. Field emission from diamond would involve the supply of electrons to the bulk material and then transport of electrons to the surface, and finally emission from the surface. Efficient emission measurements will reflect aspects of each of these processes. Sowers *et al.*[13] have suggested that nitrogen donors incorporated into diamond films are associated with additional defects that enhance field emission. Litovchenko[14] has recently suggested a physical model that could lead to a very efficient field emission and even a negative electron affinity effect in a covalent material. The qualitative idea is the presence of some small interatomic distances in the material leading to very large local electron correlations and to an effective repulsion of free electrons from essentially shallow defect states in the crystal. Strong bond compression on defects in a highly covalent material such as diamond coupled with a very high effective Fermi level would therefore make diamond a suitable candidate in light of the Litovchenko model. Should the additional feature that the defects lie in close proximity to the surface, then the potential of negative electron affinity being displayed would be enhanced.

In this paper, we shall investigate properties of charged states of substitutional N-N and O-N pairs in the diamond lattice. The *A* center in diamond which has tentatively been suggested to lie in the vicinity of the diamond surface[1] is thought to have properties that are affected by the surface and other defects present in the material. We also argue that charged states of both [N-N] and [O-N] centers can be stable in diamond, especially at very high N or O concentrations where effectively the Fermi energy in the material is quite high. Such negatively charged centers also have a shallow defect character. The repulsion between N and O also leads to relatively low values of doubly occupied N-C and O-C

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TABLE I. Reduction of 64-atom supercell K to conventional two-atom unit-cell k vectors. Symmetry labels are also indicated for the two-atom (face-centered cubic) fcc unit cell. The side length of the supercell is a_{SC} and the fcc cell a.

$K(2\pi/a_{SC})$	$k(2\pi/a)$
1:(0,0,0)	Γ:(0,0,0),Δ:($\frac{1}{2}$,0,0),Σ:($\frac{1}{2}$,0,$\frac{1}{2}$)
	L:($\frac{1}{2}$,$\frac{1}{2}$,$\frac{1}{2}$),X:(1,0,0),W:(1,$\frac{1}{2}$,0)
2:(0,$\frac{1}{2}$,$\frac{1}{2}$)	(0,$\frac{1}{4}$,$\frac{1}{4}$),($\frac{1}{2}$,$\frac{1}{4}$,$\frac{1}{4}$),(0,$\frac{1}{4}$,$\frac{3}{4}$)
	($\frac{1}{2}$,$\frac{1}{4}$,$\frac{3}{4}$),(1,$\frac{1}{4}$,$\frac{1}{4}$),(0,$\frac{3}{4}$,$\frac{3}{4}$)
3: (0,0,$\frac{1}{2}$)	($\frac{1}{4}$,0,0),($\frac{1}{2}$,0,$\frac{1}{4}$),($\frac{1}{2}$,$\frac{1}{2}$,$\frac{1}{4}$)
	($\frac{3}{4}$,0,0),($\frac{3}{4}$,0,$\frac{1}{2}$),(1,0,$\frac{1}{4}$)
4: ($\frac{1}{2}$,$\frac{1}{2}$,$\frac{1}{2}$)	($\frac{1}{4}$,$\frac{1}{4}$,$\frac{1}{4}$),($\frac{1}{4}$,$\frac{1}{4}$,$\frac{3}{4}$)

bonds but with an increased electron charge density over that of pure diamond. The compressed N-C bonds could possibly also result in a negative electron affinity in line with the mechanism proposed by Litovchenko.

II. COMPUTATIONAL ANALYSIS

Soft pseudopotentials generated through the method proposed by Troullier and Martins[15] with plane-waves of cutoff 64 Ry have been used in the present work. A cubic supercell consisting of 64 atoms was used and all atoms in the supercell were allowed to relax self-consistently. Four special supercell K points[16] have been used to obtain the charge density with electronic interactions evaluated using the local-density approximation (LDA).[17] Specific values of these K points are given in Table I and there we have indicated how these relate to the two-atom unit cell values as discussed by Harker and Larkins.[18]

We have considered neutral, negative, and positive charged forms of the defect, the latter being modeled by simply adding or removing an electron from the 64-atom supercell.

We have also considered the energy of formation of the oxygen defects which is specifically defined in the case of a simple [O-N] defect pair as:[19]

$$E_{form}=E(\mathrm{C_{62}ON})-62\mu_C-\mu_O-\mu_N+q\mu_e\,,$$

where $E(\mathrm{C_{62}O})$ is the total energy of the supercell with one C atom replaced by the O defect and another by N. The chemical potentials are μ_C for C—here taken from a calculation on pure diamond. For O, we obtain μ_O from a recently reported stable structure for a solid-state molecular form of oxygen[20,21] as discussed earlier[12,22] and the value of μ_N has been taken from a calculation on the N dimer as used in calculations of N in GaAs.[23,24] The final term in the expression for E_{form} is included to accommodate charged defects and represents the energy needed to obtain charge from some background potential. This term is necessary to maintain charge neutrality of the above expression for E_{form} as in calculations of charged forms of the defect, electrons are either added or removed from the supercell. The value of μ_e can vary between $0\leqslant\mu_e\leqslant E_g$, where E_g is the energy gap

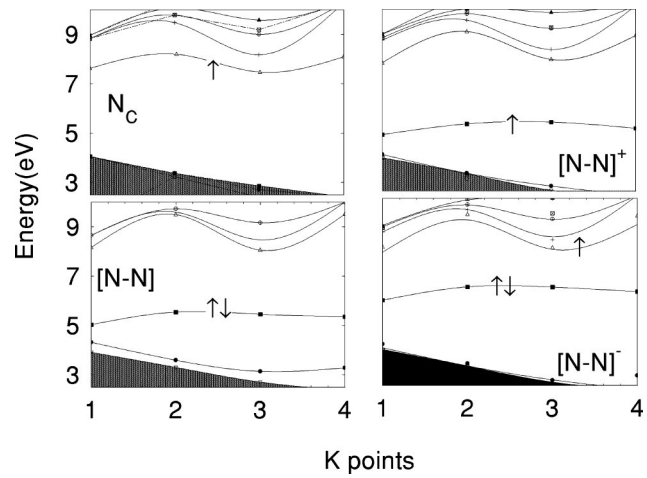

FIG. 1. Energy band of the $P1$ center (N_C) and three charged states of the A center in diamond. Four supercell K points have been used and the curve is a guide to the eye. The lower shaded region represents the fully occupied valence band.

depending upon the nature of the host material but can be calculated implicitly from the calculated Fermi energy of the defect system relative to the energy of the valence-band maximum.[19] The calculated band gap of diamond is 4.5 eV compared to 5.5 eV from experiment. It is well known that LDA severely underestimates the band-gap energy for supercell calculations and this needs to be borne in mind when considering defect energy levels. We hasten to point out that the conventional description of the Fermi level has recently been disputed by Collins[25] who has argued that the position of the Fermi level does not necessarily predict the correct charge state of a defect. Collins proposes that the charge state is influenced by the proximity of the defect to a donor or an acceptor. In light of Collins arguments, defects that are close nearest neighbors would clearly be important.

Another feature of defect aggregation is the relative energy of the aggregates compared to their separate bulk units. In the case of a simple O and N aggregate pair, this would be given from the following balance equation obtained in the calculational procedure:

$$E_{ag}=E(\mathrm{C_{62}ON})+E(\mathrm{C_{64}})-E(\mathrm{C_{63}O})-E(\mathrm{C_{63}N})$$

and this term is independent of chemical potential terms that were discussed earlier. But, as we shall see, this relationship needs to be treated with caution as it presumes exact bulk conditions which may not be the case. We recall, for example, the observations on the A center which tentatively suggest that this defect may exhibit subtle variations in prop-

TABLE II. Formation and aggregation energies for some neutrally charged defects.

Defect	E_{form}(eV)	E_{ag}(eV)
N_C	0.76	
[N-N]	−3.57	−5.09
O_C	4.79	

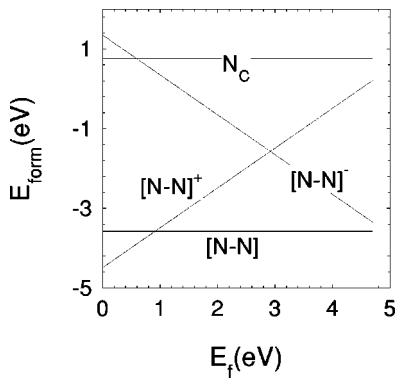

FIG. 2. Formation energies of the N_C, and the A center as $[N\text{-}N]^+$, [N-N], and $[N\text{-}N]^-$ with Fermi energy E_f.

erties as it may be found near to the surface of the diamond rather than in the bulk material.

III. RESULTS AND DISCUSSION

As implied in the Introduction, there are many factors affecting defect aggregation in diamond and the expression for the aggregation energy as presented above does not truly allow for any energetics of defect formation. The equation is simplistic from the point of view that it neglects possible roles played by secondary defects—for example, distant vacancies—or the location of the defect relative to the surface that may also indirectly accommodate any lattice relaxation and affect the aggregation energy. For this reason, we use the relation between N_C and the well-known A aggregate [N-N] to benchmark the accuracy of the present calculation. We consider the various (one-electron) energy levels and also the relative values of the defect formation and aggregation energies in several charged forms. Thereafter, we consider some different possible O-N complexes and identify their relative stabilities. When we present the defect energy levels, we recall that the conduction-band minima of bulk diamond occurs in the region $\Gamma<K<X$ of the supercell, a point that has been alluded to in a recent paper.[26]

A. *P*1 and *A* center formation

In Fig. 1, we show the defect-related band structure of N_C, $[N\text{-}N]^+$, [N-N], and $[N\text{-}N]^-$ defects in diamond and in Table II we give the calculated formation energies of these defects and also that for the O_C center. Figure 2 shows the variation of the formation energy with Fermi energy. A defect energy level emerging for both [N-N] and $[N\text{-}N]^+$ centers is located around the middle of the energy gap in agreement with early cluster model calculations[27] and this level is completely filled for [N-N]. With $[N\text{-}N]^-$ the additional electron occupies a perturbed conduction-band level, there is variation in energy of this state with K vector following that of the conduction-band showing that an extra electron is occupying a level that is pinned to the conduction-band. However, the calculated formation energy of $[N\text{-}N]^-$ shown in Fig. 2, whilst still being quite low, is always slightly higher than either $[N\text{-}N]^+$ or [N-N] meaning that it would be unstable and as such not observable even with a very high value of the Fermi energy. Table III gives the extent of lattice relation about both the neutral N_C, [N-N], $[N\text{-}N]^+$, and $[N\text{-}N]^-$ defects; again there is agreement with early cluster model calculations.[27]

TABLE III. Lattice relaxation about different charged forms of the [N-N] defect. The nearest-neighbor distance in perfect diamond is 1.54 Å. $*$ shows that earlier calculations are from Ref. (26).

Defect	d_{N-N}(Å)	d_{N-C}(Å)
$[NN]^+$	1.91	1.46
[NN]	2.13(2.14*)	1.49(1.46*)
$[NN]^-$	1.91	1.50

The chemical potential for N is taken from a calculation on the N dimer and as we can see has led to a low formation energy for N_C, consistent with correct expectations for the observed abundance of this defect as the $P1$ center in diamond. The calculated formation energy of various forms of the [N-N] center are also low implying that this center is readily formed again consistent with the observation that it is also a very common defect in diamond. Similarly, the calculated aggregation energy is defined in this case as

$$E_{ag}=E(C_{62}NN)+E(C_{64})-2E(C_{63}N)$$

also indicates that N_C aggregation to make [N-N] is very likely—as indeed is observed. This conclusion does demonstrate that the A center is a very common defect in diamond and the fact that N aggregation occurs is well documented. Now proceeding to calculations related to the interaction of N with O, we use the [N-N] results as a reference benchmark for our calculation.

B. *P*1 and interaction with substitutional O defects

Now we consider the N_C that is located directly next to O_C—in many ways, this is a similar defect to the A center. Furthermore, in line with the A center notation, we label such a defect as [O-N]. Through the formalism described above, some indication of the relative stability of the various charge forms of the [O-N] defect and the relative aggregation of O_C

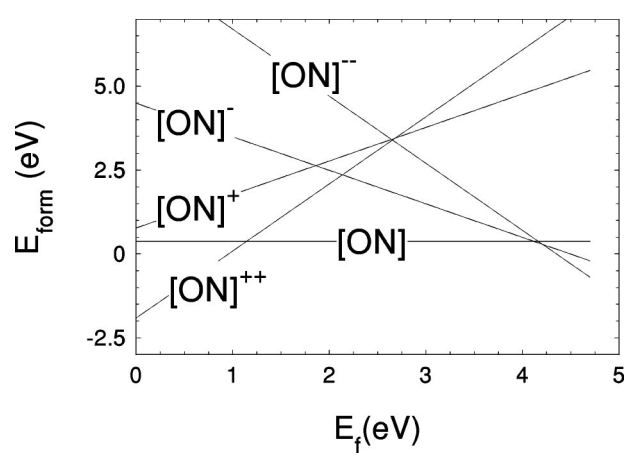

FIG. 3. Formation energies of the nearest-neighbor substitutional [O-N] pair in various charge states with Fermi energy E_f.

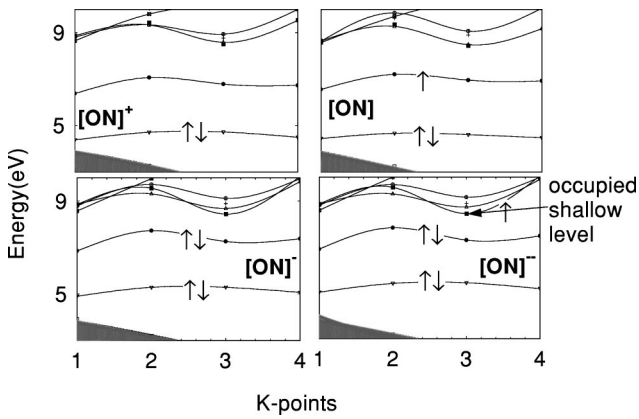

FIG. 4. Energy-band structure of various charged forms of [O-N] nearest-neighbor pairs in diamond. Vertical arrows denote electrons. The occupied shallow level shown is <0.3 eV below the last part of the conduction band and arises from the strong compression of a C-N bond as discussed in the text.

and N_C (the $P1$ center) can be obtained. In Fig. 3, we now show the calculated formation energies for various charge states of the [O-N] defect and in Fig. 4 the defect related band structure.

The behavior follows that found earlier[26] for the simple substitutional O_C, namely, that the higher the Fermi energy the more likely it is to find the defect in a negatively charged state. This is contrary to our calculations for the A center. As with simple substitutional O_C several defect levels appear in the energy gap and some of these we relate to a vacancylike character of the defect. This can be seen from the charge density about the [O-N] center. A typical charge density plot is shown in Fig. 5 specifically for the double negatively charged form of this defect, $[\text{O-N}]^{--}$. Very little charge is located between N and O and this is the origin of the vacancy character.

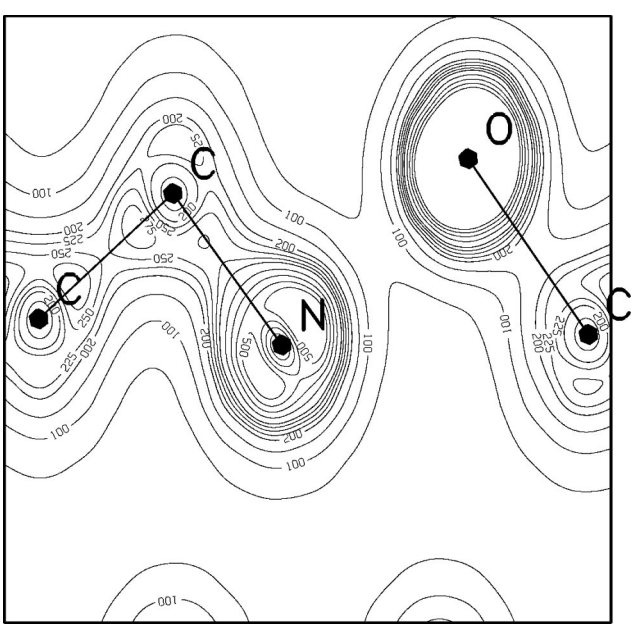

FIG. 5. Charge density about the $[\text{O-N}]^{--}$ defect in the [110] crystal plane. Ion locations are for the fully relaxed lattice. Contours are in units of $me/(\text{bohr}^3)$.

TABLE IV. Lattice relaxation about different charged forms of the [O-N] defect. The nearest-neighbor distance in perfect diamond is 1.54 Å.

Defect	d_{O-N}(Å)	d_{O-C}(Å)	d_{N-C}(Å)	d_{C-C}(Å)
$[\text{ON}]^{++}$	1.94	1.60	1.47	1.51
$[\text{ON}]^{+}$	2.15	1.52	1.45	1.51
[ON]	2.15	1.60	1.45	1.51
$[\text{ON}]^{-}$	1.97	1.57	1.48	1.51
$[\text{ON}]^{--}$	2.17	1.64	1.45	1.48

There is a related repulsion between the N and O ions which we can see from the calculated inter-ionic spacings between ions shown in Table IV and where the distance between O and N ~ 2 Å in all charged forms. Compared with the unrelaxed interionic distance in diamond of 1.54 Å, this relaxation is substantial. As the N or O ion moves relatively outward, the outer bonds between N and C are compressed and, as seen in Fig. 5, a build up of charge arises. Specific distances of the N-C and O-N bonds are also included in Table IV. Each of the three N-C bonds are substantially reduced to ~ 1.45 Å when in the defect takes the charged form $[\text{O-N}]^{--}$. The smallest value of the C-C bond length is shown in Table IV—this is only very slightly below the value of 1.54 Å for the exact diamond lattice so that the relaxation associated with N and O are quite localized. From the group theoretical point of view, the shallow highest occupied state of $[\text{O-N}]^{--}$ is a degenerate level in the point group C_{3v} of the defect symmetry. This level has an interesting origin. Following the defect levels for the different charge states as shown in Fig. 4, it is at the $[\text{O-N}]^{-}$ charge state that a slight distortion of the conduction-band states start to occur and then with $[\text{O-N}]^{-}$—such a state becomes occupied. The lower-energy states, as we have stated are associated with deep vacancy-related states. The emerging shallow level associated with the strongly compressed N-C bond.

Stability of the [O-N] defect is evident from the calculated formation energies shown in Fig. 3, the stability of the defect relative to its separate forms can be measured from the aggregation energy. Here, we make the assumption that the defect is formed from the $P1$ center and a O_C in a charged form, and aggregation energies are given in Table V. These values have to be treated with some cation as we outlined earlier but we see that the values are not far from those

TABLE V. Aggregation energies for the [O-N] center.

Defect	E_{ag}(eV)
$[\text{O-N}]^{++}$	-3.67
$[\text{O-N}]^{+}$	-2.38
[O-N]	-5.17
$[\text{O-N}]^{-}$	-4.08
$[\text{O-N}]^{--}$	-4.82

calculated for the *A* center. Thus, all charged forms of the [O-N] defect are quite stable but significantly is $[\text{O-N}]^{--}$.

IV. CONCLUSION

The *A* center [N-N] is a common defect in diamond. Calculations presented here have shown that both the positive and neutral forms of this defect are likely but any negatively charged form not so. This is consistent with our observation. Subsequently, using results of the *A* center as a benchmark to our calculations, we then argued that a similar defect to the *A* center [O-N], an adjacent substitutional O_C and N_C is stable in diamond. As with O_C, the defect has both a vacancy character and yet in the highly negatively charged form would exhibit a shallow defect character that could lead to an *n*-type conductivity. This defect introduces substantial local lattice distortion with the outward relaxation between O and N causing compression of the N-C bonds, where there is also a buildup of electronic charge relative to bulk diamond. The compressed bond is responsible for the shallow level features of the negatively charged form of the defect. At a qualitative level, the shallow *n*-type character of the charged defect $[\text{O-N}]^{--}$ coupled with a strongly localized buildup of charge, adjacent C-N bonds may possibly lead to an efficient electron emission. Furthermore, as there is some analogy of the [O-N] defect to that of the *A* center, given that ESR results have suggested that this defect is located near the diamond surface, then should [O-N] defects follow a similar behavior, this would also strengthen their potential role as shallow *n*-type centers and even possible bulk sources for negative electron affinity.

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