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Nitrogen and nitrogen-vacancy complexes and their formation in diamond

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Using a semiempirical molecular-orbital technique, incorporating Car-Parrinello molecular dynamics, the structure and properties of the common aggregates of nitrogen atoms in diamond have been investigated. Nitrogen-vacancy complexes have been examined in the same way, showing that, as is observed, it is energetically favorable for the nitrogen to form aggregates and for the vacancies to be trapped at the nitrogen, whatever its state of aggregation. The activation energy for migration of the vacancy was found to be 2.4 eV, in close agreement with experiment, and the processes by which the nitrogen complexes trap vacancies were modeled. The mechanisms involved in the migration of the single nitrogen atom and its aggregation to form pairs are explored. It is found that a vacancy-assisted mechanism has an activation energy of 4.5 eV, and a direct atomic exchange of the nitrogen with its carbon neighbor has an energy of 6.3 eV. These values straddle the experimental estimate of 5 eV and would indicate why radiation damage enhances the nitrogen aggregation. The mechanisms involved in the further aggregation of nitrogen pairs to form well-defined clusters of four nitrogen atoms were also modeled, and an activation energy of 7–8 eV found.

I. INTRODUCTION

Nitrogen is the dominant impurity in diamonds.[1–3] It is present in different forms which can be distinguished by their infrared spectra and to a lesser extent visible and electron paramagnetic resonance (EPR) data.[4–6] Rare samples show very little one phonon absorption in the infrared, and it can be shown that they contain very small concentrations of nitrogen. (These are known as Type II diamonds.) More commonly, diamonds contain much larger concentrations — up to half an atomic percent — and show characteristic infrared absorption. Synthetic diamonds produced by the conventional high pressure, high temperature techniques usually contain nitrogen as single substitutional atoms (Type Ib). In most natural diamonds, the nitrogen is present in the form of aggregates of substitutional atoms (Type Ia).

Single substitutional nitrogen has an infrared local mode of vibration at 1344 cm^{-1}, just above the Raman frequency for diamond of 1332.5 cm^{-1}, which involves only the vibration of carbon.[7] There is C_{3v} symmetry — a substantial relaxation of the nitrogen occurs away from one of its carbon neighbors, towards the plane of the other three. It is a very deep donor with an electronic level at about 1.9 eV below the conduction band edge.[8] There is an EPR signal[9] associated with this defect, P1, whose properties originally identified this structure.

The nitrogen aggregates in diamonds are, most commonly, pairs of neighboring substitutional atoms, the *A* aggregate, and groups of four around a vacancy, the *B* aggregate. These three forms of nitrogen give distinct infrared spectra which can be used to give an increasingly accurate measure of the quantity of nitrogen in those forms.[3] Diamonds containing the *A* aggregates have an absorption edge in the ultraviolet part of the spectrum at about 4 eV, which indicates that there is an electronic level deep in the energy gap. Nitrogen is also present in lesser concentrations as aggregates of three substitutional atoms neighboring a vacancy (giving rise to the optical N3 center,[10] known in EPR as the P2 center[9,11]) and in other configurations of pairs.[12,13]

More extended features called platelets appear to contain some nitrogen. They probably contain carbon interstitials, decorated by some interstitial or substitutional nitrogen, but details of their structure is still the subject of speculation and some controversy.[14–17] They also have a distinctive infrared spectrum and can be seen by x-ray diffraction.[18] However, the quantity of nitrogen involved is not known and may vary between platelets.

It can be shown (see review by Evans[19]) that when diamonds containing single nitrogen atoms are heated to about 2000 K under a stabilizing pressure, the nitrogen atoms migrate and come together at first to form *A* aggregates. At even higher temperatures (above 2600 K) the *A* aggregates start to disappear and *B* aggregates and platelets appear. It is possible to anneal the diamonds for long enough at these high temperatures to convert most of the nitrogen into *B* aggregates.

Evans derived activation energies for the diffusion of the single nitrogen atoms of 5 ± 0.3 eV,[19,20] although values of 2.6 (Ref. 21) and 3.6 eV (Refs. 22 and 23) are also quoted in the literature. Because of the uncertainties involved in annealing the diamonds under such extreme conditions, he was unable to derive similar activation energies for the diffusion energies involved in the formation of *B* aggregates.[19]

It is supposed that the nitrogen in a newly grown natural diamond is in the single substitutional form and such diamonds are type Ib, as are synthetic ones. Most natural stones spend a long period, measured in billions of years, under the earth's crust at high temperatures and pressures, before a volcanic eruption brings them to the surface. Depending on the length of that period and the temperature, the nitrogen may migrate to form *A* and then B aggregates. The form of nitrogen in natural diamonds can show something of the geological history of the stones.

Conversely, by examining the likely geological history of some natural type Ia stones containing both A and B aggregates, Evans and Harris[24] were able to estimate activation energies of 6.5–7.1 eV for the formation of the B aggregates.

The charge states of the nitrogen and nitrogen-vacancy complexes is usually neutral which limits the observations possible using EPR. However, many defects involving lattice vacancies are observed by optical spectroscopy[2,3] and show sharp zero phonon lines and vibronic side bands associated with electronic transitions between states localized on the defects. Details of the structure of many of these defects is understood in great detail.

Irradiation of diamonds by electrons or neutrons produces vacancies (V), which are observed as the GR1 (Ref. 25) with a zero-phonon line at 1.673 eV or the ND1 (Ref. 26) (3.150 eV) optical centers, in the neutral or negative charge state, respectively.[27] Neutral vacancies become mobile at about 900 K, with an activation energy of 2.3 ± 0.2 eV, and are captured by the nitrogen aggregates to form other optical centers. In type Ib diamonds, the nitrogen-vacancy (NV) optical center,[28] which has a zero phonon line at 1.945 eV, is produced. In type Ia diamonds, the A aggregates trap vacancies to form H3 optical centers[29] (2.463 eV) or, if negatively charged, H2 centers[30] (1.257 eV); the B aggregates trap vacancies to form H4 centers[31] (2.498 eV).

The H3 defect consists of two nitrogen substitutional atoms bound to the same vacancy (N-V-N), which involves some reordering when the A aggregate nitrogen pair traps the vacancy (N-N-V). The H3 center has been investigated thoroughly experimentally[29] and its structure and vibronic properties are well established. It has also been studied theoretically in some detail by an *ab initio* local density technique,[32] with good agreement with the experimental data.

The H4 defect, formed when a B aggregate traps a vacancy, has C_{1h} symmetry and probably forms[33] when one of the nitrogen atoms of the B aggregate moves into the trapped vacancy (see Fig. 1). It has also been modeled theoretically[32] in the same way as H3.

When the diamond is irradiated, even with a low dose creating a much lower vacancy concentration than that of nitrogen, then the nitrogen aggregation is greatly enhanced.[34] This may indicate that a vacancy-assisted mechanism has a lower activation energy than the normal nitrogen migration or that the vacancy-assisted mechanism is the normal one and the limiting step is the capture of one of the rare vacancies by the nitrogen. These cases could be distinguished by examining the dynamics of the aggregation. If the migration is vacancy related, each vacancy must be involved in the migration of many different nitrogen atoms.

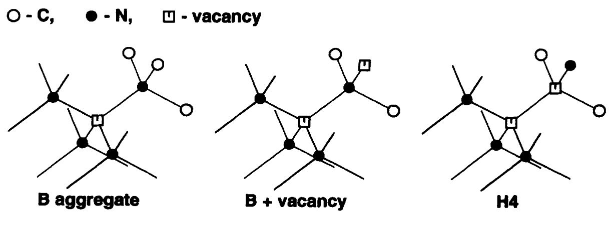

FIG. 1. The B aggregate of nitrogen and the H4 defect.

In this paper, the molecular orbital technique described in Sec. II has been used to explore the structure and energy of the nitrogen and nitrogen-vacancy complexes already described. The results are presented in Secs. III and IV. In Sec. V, estimates of the energies of the complexes with respect to their isolated components show whether aggregation is likely to take place, but in order to study the dynamics, detailed models of the processes must be explored. Calculations of the energies of the saddle points in the migration path of the vacancy (Sec. VI) and nitrogen (Sec. VI) show which processes are involved in their aggregation.

II. THEORETICAL MODEL

The complete neglect of differential overlap (CNDO) molecular-orbital method is a self-consistent semiempirical program which has been used successfully to calculate the properties of defects in diamond.[35–37] The version we use here incorporates Car-Parrinello molecular dynamics.[38,39] The empirical parameters were derived to reproduce the band structure of pure diamond[40] and have been used for other nitrogen-related defects in diamond.[36,37,41]

Two atomic clusters were used, one of 69 atoms centered on an atom site and the other of 74 atoms centered on a bond center. In each case the outer atoms consisted of only the sp^3 hybrids directed into the cluster to eliminate dangling bonds and the problems associated with the hydrogen termination of clusters.

In comparing the energies of different defects, there can be some ambiguity in deciding which cluster energies to use. There is often a problem associated with the Fermi energy being at different absolute levels particularly when the energies of the different charge states of a defect cluster are compared,[42] but in the present work the valence band levels did not vary in energy significantly. Similarly, comparing the energies of a defect in different clusters or at different positions in the same cluster can cause discrepancies. The defect energies quoted below are all comparisons between the total energies of the defect in a cluster and the same cluster containing no defect; for example, the single nitrogen substitutional energy E_N in an n atom cluster of diamond is

$$E_N = E(NC_{n-1}) - E(C_n) \ . \tag{2.1}$$

On the other hand, the energies of complex defects are quoted relative to the energies of their constituent simple defects, calculated in the same position in the same cluster, for example, for the NV center $E_{\rm NV}$:

$$E_{\rm NV} = E(NVC_{n-2}) - E(NC_{n-1}) - E(VC_{n-1}) + E(C_n) \ . \tag{2.2}$$

III. NITROGEN AGGREGATES

A. Single substitutional nitrogen

A nitrogen atom replacing the central carbon one in the 69 atom cluster undergoes a ⟨111⟩ distortion so that one of its four carbon-nitrogen bonds is elongated by about 24%. Previous calculations showed that this relaxation was considerably smaller and strongly dependent on the cluster size.[36] Although the earlier work used the same CNDO approximations and parameters, the relaxation was done by moving atoms explicitly, which is much less reliable than the dynamical method used here. In the 74 atom cluster the nitrogen-carbon bond length was elongated by 25%. Briddon *et al.*[16,17] show in their calculations that this ⟨111⟩ distortion results from the population of an antibonding orbital between the nitrogen and one of its carbon neighbors by the nitrogen's fifth valence electron. They show that the spin of this odd electron is largely concentrated on the unique carbon neighbor rather than on the nitrogen, in agreement with the EPR data.[9] Their calculations give a carbon-nitrogen bond elongated by 28%, with both the carbon and nitrogen moving by about 0.2 Å (see Table I). The carbon's relaxation away from the nitrogen strengthens its bonds to its carbon neighbors and gives rise to the local mode at 1344 cm^{-1}, which involves the vibration of that carbon atom and not the nitrogen. The electron densities calculated here agree qualitatively with all these conclusions, although the local mode frequency was not reproduced. The energy of this defect [see Eq. (2.1)] is 6.1 eV and does not seem to be dependent on the cluster size.

B. The *A* center N-N

The calculations showed that the two neighboring nitrogen substitutional atoms relaxed away from each other in both clusters with an elongation of the N-N bond of about 30% compared to the normal carbon bond length (2.0 Å). The nitrogen bond to the neighboring carbon showed a reduction of 4%. This compares with Briddon's values of about 38% and 5% (Refs. 16, 17, 43 and 44) (see Table I). The total energies of the *A* centers were 10.2 and 10.1 eV in the two clusters, corresponding to an energy reduction of 2 eV relative to two isolated single nitrogen substitutional atoms. The charge density in a (110) plane including the two nitrogen atoms and two of their carbon neighbors is shown in Fig. 2(a). The strong anti-bonding nature of the N-N bond and its elongation can be seen clearly. The energy gain on aggregation of the nitrogen into pairs is due to the lowering of the nitrogen donor level when occupied by the two excess electrons.

TABLE I. A comparison of the geometry of nitrogen defects with *ab initio* calculations (Refs. 16, 17, 32, 43 and 44). All lengths are quoted relative to the normal C-C bond length in diamond.

Defect	Bond	*Ab initio* results	Present calculations
N	C–N	1.28	1.25
	C_3–N	0.95	0.96
A	N–N	1.38	1.30
	N–C	0.96	0.96
B	N–C	0.96	0.96

C. The *B* center

The Loubser–van Wyk[33] model of the *B* center is a tetrahedral arrangement of four substitutional nitrogen atoms around a vacancy. The present calculations show that this configuration has an energy of 12.2 eV above that of an isolated vacancy, or −12 eV relative to four isolated nitrogens and a vacancy. This means that there is an energy gain of 8.2 eV when two *A* centers and a vacancy come together to form a *B* center. However, if a vacancy is not already present, the energy to form the *B* center and a distant carbon interstitial is 5.5 eV. The nitrogens relax outwards by 9.5% from the vacancy, reducing the bond length to the neighboring carbons to

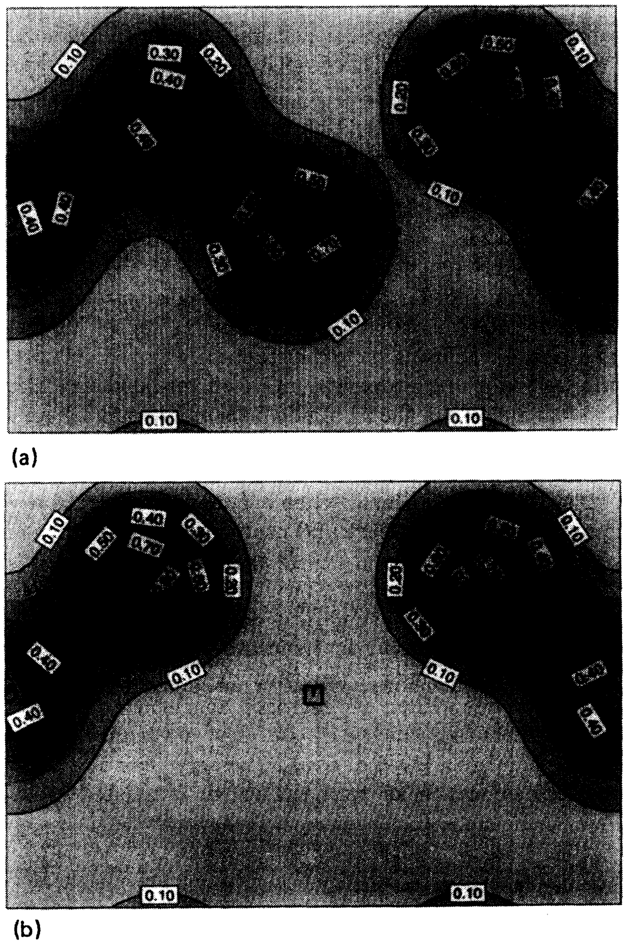

FIG. 2. The valence charge density in a (110) plane including (a) an *A* center and (b) a *B* center. The positions of the nitrogen atoms are shown by filled circles, carbon atoms by open circles, and the vacancy by a square. Only two of the *B* center's four nitrogen atoms are in the (110) plane. The units are electronic charge per cubic atomic unit.

96% of the normal value. This agrees closely with Briddon's structure.[43,44] A similar charge density plot to that of the *A* center is shown in Fig. 2(b).

The similar defect where the four nitrogen atoms are bonded tetrahedrally to a single carbon atom has a higher energy of 30.5 eV, implying that it is unlikely to form from two *A* centers, or indeed from four isolated nitrogen atoms. There is an energy gain of 4.6 eV if it transforms to a *B* center by expelling a carbon interstitial, but a much larger gain of 18.3 eV if it achieves this transformation by trapping a vacancy. (Note the comments in Sec. IV on the reliability of the interstitial comparison — the calculation of the energy gain is likely to be show a greater value than 4.6 eV if the vacancy is modeled with its own orbitals. 4.6 eV should be regarded as an lower limit.)

D. The N3 center

Three substitutional nitrogen atoms in a triangular arrangement, each neighboring a common vacancy is the accepted structure for the N3 optical center and the P2 EPR defect.[11,12] In these cluster calculations the C_{3v} symmetry was preserved, with the nitrogen atoms relaxing away from the vacancy by about 12.5%. The bonds between the nitrogen atoms and their carbon neighbors was reduced to 98% of a normal bond length. The spin associated with the center was largely localized on the sole carbon neighbor to the vacancy, as the EPR data show. The energy of the defect, 8.9 eV above that of an isolated vacancy, or -9.3 eV relative to three nitrogens and a vacancy, is more stable than the smaller aggregates of nitrogen. Like the B center, it is not likely to form unless a vacancy is present; the N3 and distant self-interstitial is 4.1 eV less stable than three distant nitrogen atoms (but note Sec. IV).

It is interesting to look at the equivalent defect with no vacancy (an alternative model for the N3 center.[10,11]) The energy of 18.9 eV shows that it is not energetically favorable for it to form from three distant nitrogen atoms.

IV. NITROGEN-VACANCY CENTERS

Lowther[45] has shown that the nitrogen-vacancy complexes are well modeled by considering the nitrogen merely as a source of charge to be trapped at a vacancy whose symmetry may be lowered by the neighboring nitrogen. The properties of the centers are determined by the vacancy's electronic states. Without placing atomic orbitals at the vacancy site it is difficult to get a good model of the vacancy's electronic structure.[35] If there are atomic orbitals at the vacancy's site, its migration cannot be treated sensibly. Since the object of this work was to examine the migration of defects, the vacancy was modeled without its own orbitals, and the models of the nitrogen-vacancy complexes are examined critically with their possible shortcomings in mind. Comparing the energy of a defect containing a vacancy with that of the isolated vacancy is more reliable than including an interstitial to conserve atoms in the comparison.

A. NV center

There is some relaxation of the nitrogen away from the vacancy — about 8% of the bond length. The spin is located on the carbon neighbors to the vacancy, that is, as near as this model allows to the vacancy itself, as Lowther's model[45] would suggest. It is more stable than its constituent defects [see Eq. (2.2)] by 4.7 eV.

B. H3 center

This defect has been modeled in detail by Jones *et al.*[32] and the structure obtained here is quite similar. The two nitrogen atoms neighboring the vacancy relax away from it by about 9% and the two carbon neighbors to the vacancy also relax away by 10%. The occupied band gap state is localized more on these carbon atoms than the nitrogen, as Jones *et al.*[32] also find. The energies of the band gap states are not as reliable as those of Jones *et al.*, for the reasons discussed, but the qualitative agreement with their wave functions[46] is good. The total energy of the H3 center relative to two separated nitrogen atoms and a distant vacancy is -7 eV, 5 eV more stable than the *A* center and a distant vacancy.

A vacancy trapped next to an *A* aggregate (N-N-V) probably forms as an intermediate configuration in the formation of H3 (N-V-N) centers. In these calculations this defect has an energy 1.1 eV below that of the *A* aggregate and a distant vacancy, or 4 eV above the energy of the H3 center.

C. H4 center

The H4 center forms when the *B* center captures a vacancy, with some reordering of the atoms to form a structure in which a divacancy has three nitrogen neighbors to one vacancy and one nitrogen neighboring the other vacancy (shown in Fig. 1). According to the model, of Jones *et al.*[32] it is the second of these vacancies which dominates the electronic structure. The electron density near this second vacancy looks quite similar to the equivalent calculation around the H3 center, as Jones *et al.* find and use to explain why the H3 and H4 centers have very similar properties.[46] These calculations show that the energy of this defect is -16.9 eV compared to the constituent defects, or 4.9 eV more stable than the *B* center and distant vacancy.

The intermediate configuration where the vacancy is next to the *B* aggregate (B-V) has an energy 10.9 eV higher than H4.

V. AGGREGATION ENERGIES AND MIGRATION

The energies of the defects discussed in Secs. III and IV are summarized in Fig. 3. It can be seen clearly that it is energetically favorable for nitrogen to aggregate into pairs, threes and fours, the latter two including a vacancy. It is also favorable for the nitrogen complexes to capture a vacancy. This can be seen by considering that the sp^3 hybrids of the carbon combine to form the bonding or-

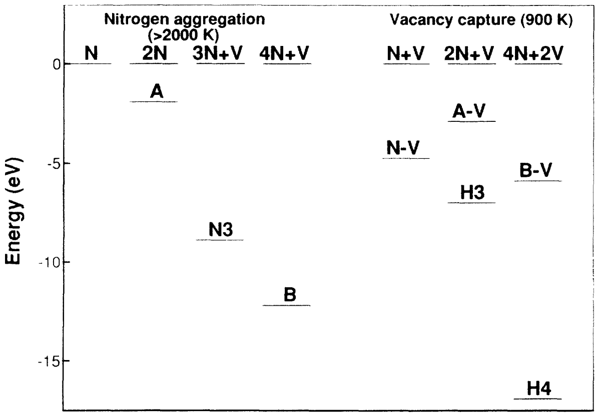

FIG. 3. The energy of the nitrogen and nitrogen-vacancy complexes discussed in the text. – denotes defects at first neighbor positions and + denotes distant defects.

bitals of the valence band and the antibonding orbitals of the conduction band. Nitrogen's extra electron populates the antibonding orbitals, which leads, in the case of the single nitrogen and the *A* center, to a lengthening of the bond concerned. When more nitrogen atoms aggregate, there is both elastic energy required to accomodate the lengthened bonds and the extra energy of more high energy antibonding orbitals. The larger aggregates are only stable if a vacancy, with its relatively low energy band gap electronic levels and inward relaxation, is present. All of the nitrogen aggregates can capture a vacancy. These results agree qualitatitvely with experiment, but in order to examine the quantitative results, intermediate structures in the migration processes must be explored.

The migration of nitrogen, or any other defect, will involve a series of steps over a saddle point configuration, into another stable or metastable site. For example, the migration of a vacancy to be trapped at a nitrogen atom involves many steps in which a neighboring carbon surmounts an energy barrier before dropping into the vacancy. Then when it is close to the nitrogen atom the energies of such configurations as N-C-C-V, N-C-V, and N-V as well as the energy barriers between them will determine the kinetics of nitrogen-vacancy aggregation. It is the energy barrier heights which determine the activation energy for migration.

Nitrogen atoms are heavier than the lattice carbon atoms, so their motion is unlikely to be decoupled from the lattice vibrations in the way that light interstitials could hop or tunnel through the lattice. The motion of the defect and its surrounding atoms must be considered altogether. As the migrating atoms move towards an energy barrier as part of their thermal vibration, the lattice atoms can move to lower the barrier in response to forces the migrating atoms impose on them. For this reason, it is appropriate to calculate saddle point energies allowing all the atoms to relax around the migrating atom which is fixed at the saddle point. To calculate the migration path, it is then released and allowed to drop into its stable configuration, using the molecular dynamics of the program. This procedure means that once we select a saddle point position for the migrating atom the rest of the path will follow the route of lowest energy, but the results are dependent on selecting the correct migration path and saddle point.

VI. VACANCY MIGRATION

Vacancy migration from site to site must involve one of its neighboring carbon atoms moving through a saddle point into the vacant site. The saddle point position for that carbon atom is calculated to be midway along the carbon-vacancy bond, as would be expected by symmetry arguments, with the neighboring atoms relaxed. The barrier energy for such a configuration is calculated to be 2.4 eV. This should be the activation energy for vacancy migration and is in pleasing and probably fortuitous agreement with the experimental value of 2.3±0.2 eV.[27]

As explained in Sec. I, the vacancies are trapped by the nitrogen aggregates under suitable annealing conditions. The energies of the metastable configurations in the capture of the vacancy by a single nitrogen are most easily explained in the form

N + V	→···	N-C-V	→	N-V	→	V-N
0.0	2.4	−2.0	−0.2	−4.7	−0.4	−4.7

with all energies (in eV) relative to the isolated defects. The + sign has been used to denote distant defects and the – to denote atoms bonded at next neighbor positions in the lattice. There is a very much higher barrier to the nitrogen-vacancy interchange than the 0.8 eV suggested by Davies and Hamer[28] from a simple two potential well model and their optical data.

For vacancies captured by an *A* aggregate, there is an important final step in which the N-N-V reorders to form the N-V-N of the H3 defect:

N-N+V	→···	N-N-C-V	→	N-N-V	→	N-V-N
0.0	2.4	3.4	5.1	−1.0	3.0	−5.1

Although the main part of this migration would be governed by the vacancy's migration energy, the final steps in the process involve a higher activation energy. There is some evidence for such an effect in the kinetics of the process.[27,47]

A similar reordering takes place when the *B* aggregate captures a vacancy forming an H4 center (Fig. 1), although in this case there is a very small barrier to reordering, and a large energy gain when it takes place:

B + V	→···	B-V	→	H4
0.0	2.4	6.0	6.5	−4.9

VII. NITROGEN MIGRATION

Three mechanisms by which the nitrogen substitutional atoms could migrate are explored: a simple interchange of the nitrogen with a carbon neighbor, via interstitial sites, or by a vacancy assisted mechanism.

A. Interchange with a neighbor

In essence, the nitrogen would have to break its bonds with three of its four carbon neighbors (the fourth being already broken), move past one of them, and take its place in the next lattice site. A number of routes were explored and the energy of the lowest energy saddle point, at the point where the atoms pass each other, is surprisingly low — only 6.3 eV above the nitrogen's energy at a substitutional site.

B. As an interstitial

The migration energy of a nitrogen interstitial N_i has already been calculated in this way[37] and is found to be near 1 eV. This means that any nitrogen interstitials would migrate and be trapped readily even at room temperature. The displacement of the nitrogen substitutional atom into an interstitial position leaving a vacancy behind had an energy of about 11 eV. However, if radiation damage produces vacancies, it must also produce interstitials C_i, and one of these self-interstitials could displace the substitutional nitrogen into an interstitial position:

$$\begin{array}{ccccccc} C_i + N & \to\cdots & C_i\text{-}N & \to & C\text{-}N_i & \to & N_i\text{-}C \\ 0.0 & 1.0 & -1.3 & -2.2 & -2.5 & -1.5 & -2.5 \end{array}$$

The carbon interstitial's migration energy is very similar to that of the nitrogen interstitial, and even if this process takes place, it is not the high temperature aggregation process that Evans describes.[3]

C. Vacancy-assisted migration

All the processes involved in a vacancy-assisted migration were examined in Sec. VI. A vacancy must migrate, be trapped by a nitrogen atom, interchange sites with that atom, move away from that nitrogen, and be trapped by another or the same nitrogen, for the next step. The step which needs the highest energy in this cycle is the dissociation of the NV center of 4.5 eV.

This process does not consume vacancies, so a very small number may be involved in the migration of many nitrogen atoms and the vacancy formation energy has not been included in the activation energies quoted. However, the thermal equilibrium concentration of vacancies in uniradiated diamond at the temperatures at which the nitrogen migration occurs is many orders of magnitude smaller than the concentration of nitrogen.

Two mechanisms for the nitrogen migration are proposed: the direct interchange of atoms with an activation energy of 6.3 eV, reasonably close to Evans's[19] estimate of 5 eV, and a vacancy-related mechanism with an activation energy of 4.5 eV. In uniradiated diamonds the former process would dominate, with any vacancies present speeding the process to give an apparent lowering of activation energy. In irradiated samples, the latter process would give the enhanced aggregation which is observed.[13,34]

VIII. THE MIGRATION OF *A* CENTERS

The mechanisms for the migration of the *A* centers seem most likely to involve their dissociation. Although Evans[19] saw no evidence for this, he did observe the formation of N3 centers as the *B* centers formed, which implies that some single nitrogen atoms were being trapped by *A* centers. As before, the migration could be a vacancy-related process or a direct interchange of atoms. Other mechanisms, where the nitrogen pairs migrate as a unit, defeated the imagination of the author.

A. Vacancy-related dissociation of the *A* center

Most of the steps involved in this process have already been discussed in Sec. IV B, but these energies would suggest a very high dissociation energy for the H3 defect of 8.1 eV. An alternative path, by which one of the carbon neighbors to the vacancy migrates into it, has a saddle point energy of 1.1 eV, giving a dissociation energy by this path of 7.2 eV. Since the aggregation of *A* centers to form *B* centers occurs at a much higher temperature than the formation of the *A* centers, there is likely to be a greater concentration of vacancies to be involved in this process. The creation of the *B* center (and N3 center) needs the presence or creation of a vacancy. It is not clear whether the vacancies involved are created (with a self-interstitial) during the nitrogen migration process, and assist in that migration, or only as a consequence of the aggregation of the nitrogen. In either case self-interstitials will be created which condense into platelets, perhaps with some nitrogen also included.[48]

B. Direct interchange of atoms

The saddle point energy in the interchange of one of the nitrogen atoms in the *A* center with one of its carbon neighbors is 8 eV.

The temperatures are very high (over 2000 K in laboratory conditions) when these processes occur. It is probable that more than one mechanism is important, as in the formation of A centers. Both the mechanisms explored here, with energies of 7–8 eV and perhaps some other quite different ones, may contribute to the aggregation of nitrogen to form *B* centers.

IX. CONCLUSIONS

The energies and structures of nitrogen and nitrogen-vacancy complexes have been calculated and the results show that it is energetically favorable for the nitrogen to aggregate and the nitrogen to trap vacancies. The gain in energy when two distant single nitrogen atoms form a pair is 2 eV, and when two pairs and a distant vacancy form a *B* aggregate there is a further gain of 8.2 eV. A single nitrogen atom traps a vacancy with an energy gain of 4.7 eV. An *A* aggregate gains 5 eV and a *B* aggregate gains 4.9 eV on trapping a vacancy to form the H3 and H4 centers, respectively.

The mechanisms for migration of the single nitrogen atom are shown to be both a vacancy-assisted one and a direct interchange of atoms with an activation energy for migration of the single nitrogen of 4.5 eV and 6.3 eV, respectively, both near Evans's experimental estimate of 5 eV. The migration of the *A* centers to form *B* centers probably involves their dissociation, which has an energy of 8 eV, or 7.2 eV if a vacancy is present. These energies compare well with Evans's estimates of around 7 eV.

The reliability of such calculations is difficult to gauge and they have been compared to experimental results or other calculations whenever possible. The original aim of building up a good *qualitative* model of the nitrogen and nitrogen-vacancy complexes in diamond and their formation was surpassed by results which give a very reasonable *quantitative* picture, agreeing well with available experimental data.

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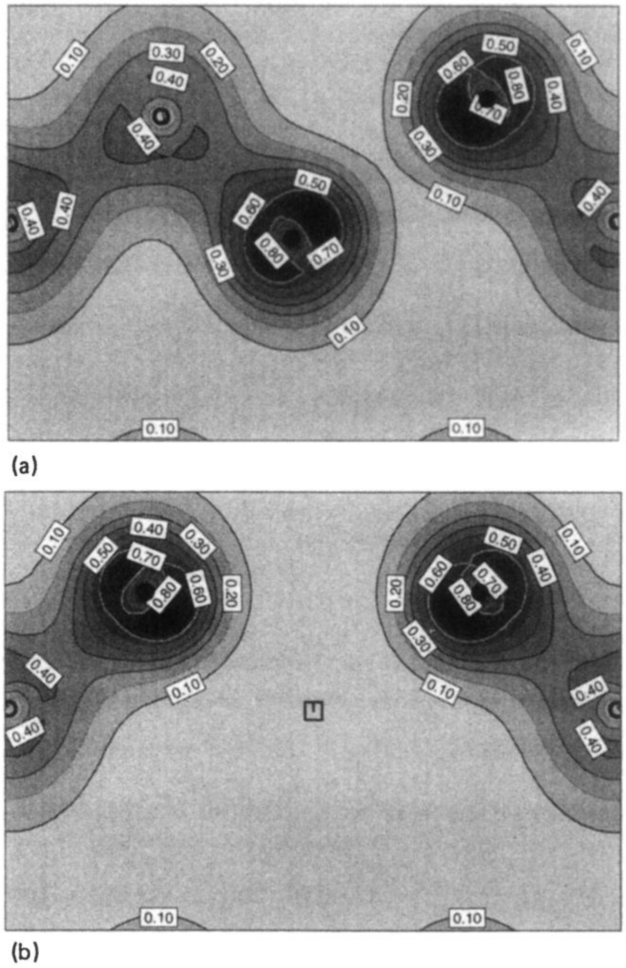

FIG. 2. The valence charge density in a (110) plane including (a) an *A* center and (b) a *B* center. The positions of the nitrogen atoms are shown by filled circles, carbon atoms by open circles, and the vacancy by a square. Only two of the *B* center's four nitrogen atoms are in the (110) plane. The units are electronic charge per cubic atomic unit.