



## Diffusion of nitrogen in diamond and the formation of A-centres



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### ABSTRACT

It has long been understood that nitrogen in diamond energetically favours aggregated forms as a consequence of the reduction in the number of dangling bonds. Thus heating to around 1500 °C leads to the formation of A-centres, which are close-by pairs of substitutional N atoms. However, the *mechanism* by which N moves through the diamond lattice to form the aggregates is much less clear, although for some time it has been generally thought that it may be mediated by lattice vacancies. In this study, we review the energetics of this mechanism in comparison to one based upon self-interstitials, and show that the available experimental evidence is much more consistent with an interstitial mechanism than one based upon lattice vacancies.

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### 1. Introduction

This paper is concerned with the mechanisms by which nitrogen impurities diffuse to form close-by pairs called A-centres when type-Ib diamonds are heated around 1500 °C. Experimental investigations [1–5] have established that the aggregation process is enhanced by radiation [5], by the presence of transition-metal impurities present in synthetic diamonds grown with a metal catalyst [2–4], and is reduced by increasing hydrostatic pressure [2]. The growth of A-centres has been found, in early stages, to obey second order kinetics suggesting a diffusion controlled process and activate [1] with an energy 5 eV, or in a later study  $5.5 \pm 0.7$  eV which used synthetic diamonds grown with a cobalt catalyst [2]. However, a nickel catalyst, and to a lesser extent a cobalt one, leads eventually to pronounced departures from second-order kinetics [3] and suggests a transient enhanced mechanism with the aggregation rate decreasing with time due to the simultaneous loss of a Ni or Co defect.

Nitrogen is expected to diffuse through diamond in a similar way to dopant diffusion in other semiconductors like silicon or germanium. In these cases, the diffusing species is a complex formed by the dopant trapping a mobile vacancy ( $V_C$ ) or self-interstitial ( $I$ ). To a large extent because the binding energies of  $V_C$  or  $I$  with the dopant are so small, the activation energy of diffusion in these materials is close to the formation energy of the native defect [6]. However, these quantities when calculated using density-functional methods are very large in diamond. It seems that these energies are overestimated and/or there are internal sources of vacancies or interstitials, eg dislocations, within diamonds which lead to the creation of an  $NV_C$  complex, or the interstitial nitrogen  $N_i$  centre [7] at the temperature where aggregation occurs

(1500 °C). For example, it has been suggested that heat treatment of synthetic diamonds leads to a transformation of Ni related defects, which results in the formation of carbon interstitials [8]. These would then promote the diffusion of nitrogen and the formation of A-centres [2]. This is supported by the simultaneous observation of the loss of centres associated with substitutional Ni impurities, and the growth of Ni-vacancy defects. At the same time, an interstitial related nitrogen centre labelled H1a is formed [2–4]. The H1a centre is a carbon interstitial that has been trapped by an A centre [9,10]. We denote this defect by  $(N_2)_C$ , as it can be thought of as an  $N_2$  pair substituting for a host carbon atom, with the N–N bond aligned along [001]. It can also be thought of as the product of the reaction when interstitial nitrogen  $N_i$  is trapped by a substitutional N defect. To form an A-centre, H1a must dissociate (releasing  $I$ ) at the aggregation temperature. The dissociation of  $(N_2)_C$  is consistent with the loss of H1a between 1400 °C and 1600 °C, without the appearance of any new interstitial related defect [10]. Thus in synthetic diamonds following anneals around 1500 °C, we expect H1a to be particularly rich in regions where the concentration of Ni or Co is highest, e.g. in (111) growth sectors. It is then these regions where A-centres should be most abundant and such a correlation has been noticed previously (see Ref. [11], section D). In this paper, we shall show that it is a self-interstitial and not a vacancy that is primarily responsible for the diffusion of nitrogen. This is further supported by the absence of any vacancy-nitrogen defect that would be formed during the heat treatment if vacancies were produced [3].

Similarly, electron irradiation of synthetic or natural type-Ib diamonds leads to an enhancement in the aggregation rate of nitrogen which has been, without direct evidence, attributed to vacancy mediated diffusion of nitrogen [5]. This model assumes that mobile  $V_C$  migrates and is trapped by substitutional nitrogen ( $N_s$ ) to form the vacancy-nitrogen or  $NV_C$  defect and these in turn are mobile at 1500 °C and are

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trapped by further  $N_s$ , resulting in di-nitrogen vacancy defects,  $N_2V_C$ . These would have to dissociate via emission of a vacancy to yield A-centres. We note, however, that an interstitial mediated enhanced diffusion mechanism could equally well account for the data.

To summarise, there are two plausible mechanisms for the formation of A-centres. The diffusion of nitrogen is controlled either by self-interstitials or by vacancies. Each mechanism involves three stages. First, interstitials or vacancies have to be produced, secondly at the temperature at which aggregation is known to occur (1500 °C), these are mobile and are trapped by  $N_s$  forming  $N_i$  or  $NV_C$ . In turn,  $N_i$  or  $NV_C$  must be mobile at 1500 °C and must not dissociate before being trapped by another  $N_s$  forming  $(N_2)_C$  or  $N_2V_C$ . Thirdly,  $(N_2)_C$  or  $N_2V_C$  must dissociate at 1500 °C, leading to A-centres, freeing  $I$  or  $V_C$  that can catalyse further aggregation. Such mechanisms could explain the very large, ~80%, transformation of  $N_s$  into A-centres after 10 h [3].

A third mechanism of diffusion is an exchange of an N atom with a neighbouring carbon atom but this, besides having very high energy [9], is ruled out as it cannot account for the effect of radiation or the presence of transition metals.

## 2. Energetics of defects involved in N diffusion

To analyse the process of nitrogen aggregation, we require the formation and migration enthalpies of various defects. The former, denoted by  $E_f$ , is given by

$$E_f = E_{\text{cell}} - \sum_i N_i \mu_i \quad (1)$$

Here  $E_{\text{cell}}$  is the energy of the cell containing the defect, and  $\mu_i$  and  $N_i$  are the chemical potential and number of atoms of species  $i$ , respectively, making up the defect. The formation energy  $E_f$  is related to the equilibrium concentration of the defect by  $C = N \exp(S_f/k) \exp(-E_f/kT)$ . Here  $N$  is the density of atoms in diamond and  $S_f$  is the entropy of formation.

Values of  $E_f$  (at zero pressure) and the migration energies of various defects are taken from previous density functional theory calculations [9,12–15] and are given in Table 1. We note that the values used are consistent with relevant recently published values [16]. We should remark that LDA and GGA calculations of the formation energy of the vacancy exceed by about 1 eV the energy calculated by a quantum Monte Carlo calculation, which gives the vacancy formation energy to be around 6 eV [17].

## 3. Self-diffusion and the diffusion of nitrogen

In the simplest case, the diffusion constant of nitrogen is related to the product of the equilibrium fraction of nitrogen present as  $NV_C$  or  $N_i$  and their diffusivities [6]. Thus the diffusion constant is

$$D = D_0 \exp\left(-\frac{E_f + E_m}{kT}\right) \quad (2)$$

**Table 1**

Formation ( $E_f$ ) and migration ( $E_m$ ) energies of defects in diamond (eV) taken from Refs. goss-PRB-63-195208, goss-PRB-70-235208, jones-PSSA-204-3059, pinto-PSSA-209-1765, and newton-DRM-11-618. The chemical potential of nitrogen is taken such that the formation energy of  $N_s$  is zero. Values in parentheses are those that best describe the data, as described in the text.

Defect	$N_s$	A-centre	$(N_2)_C$	$N_2V_C$
$E_f$	0	−4.0	2.4	−2.2
Defect	$V_C$	$I$	$NV_C$	$N_i$
$E_f$	6.0 (4.1–5.1)	12.3 (9.4–10.4)	2.5	6.7
$E_m$	2.3	1.6	4.9 (4.4)	1.8

and

$$D_0 = \nu a^2 \exp\left(\frac{S_f + S_m}{k}\right) \quad (3)$$

Here  $E_f$  and  $E_m$  are the formation and migration enthalpies of  $N_i$  or  $NV_C$ ,  $\nu$  is a jump frequency, typically  $10^{13}$  Hz and  $a$  the jump distance. For self-diffusion the diffusion constant is given by this expression but  $E_f$ ,  $E_m$  and  $S_m$  refer to the formation energies, migration energies and their entropies for a vacancy and interstitial. We expect that the activation energy for vacancy assisted diffusion is significantly different from interstitial assisted diffusion so that only one process needs to be considered.

In the absence of a significant entropic term, we expect  $D_0$  to be  $\sim 10^{-3}$  cm<sup>2</sup>/s, but experiments on self-diffusion [19] show  $D = 0.4 \exp(-6.8 \pm 1.6 \text{ eV}/kT)$  cm<sup>2</sup>/s and suggest the entropic term  $S_f + S_m$  of about 6 k. The migration energies of  $I$  and  $V_C$  are known from experiment [18,20] to be 1.6 eV and 2.3 eV, respectively, and are not expected to vary greatly with pressure. However, we shall see later (Sec. 6) that there is a strong pressure dependence on the formation energies of  $V_C$  and  $I$  as the creation of either of these defects leads to a significant increase in volume of the crystal. At 10 GPa, we find  $E_f$  for  $V_C$  or  $I$  to increase over their zero pressure values by  $\sim 0.35$  eV.

### 3.1. Self-diffusion

Let us suppose that self-diffusion occurs by a vacancy mechanism. Then the vacancy formation energy, at zero pressure, would have to be  $4.1 \pm 1.6$  eV so that the sum of the formation and migration enthalpies, as well as the pressure term at 10 GPa, is the experimental [19] activation energy of  $6.8 \pm 1.6$  eV. The value of the formation energy,  $4.1 \pm 1.6$  eV, should be compared with the theoretical [17] formation energy of the vacancy of 6.0 eV. Clearly the extreme experimental value is almost compatible with theory, although the entropic term  $S_m + S_f$  would then have to be about 18 k. Such a value seems far too large and we are more inclined to the view that the vacancy formation energy is much less than the theoretical value, and more probably between 4 and 5 eV. This may be explained if there are vacancy clusters in the diamond whose dissolution leads to a supersaturation of vacancies. Such clusters appear to exist in brown diamonds [19] but these dissociate at temperatures around 2200 °C, while the diffusion experiments were carried out from 1800 to 2100 °C.

If instead self-diffusion proceeded by an interstitial mechanism, then as both experiment [18] and theory [9] place  $E_m(I)$  around 1.6 eV, we would require  $E_f(I)$  at zero pressure to be  $4.8 \pm 1.6$  eV in order for the activation energy to be 6.8 eV. The density functional estimate [21] for  $E_f(I)$  is 12.3 eV and clearly much greater than the estimate obtained from the experimental data. Another estimate of 23 eV has been given, but this refers to a different and less stable structure [22,23]. Nevertheless, we believe that a figure of 12.3 eV is still too big and a value around 9–10 eV is more credible. However, this is still far too large to account for self-diffusion. We conclude that interstitial mediated self-diffusion does not occur and self-diffusion proceeds by a vacancy route with a vacancy formation energy at zero pressure around 4 to 5 eV.

### 3.2. Temperature and activation barriers for nitrogen related reactions

There are very few studies which report activation energies of defect related reactions in diamond. Rather the temperature at which a process takes place is the only information that is available. We suppose that the temperature and activation energy  $W$  are related by the requirement that one jump or atomic rearrangement occurs in 1 s. Such rates are relevant for laboratory experiments but do not reflect rates in natural diamonds exposed to much lower temperatures. We take the jump rate to be  $\nu \exp(S_w/k) \exp(-W/kT)$  with  $\nu \sim 10^{13}$  Hz, and note that the corresponding barrier at 1500 °C is 4.6 eV assuming that the entropic term  $S_w$  is zero. However, if  $S_w$  is taken to be 6 k, the same as found

for self-diffusion, then the barrier would be 5.5 eV. In the following analysis, we give barriers for both  $S_W = 0$  and 6 k.

Previous theoretical investigations mainwood [24] of the diffusion of nitrogen using CNDO methods found for vacancy mediated diffusion an activation energy for the growth of A-centres of 4.5 eV. However the path for  $NV_C$  diffusion is unclear, and appears to be at variance with similar studies in silicon.

#### 4. Interstitial mediated diffusion of nitrogen: synthetic diamond

Two types of experiments on the formation of A-centres have previously been carried out. Both have used synthetic diamond which has been grown by a heat treatment ( $\sim 1400$  °C) carried out at high temperatures and pressures in the presence of a Ni or Co catalyst. Most of the nitrogen is then present as single substitutional defects.

In the first experiment the synthetic diamond was annealed for varying durations around 1500 °C and the concentration of A-centres found [2–4].

The second type of experiment monitors the growth of A-centres in annealed ( $T \sim 1500$  °C) synthetic diamonds that have been irradiated.

Growth using a Ni or Co catalyst increases the aggregation rate while hydrostatic pressure noticeably decreases it. The effect of Ni has been attributed to the release of carbon interstitials created by a transformation of Ni or Co defects. Support for this has been provided by EPR experiments [8] where the loss of substitutional Ni (epr centre labelled W8) and the creation of a Ni-vacancy defect (labelled NE4) is assumed to be accompanied by the release of an interstitial. The interstitial is mobile [18] at 300 °C, and is expected to be strongly trapped by  $N_s$ , as the binding energy of the interstitial with nitrogen (Table 1) is 5.6 eV. Once formed  $N_i$  cannot dissociate at 1500 °C but is mobile at this temperature. Evidence for this comes from previous theoretical calculations as the migration barrier of the nitrogen interstitial  $N_i$  is only 1.8 eV, and  $\sim 0.2$  eV above that for the self-interstitial [13]. Hence, at a relatively low temperature, mobile  $N_i$  would be trapped by further  $N_s$  forming the di-nitrogen species which in this case is  $(N_2)_C$ . This defect is the well known H1a centre and is detected in infra-red absorption studies on annealed synthetic diamonds [11] or irradiated diamonds [10] through its vibrational mode at  $1450\text{ cm}^{-1}$ . H1a forms at 320 °C in irradiated type-Ia diamonds by the capture of  $I$  by an A-centre. It is formed at 650 °C in synthetic type-Ib diamonds, when mobile  $N_i$  is trapped by  $N_s$  [11]. To form an A-centre, the  $(N_2)_C$  defect must dissociate. Indeed, H1a is lost following anneals [10] around 1500 °C and since A-centres are created at this temperature we suppose the dissociation reaction:



occurs.

We can estimate the barrier for the dissociation of  $(N_2)_C$  from the formation and migration energies given in Table 1. The barrier is the change in energy of the reaction plus the energy necessary to transport  $I$  away from the A-centre. Hence, the barrier for Eq. (4) is  $\Delta E_f + E_m(I)$ , where  $\Delta E_f$  is the energy change caused by the reaction. Leaving the value of the formation energy of the interstitial  $E_f(I)$  for the moment, we find the barrier is  $E_f(I) - 4.8$  eV. Clearly the barrier increases with the formation energy of the interstitial and as the dissociation occurs around 1500 °C when A-centres are formed, we would anticipate that the dissociation barrier lies between 4.6 eV and 5.5 eV, assuming entropic values of 0 k to 6 k. This places  $E_f(I)$  in the range of 9.4–10.1 eV, and implies that previous calculated estimates of the formation energy are overestimates of  $\sim 15$ –30%.

It is important to note that the dissociation of  $(N_2)_C$  should lead to the formation of the A-centre rather than a de-binding with the loss of  $(N_2)_C$  through the formation of  $N_s$  and  $N_i$ . The barrier for dissociation is 6.1 eV as judged from the energies given in Table 1. Provided then that  $E_f(I)$  is lower than 10.9 eV, the barrier to dissociation  $(N_2)_C$  into  $N_s$  and  $N_i$  is higher than the barrier to form A-centres.

Finally, we note that  $N_i$  itself will migrate as a unit rather than dissociate into  $N_s$  and  $I$  if the migration barrier is less than its dissociation barrier. That this is the case comes from an inspection of the relative energies. The dissociation barrier is

$$E_f(N_s) + E_f(I) + E_m(I) - E_f(N_i),$$

or  $E_f(I) - 5.1$  eV. This exceeds the migration energy of  $N_i$  if  $E_f(I)$  exceeds 7 eV, which we shall take as the lower limit of  $E_f(I)$  for an interstitial mediated aggregation process to be valid.

In conclusion, provided  $E_f(I)$  is around 9.4–10.4 eV,  $N_i$  will diffuse (and not dissociate) around 600 °C, and be trapped by  $N_s$ , forming  $(N_2)_C$ . This is stable until about 1400–1600 °C where it dissociates into an A-centre and a self-interstitial.  $I$  can then lead to additional A-centres being formed and will continue until it is captured by traps deeper than  $N_s$ , such as dislocations.

In summary, provided there is an initial supply of interstitials, nitrogen atoms will cluster and lead to A-centres at 1500 °C. We shall return to the matter of the formation of the self interstitials in Sec. 6.

#### 5. Vacancy mediated diffusion of nitrogen

We now investigate whether the aggregation of N can be attributed to vacancy assisted diffusion in annealed synthetic or irradiated diamonds. The migration energy of V, 2.3 eV, is low enough to permit diffusion around 600 °C and V will be trapped by  $N_s$  forming  $NV_C$  centres. The barrier for the migration of  $NV_C$  has been calculated [15] to be 4.9 eV. The dissociation barrier for  $NV_C$  into  $V_C$  and  $N_s$  is  $E_f(V_C) + E_f(N_s) - E_f(NV_C) + E_m(V_C)$ , or  $E_f(V_C) - 0.2$  eV using the values in Table 1. Hence if  $E_f(V_C)$  is more than 5.1 eV,  $NV_C$  will migrate rather than dissociate which seems to be process that occurs. However, the migration energy and dissociation barrier of  $NV_C$  are close together and the mode by which VN disappears is uncertain.

The dissociation barrier of  $N_2V_C$  into an A-centre and vacancy is  $E_f(V_C) + E_f(A\text{-centre}) - E_f(N_2V_C) + E_m(V_C)$ , or using the values in Table 1,  $E_f(V_C) + 0.5$  eV. This is greater than the dissociation barrier of  $N_2V_C$ . Clearly, as the migration of VN is easier than that of  $N_2V_C$ ,  $NV_C$  should disappear at a lower temperature than  $N_2V_C$ , leading to a temperature range where  $N_2V_C$  is stable in the aggregation process.

The neutral charge state of  $N_2V_C$  is responsible for the H3 optical centre while the negatively charged form is labelled H2. Annealing experiments show that H2 is formed around 1400 °C (see Fig. 10 of Ref. [25]) and the same experiments show that H2 and H3 are stable to about 1700 °C (see Fig. 4 of Ref. [25]). This rules out A-centre creation at 1500 °C and thus we can exclude the vacancy assisted mechanism for nitrogen aggregation occurring at this temperature because H2 and H3 are stable at this temperature.

To conclude, assuming a supply of free vacancies,  $N_2V_C$  defects are formed from  $NV_C$  around 1400 °C but are too stable to dissociate at 1500 °C. They do dissociate around 1700 °C, but this mechanism cannot explain A-centre production at 1500 °C.

In summary, we have shown that the formation of A-centers at 1500 °C is an interstitial mediated process and not a vacancy one. This assumes a supply of interstitials. There is a free supply of  $I$  in irradiated diamonds, but we now need to investigate their formation in synthetic diamond grown with Ni or Co catalysts.

#### 6. Formation of interstitials in synthetic diamonds

An interstitial could be created by a grown-in Ni defect transforming to a Ni-vacancy centre with the release of an interstitial. Capture of  $I$  by  $N_s$  would then lead to a supersaturated concentration of  $N_i$ . These are mobile at the aggregation temperature  $\sim 1500$  °C, and become trapped by  $N_s$  leading to the formation of  $(N_2)_C$ . The dissociation of these defects leads to A-centres. There are four clearly identifiable steps. The first is the creation of  $N_i$  along with a Ni-vacancy defect as in the reaction:

$Ni_s \rightarrow NiV + I$ . The remaining steps are as discussed above, being the creation of  $N_i$ , the creation of  $(N_2)_C$  from a mobile  $N_i$  defect, and the dissociation of  $(N_2)_C$  resulting in A-centres and release of  $I$ . To be effective the overall reaction should be exothermic.

We now investigate the changes in energy for these reactions and conclude that the net process is exothermic provided the formation energy of the interstitial  $E_f(I)$  is less than about 9 eV.

If the Ni defect were  $Ni_s^-$  as suggested previously [8], then  $\Delta E_f$  for the first reaction  $Ni_s^- \rightarrow (NiV_C)^- + I$ , is given by  $E_f(NiV_C^-) + E_f(I) - E_f(Ni_s^-)$ . DFT calculations [26] give this to be  $E_f(I) - 5.3$  eV. The barrier to the process is this energy change together with the migration energy of  $I$ , leading to the barrier of  $E_f(I) - 3.7$  eV. Changes in formation energy and barriers to the processes for all four stages are given in Table 2.  $\Delta E_f$  for the second reaction is  $6.7 - E_f(I)$  eV, and the overall energy increase for the first two reactions together is only 1.4 eV (it is independent of the formation energy of the self-interstitial).

$\Delta E_f$  for the third reaction, where mobile  $N_i$  is trapped by  $N_s$  forming the H1a centre, is found from Table 1, and is strongly exothermic:  $\Delta E_f = -4.3$  eV. Finally, for reaction 4, the dissociation of  $(N_2)_C$  and the formation of A-centres, leads to an energy change of  $E_f(I) - 6.4$  eV. The overall energy change, for the four reactions starting from  $Ni_s^-$  and yielding A-centres, together with a free interstitial, is  $E_f(I) - 9.3$  eV and is negative (exothermic) if  $E_f(I)$  is less than 9.3 eV. Consequently there would be a spontaneous tendency for A-centres to be produced with a loss of  $Ni_s^-$  defects.

The rate determining step for the whole process is the first reaction which has a barrier of  $E_f(I) - 3.7$  eV. This needs to be in the 4.6–5.6 eV range if the reaction takes place around 1500 °C and places  $E_f(I)$  to be 8.3–9.3 eV. This again is reasonably close to our estimate. The interstitial formed in the process can catalyse the formation of other A-centres but can also be lost through trapping by dislocations. Consequently the process continues only if there are sources of interstitials present. In spite of the EPR evidence for the formation of the Ni vacancy centre in the temperature range 1330–1630 °C, other experiments have shown that there is loss of Ni from substitutional sites [3] but only at anneal temperatures above 1600 °C although. Nevertheless, self-interstitials continue to be generated as H1a defects are observed. Further experiments are required to resolve this inconsistency.

## 7. Effect of pressure on the formation of A-centres

We turn now to the effect of pressure on the formation of A-centres. It is known that pressure reduces the generation rate of A-centres in irradiated synthetic diamonds [2]. It probably reduces the concentrations of interstitials that assist in the diffusion. This can be explained if the formation energy of the interstitial is increased and this would be the case if the crystal volume increased when interstitials or vacancies are created. Pressure manifests itself by adding a term  $p\Delta V$  to the formation energy of the interstitial. A similar argument can be given if vacancies assist in the diffusion process.

When  $I$  is formed, the change in volume  $\Delta V$  is due to two processes. The first removes an atom from the surface and the second inserts the atom into the crystal. The first step reduces the crystal volume by the atomic volume  $\Omega$  or  $a_0^3/8$ . The second step increases the volume as the

inserted atom compresses its environment. It is this second step that is measured in X-ray studies of the lattice parameter. It turns out [21] that the second step leads to a volume increase of  $1.9\Omega$ , so the net increase is  $0.9\Omega$ .

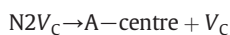
If a vacancy is created, an atom is removed from the bulk but this does not lead to any significant change in lattice parameter [21]. The atom is added to the surface increasing the crystal volume by  $\Omega$ . So  $\Delta V$  is positive for both  $I$  and  $V_C$  thermal formation. This decreases the generation rate of A-centres in electron irradiated diamond by a factor  $\exp(-p\Delta V/kT)$  which is about 0.12 at 1500 °C and a pressure of 10 GPa. This is comparable with the experimental data [2].

## 8. Nitrogen aggregation in diamonds free from transition metals

We now discuss the aggregation process for experiments on natural Ib diamonds carried out in the laboratory and not in nature where the time scales are completely different.

In the absence of metal precipitates, it is unlikely that diffusion cannot occur with the aid of interstitials unless the material is irradiated. Thus in heat treated but not irradiated diamond, a vacancy assisted aggregation mechanism is likely to occur when  $N_2V_C$  is formed. This occurs by migration of  $NV_C$  until it is trapped by  $N_s$  forming  $N_2V_C$ . The barrier for this process is the sum of the formation and migration energies of  $NV_C$ , i.e.  $2.5 + 4.4$  or  $6.9$  eV. This energy is close to the activation energy for self-diffusion.

In turn  $N_2V_C$  must dissociate but such a mechanism requires an annealing temperature of  $\sim 1800^\circ\text{C}$ . This follows as the dissociation barrier of



is  $E_f(V_C) - 4.0 + 2.3 + 2.2 = E_f(V_C) + 0.5$  eV. For  $E_f(V_C)$  in the range of 4.6 to 5.6 eV,  $N_2V_C$  dissociates around 1700–1800 °C.

## 9. Conclusions

We have found that it is not possible to reconcile the theoretical formation energies of the self-interstitial or vacancy with experimental estimates. They appear to be  $\sim 30\%$  greater than required to explain data regarding A-centre formation. Paradoxically, the calculated migration energies of  $V_C$  and  $I$  as well as  $NV_C$  agree with experimental values. We do not know the reason for the discrepancy but even for diffusion in Si there are continuing problems in matching experimental and theoretical diffusion activation energies.

Self-diffusion studies in diamond koga-PRB-72-024108 point to a far higher concentration of vacancies at the temperature  $\sim 2000^\circ\text{C}$  than given by a formation energy of 6 eV. It may be there are internal sources of vacancies. Alternatively the formation energies of  $V_C$  and  $I$  are overestimated. If this is the case there is broad agreement with the activation energy for vacancy assisted self-diffusion, and the stability and formation temperatures of  $NV_C$ ,  $N_i$ ,  $N_2V_C$  and  $(N_2)_C$ .

Using the reduced formation energies of  $V_C$  and  $I$  we have shown the following:

1. Self-diffusion occurs by a vacancy mechanism, with vacancies being generated thermally with a formation energy around 4.5 eV at 10 GPa. This implies a concentration of vacancies around 1 ppb at 2400 °C. The effect of pressure is to reduce the self-diffusion rate as the introduction of a vacancy is accompanied by an increase of the crystal volume equal to the volume of an atom. Thus the activation energy is increased by 0.35 eV for a pressure of 10 GPa. Similarly, the interstitial gives a net volume increase of  $\Delta V = 0.9\Omega$ . This decreases the rate for the production of self-interstitials by  $\exp(-p\Delta V/kT)$ . For  $p = 10$  GPa and  $T = 1500^\circ\text{C}$ , the rate decreases by a factor of 8. The experimental value klawi-DRM-6-1643 is about a factor of 10.

**Table 2**

Reaction energies at zero-pressure,  $\Delta E_f$  (eV), and barriers leading to A-centre formation. Note that reaction 1 where Ni transforms to a Ni-V defect has the greatest barrier and is then the rate determining step. Note also that the overall energy change leading to A-centres is negative (exothermic behaviour).

Step	Reaction	$\Delta E_f$	Barrier
1	$Ni_s^- \rightarrow (NiV_C)^- + I$	$E_f(I) - 5.3$	$E_f(I) - 3.7$
2	$I + N_s \rightarrow N_i$	$6.7 - E_f(I)$	1.6
3	$N_i + N_s \rightarrow (N_2)_C$	- 4.3	1.8
4	$(N_2)_C \rightarrow I + A\text{-centre}$	$E_f(I) - 6.4$	$E_f(I) - 4.8$



2. Diffusion of nitrogen in synthetic crystals grown with a metal catalyst is limited by two stages in the aggregation process. The first is the rate at which interstitials are introduced possibly by the transformation of grown-in Ni or Co defects. The reaction where substitutional  $N_i$  is transformed into a Ni-vacancy defect with the production of interstitial nitrogen,  $N_i$ , is exothermic when the binding energy of the interstitial with nitrogen is taken into account. The second is the rate at which H1a centres ( $(N_2)_C$ ) dissociate into A-centres and a self-interstitial. These reactions can occur at 1500 °C only if the formation energy of an interstitial is about 9.4 eV, which is 30% lower than the calculated value.
3. The question arises as to the mechanisms for nitrogen aggregation in annealed natural type-Ib diamonds without metal catalysts providing a source of interstitials. If  $I$  or  $V_C$  were created thermally then it seems that the interstitial route is too slow as the sum of the activation energy for the formation and migration energies of  $N_i$ , together with the pressure term, is  $6.7 + 1.8 + 0.35 = 8.9$  eV. For diffusion mediated by  $NV_C$ , the diffusion activation energy is  $2.5 + 4.4 + 0.35 = 7.3$  eV at 10 GPa. Thus we predict a vacancy mechanism with a similar activation energy to that of self-diffusion. Assuming that the pre-exponential factors are similar, we expect A-centre formation to occur around 1800–2100 °C in such materials which includes annealed natural diamonds.

Despite the factors noted above that provide a clear indication of the different roles played by  $I$  and  $V_C$  in the aggregation of nitrogen into A-centres, there remain some important questions to address. First, what is the origin of the theoretical overestimate of the formation energies of the native defects. This might be answered by using more accurate quantum-chemical models. Second, it would be helpful if further experiments were undertaken to check the diffusion results published so far.

Finally, it is known that A-centres transform into other defects [1] at annealing temperatures around 2000 °C especially N3 and B-centres which contain three and four N atoms and a lattice vacancy, together with the formation of a self-interstitial aggregate called a platelet. The energetics of the growth of platelets have been investigated previously [12] where it is shown that the platelet grows by vacancy emission. The vacancy is probably trapped by an A centre forming the H3 centre discussed above and the diffusion of this centre and its subsequent capture by a second A centre or even substitutional nitrogen leads directly to B and N3 centres.

## Prime novelty statement

The submitted article presents a detailed examination of the energetics of nitrogen aggregation into A-centres in diamond. The paper shows that based upon the current understanding of the formation and migration barriers for N, lattice vacancies and self-interstitials, in contrast with long-standing assumptions, an interstitial mediated aggregation mechanism is the most plausible.

## References

- [1] T. Evans, Z. Qi, *Proc. R. Soc. Lond. Ser. A* 381 (1982) 159.
- [2] I. Kiflawi, H. Kanda, D. Fisher, S.C. Lawson, *Diamond Relat. Mater.* 6 (1997) 1643.
- [3] D. Fisher, S.C. Lawson, *Diamond Relat. Mater.* 7 (1998) 299.
- [4] I. Kiflawi, H. Kanda, A. Mainwood, *Diamond Relat. Mater.* 7 (1998) 327.
- [5] A.T. Collins, *J. Phys. C* 13 (1980) 2641.
- [6] P.M. Fahey, P.B. Griffin, J.D. Plummer, *Rev. Mod. Phys.* 61 (1989) 289.
- [7] Based upon quantum-chemical simulations, interstitial nitrogen is currently thought to form a [001]-split interstitial configuration goss-PRB-70-235208, where N-C pair share a single host site. It may be viewed as a complex of a self-interstitial and a substitutional nitrogen centre, with formation and dissociation reactions between the constituent components, as well as migration processes, being explored in detail in Ref. goss-PRB-70-235208.
- [8] V.A. Nadolinny, A.P. Yelisseyev, J.M. Baker, D.J. Twitchen, M.E. Newton, B.N. Feigelson, O.P. Yuryeva, *Diamond Relat. Mater.* 9 (2000) 883.
- [9] J.P. Goss, P.R. Briddon, S. Papagiannidis, R. Jones, *Phys. Rev. B* 70 (2004) 235208.
- [10] S. Liggins, M.E. Newton, J.P. Goss, P.R. Briddon, D. Fisher, *Phys. Rev. B* 81 (2010) 085214.
- [11] I. Kiflawi, A. Mainwood, H. Kanda, D. Fisher, *Phys. Rev. B* 54 (1996) 16719.
- [12] J.P. Goss, B.J. Coomer, R. Jones, C.J. Fall, P.R. Briddon, S. Öberg, *Phys. Rev. B* 67 (2003) 165208.
- [13] J.P. Goss, B.J. Coomer, R. Jones, T.D. Shaw, P.R. Briddon, M. Rayson, S. Öberg, *Phys. Rev. B* 63 (2001) 195208.
- [14] R. Jones, L. Hounscome, N. Fujita, S. Öberg, P.R. Briddon, *Phys. Status Solidi A* 204 (2007) 3059.
- [15] H. Pinto, R. Jones, D.W. Palmer, J.P. Goss, P.R. Briddon, S. Öberg, *Phys. Status Solidi A* 209 (2012) 1765.
- [16] P. Deák, B. Aradi, M. Kaviani, T. Frauenheim, A. Gali, *Phys. Rev. B* 89 (2014) 075203.
- [17] R.Q. Hood, P.R.C. Kent, R.J. Needs, P.R. Briddon, *Phys. Rev. Lett.* 91 (2003) 076403.
- [18] M.E. Newton, B.A. Campbell, D.J. Twitchen, J.M. Baker, T.R. Anthony, *Diamond Relat. Mater.* 11 (2002) 618.
- [19] K.T. Koga, M.J. Walter, E. Nakamura, K. Kobayashi, *Phys. Rev. B* 72 (2005) 024108.
- [20] G. Davies, S.C. Lawson, A.T. Collins, A. Mainwood, S.J. Sharp, *Phys. Rev. B* 46 (1992) 13157.
- [21] J.P. Goss, R. Jones, P.R. Briddon, *Phys. Rev. B* 65 (2001) 035203.
- [22] J. Bernholc, A. Antonelli, T.M. Del Sole, Y. Bar-Yam, S.T. Pantelides, *Phys. Rev. Lett.* 61 (1988) 2689.
- [23] J. Shim, E.-K. Lee, Y.J. Lee, R.M. Nieminen, *Phys. Rev. B* 71 (2005) 035206.
- [24] A. Mainwood, *Phys. Rev. B* 49 (1994) 7934.
- [25] A.T. Collins, A. Connor, C.-H. Ly, A. Shareef, P.M. Spear, *J. Appl. Phys.* 97 (2005) 083517.
- [26] R. Larico, J.F. Justo, W.V.M. Machado, L.V.C. Assali, *Phys. Rev. B* 79 (2009) 115202.