Theory of Aggregation of Nitrogen in Diamond

R. Jones and J. P. Goss

A. INTRODUCTION

Modelling defects using atomistic and quantum-mechanical techniques provides us with a powerful method for identifying the microscopic structure of centres observed in experiment. Properties including the energies and lifetimes of optical transitions [1], local vibrational modes and vibrational resonances [2] have proved particularly powerful for nitrogen in diamond. However, processes involving the motion of nitrogen through the lattice are still not fully understood, and the literature is noticeably sparse concerning the modelling of these problems. Several levels of theory can be applied to the simulation of defects in crystalline material, ranging from potentials gained from parameterisation using experimental observations, to so-called *ab initio* which use no experimental input, the details of which are in the literature.

B. NITROGEN IN DIAMOND

Nitrogen is the most common impurity found as point defects, and is found in all types of diamonds. The form in which the majority of nitrogen is present is often used to classify the material. In natural type Ib and CVD diamonds, N is present as a substitutional defect, either present as a neutral or positive charged species. The neutral defect does not possess tetrahedral symmetry but undergoes a trigonal distortion with N and one of the C atom moving away from each other along (111) [3, 4, 5, 6] (FIGURE [1]). This is responsible for the yellow/brown colouration of synthetic diamonds grown without nitrogen getters.
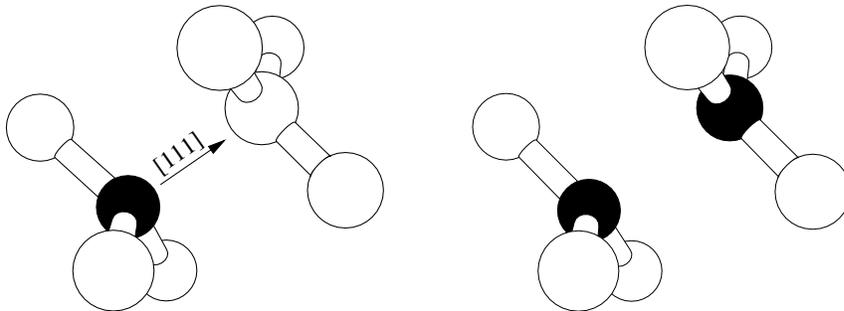
FIGURE 1 Schematics of the single substitutional nitrogen (left) and A-centre (right) showing the dilation of the bond adjacent to nitrogen. Nitrogen atoms are indicated in black.

Modelling [2] using *ab initio* local density functional cluster theory [7] successfully accounted for the vibrational modes of the defect, as well as its reorientation barrier [8]. The migration barrier by exchange with a carbon neighbour has been calculated to be 6.3 eV [6].

The aggregation of N into A-centres, which is a complex made up from two neighbouring N atoms at adjacent lattice sites (FIGURE [1]), is well established experimentally and occurs during extended heat treatments [9]. The defect was identified by Davies [10] from the symmetry of the 3.8 eV absorption line and its behaviour in diamonds containing ^{15}N. Theory [2] confirmed that the A-centre gives vibrational resonances at 1282, 1203, 1093 and 480 cm^{-1}.

Further aggregation of nitrogen leads to the B-centre which is made up from four nitrogen atoms surrounding a lattice vacancy (FIGURE [2]). These VN$_4$ defects also formed during extended anneals gave vibrational bands around the observed ones at 1332, 1171, 1093, 1003 and 780 cm^{-1}. It is thought that the aggregation of four nitrogen atoms makes it energetically favourable to form a vacancy-interstitial pair resulting in the B-centre and a self-interstitial, which in turn aggregate to form the well-known (001)-orientated platelets [11]. Material that contains mainly aggregated nitrogen is termed type Ia, and may possess predominantly A centres (type IaA), B centres (type IaB) or a mixture (type IaAB). The first-principles modelling suggested that the B-centre, like the A-centre, should be optically active. However, no absorption band has been so far identified. It is not clear whether the A-centre migrates as a unit to form the B-centres, or that they dissociate during the annealing stage and form VN$_4$ from individual N atoms.
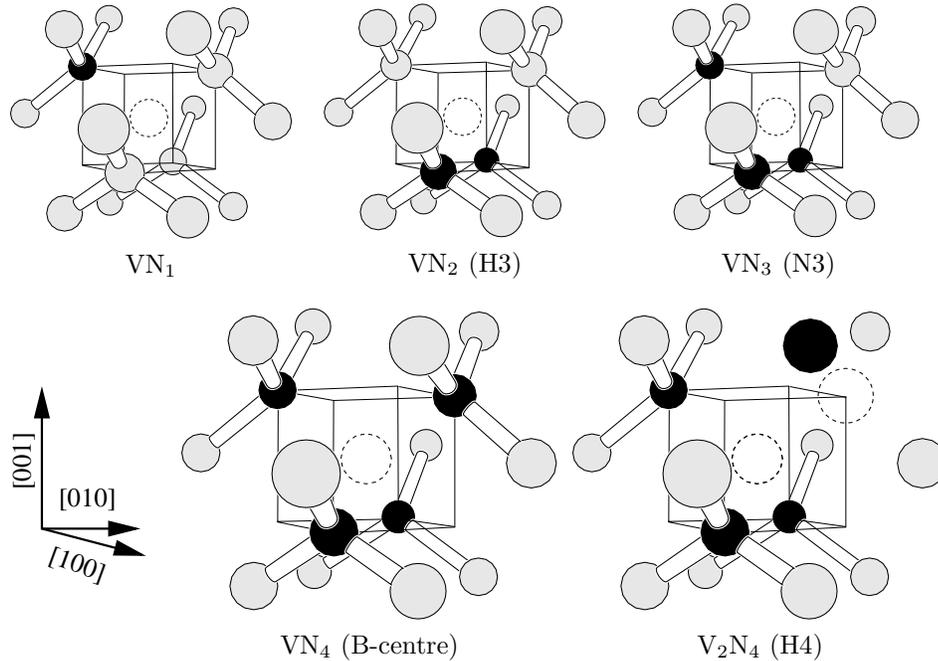
FIGURE 2 Schematics of the vacancy-nitrogen complexes. Nitrogen atoms are indicated in black, carbon in grey and the vacant sites by a dashed empty circle.

Other complexes made up from nitrogen and vacancies are also present in the material,

especially when the samples have been irradiated (see FIGURE [2]). Many vacancy-nitrogen defects have been modelled. The VN_2 or H3 centre and V_2N_2 or H4 centres in Refs. [2, 6, 12], while the optical properties of VN and VN_3 have been discussed in Ref. [1, 13]. It has been suggested that vacancies may enhance the motion of nitrogen through the lattice [14], and the activation barrier for this process has been estimated at 4.5 eV [6], lower than that of concerted exchange. A peculiarity surrounds the optical lines of the VN_3 defect. This centre gives rise to a set of lines N2-N4. However, more than the manifold of states arising from the sp^3 orbitals on the atoms bordering the vacancy are required to explain the optical properties of this complex. Additional levels are found from the first principles modelling [13].

Nitrogen interstitials have been described in a combined theoretical and experimental study [15]. There are some peculiarities associated with the centre, not least of which is the very high thermal stability of the experimental observables associated with this centre. The properties of the H1a peak are highly dependent on the material type (Ia or Ib), but in all cases an anneal to $1400°C$ is required to reduce the intensity of this local mode around 1450 cm^{-1}. However, this is still likely to be the most mobile form of nitrogen with an estimated migration barrier of 1 eV [6], and it is possible that self-interstitials catalyse the aggregation of nitrogen via migration of interstitial nitrogen.

Synthetic material grown via the high-temperature, high pressure method often contains relatively large concentrations of Ni. Recent work has focussed on nickel–nitrogen–vacancy centres where it appears that substitutional Ni can kick out an interstitial and spontaneously form a nickel-vacancy centre which is stabilised by nitrogen. These complexes have also been modelled [16], although processes behind the aggregation of nitrogen to the Ni-vacancy complex remain to be explored.

C. CONCLUSIONS

In conclusion, modelling of point defects involving N is fairly advanced and reliable structures, energetics, vibrational modes can be found although the calculation of optical transition energies continues to cause problems. The current understanding of the processes governing the motion of nitrogen through diamond on the other hand is less well developed.

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