A FIRST PRINCIPLES STUDY OF NICKEL DEFECTS IN SYNTHETIC DIAMOND

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Abstract. Spin-polarised local density functional cluster calculations are carried out on isolated interstitial (Ni_i^+) and substitutional (Ni_s^-, Ni_s^+) impurities in diamond and on Ni_i^+-B_s^-, Ni_s^+-B_s^- and Ni_s^--N_s^+ complexes. Ni_i^+ (S=1/2) lies at the T_d site. Ni_s^- (S=3/2) is shown to be stable and remains on-site in agreement with experimental results. Donor-acceptor complexes of Ni, namely Ni_i^+-B_s^-, Ni_s^--N_s^+ and Ni_s^+-B_s^- are stable trigonal defects which have a number of gap levels. Optical transitions are expected between some of these levels. We argue that there is no convincing evidence for Ni_i defects.

Introduction

Ni impurities are known to occur in synthetic diamonds grown using the high-pressure temperature-gradient method with solvent-catalysts containing Ni. Although there have been extensive experimental studies to ascertain the nature of nickel-related optical and electron paramagnetic resonance (EPR) centres, their composition and structure is still mostly undetermined. It is the aim of this work to investigate candidate structures for the various optical and paramagnetic centres. Theoretical considerations [1, 2] suggest that Ni_i^+ has an electronic configuration $t_2^6e^3$, with S=1/2 and Ni_s^- has the configuration $e^4t_2^3$ with S=3/2, if Hund's rule operates. There is evidence from EPR studies [3] that the latter defect exists as the hyperfine interaction with twelve second neighbours unambiguously identifies the substitutional site. However, the evidence for Ni_i^+ is less convincing. There are two EPR centres with S=1/2: NIRIM-1 and NIRIM-2 that have been tentatively assigned [4] to Ni_i^+ and Ni_i^+-X^- complexes, where X is unknown. No resolved hyperfine interactions with C neighbours or with X are detected. These centres are seen in material containing Ni and B, although they are apparently not seen if [B] exceeds a certain value. They coexist with the Ni_s^- which is the main argument against an assignment to Ni_s^+. However, since the material is inhomogeneous, Ni_s defects in different charge states could easily arise. The NIRIM-1 centre has T_d symmetry for $T > 25$ K and C_{3v} at 4 K, whereas NIRIM-2 is always C_{3v}. The latter may be correlated with the ${}^2E \rightarrow {}^2A$, 1.40 eV optical defect [5]. Other optical lines occur at 2.51 eV associated with Ni_s^-, 1.683 eV assigned to Ni_s^--N_s^+ [6], and unassigned transitions at 1.883, 2.56 and 3.1 eV.

We describe here local density functional cluster calculations, using the AIMPRO code, on large H-terminated clusters containing the defects. The clusters used in the present study consisted of 71 atoms centred on the Ni impurity atom. Substitutional defects are modelled using the tetrahedral cluster $NiC_{34}H_{36}$, and interstitial defects in $NiC_{30}H_{40}$, centred on a T_d site. Details of the method have been given elsewhere [7].

Interstitial Ni^+. The Ni atom in this S=1/2 defect was displaced along $\langle 111 \rangle$ from the T_d interstitial site towards one of the C neighbours by 0.4 Å, and then Ni and its nearest neighbours were allowed to relax. The Ni atom returned to the the T_d site with the four nearest C neighbours a distance of 1.72 Å. These results disagree with the C_{3v} symmetry found previously [8, 9]. The six next-nearest neighbours were at 1.78 Å. When the cluster was relaxed with all atoms allowed to move, the final T_d structure has Ni-C nearest neighbour lengths of 1.84 Å and next nearest neighbour lengths of 2.00 Å: a clear indication that restricting the relaxation to nearest neighbours is insufficient.

In order to ascertain whether the T_d symmetry found is stable against $\langle 111 \rangle$ distortions, the total energy of the cluster was calculated for various Ni $\langle 111 \rangle$-displacements for two cases. Firstly, only the Ni atom is moved, and secondly the surrounding neighbours are allowed to relax as well. The resulting potential profiles are plotted in Fig. 1. This graph shows that in both cases the *global* energy minimum is to be found at the T_d site.

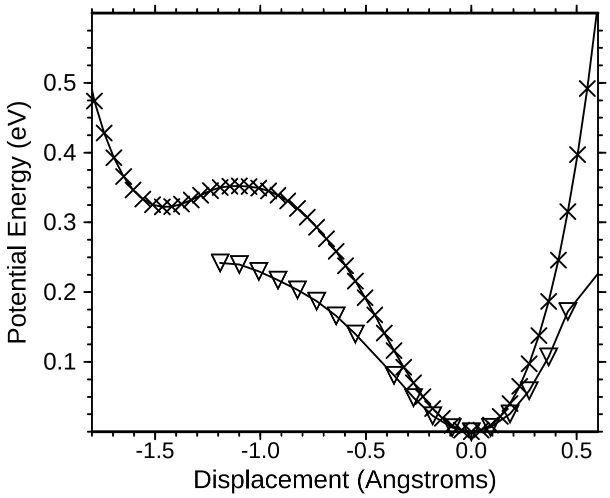

Fig. 1: The variation of potential energy with $\langle 111 \rangle$ displacement of the interstitial nickel atom from the relaxed structure. The curve shown with $\times$'s denotes case (i) when the four surrounding carbon atoms are not relaxed at each Ni position, and the curve shown with $\triangle$'s denotes case (ii) when the four nearest neighbours are free to relax.

The energy levels of the defect are shown in Fig. 2 (a,b) and Table 1 lists the low energy allowed optical transitions. Our method can only describe these levels and energies approximately. The electronic structure consists of an $e^{\downarrow}$-level occupied by a hole. The fully occupied $e^{\uparrow}$-level lies 4.6 eV below an unoccupied $a_1^{\uparrow}$. The highest filled levels then are $e^{\uparrow\uparrow}e^{\downarrow}$ as expected.

Table 1: The dipole-allowed transitions for the centres studied in this paper. All transition energies [eV], ΔE, are found from the difference between the calculated Kohn-Sham eigenvalues.

Ni_i^+		Ni_i^+-B_s^-		Ni_s^-		Ni_s^--N_s^+		Ni_s^+		Ni_s^+-B_s^-	
Trans.	ΔE	Trans.	ΔE	Trans.	ΔE	Trans.	ΔE	Trans.	ΔE	Trans.	ΔE
$e^{\uparrow}\rightarrow a_1^{\uparrow}$	4.6	$e^{\uparrow}\rightarrow a_1^{\uparrow}$	3.7	$t_2^{\uparrow}\rightarrow a_1^{\uparrow}$	3.1	$a_1^{\uparrow}\rightarrow e^{\uparrow}$	1.4	$e^{\uparrow}\rightarrow t_2^{\uparrow}$	2.45	$e^{\uparrow}\rightarrow a_1^{\uparrow}$	1.1
$t_2^{\downarrow}\rightarrow e^{\downarrow}$	1.4	$a_1^{\downarrow}\rightarrow e^{\downarrow}$	1.8	$t_2^{\uparrow}\rightarrow e^{\uparrow}$	3.8	$e^{\uparrow}\rightarrow a_1^{\uparrow}$	3.5	$t_2^{\uparrow}\rightarrow a_1^{\uparrow}$	3.5	$a_1^{\uparrow}\rightarrow e^{\uparrow}$	2.0
$e^{\downarrow}\rightarrow a_1^{\downarrow}$	3.1	$e^{\downarrow}\rightarrow a_1^{\downarrow}$	2.4	$e^{\downarrow}\rightarrow t_2^{\downarrow}$	1.7	$a_1^{\downarrow}\rightarrow e^{\downarrow}$	0.2	$e^{\downarrow}\rightarrow t_2^{\downarrow}$	2.1	$e^{\uparrow}\rightarrow a_1^{\uparrow}$	2.9
						$e^{\downarrow}\rightarrow a_1^{\downarrow}$	2.6			$a_1^{\downarrow}\rightarrow e^{\downarrow}$	1.8
										$e^{\downarrow}\rightarrow a_1^{\downarrow}$	2.9

It has been suggested that this defect is responsible for the NIRIM-1 EPR centre [4]. At low T, the T_d symmetry would be unstable and, if the defect assumed C_{3v} symmetry, the $e^{\downarrow}$-level would be split by spin-orbit interaction, hence stabilising the distortion. We expect that the magnitude of the splitting would be about the same as that found in the 1.40 eV optical centre (although the two defects are distinct as they have different room-temperature symmetries): namely 2-3 meV. This suggests that the distortion would disappear above about 20 K. In spite of the agreement with the properties of the NIRIM-1 centre, we do not consider that NIRIM-1 is Ni_i^+. This is because, in addition to arguments given later, in diamonds containing larger concentrations of [B], no further EPR defects are reported. Yet if Ni_i was present, we would expect it to assume the state Ni_i^{++} with S=1 in the configuration $e^{\uparrow\uparrow}$. However, no centres with this spin have been detected.

The Ni_i^+-B_s^- complex. A C-neighbour of Ni_i was replaced by B and the cluster re-relaxed. Ni moved slightly away from the T_d site along $\langle\bar{1}\bar{1}\bar{1}\rangle$, by 0.16 Å. B was displaced along $\langle 111\rangle$, with a Ni-B bond-length of 1.98 Å. The three C neighbours also relaxed outwards with final Ni-C bond-lengths of 1.87 Å.

The energy levels are comparable with Ni_i^+, Fig. 2 (c,d), showing the role of B is mainly in providing an electrostatic field. The $e^{\downarrow}$-level still contains a single hole but the C_{3v} symmetry splits the lower lying $t_2^{\downarrow}$-state associated with the Ni_i^+ into an e-state lying above an a_1-state. The lowest energetic optical transition would then be between the $e^{\downarrow}$-level and the $a_1^{\downarrow}$-level 1.8 eV below. Other transitions are given in the Table 1. We note that the e state containing the hole has a nodal surface running through the B atom, and only a very small hyperfine interaction with B would therefore be expected. The $a_1^{\downarrow}$ does overlap B, and this might lead to an observable splitting in the optical transition caused by the different B isotopes.

Again, it is tempting to suggest that the C_{3v} symmetry, the ${}^2E$ ground state, the effective spin of S=1/2 and the approximate agreement with an optical transition at 1.40 eV (although no splitting by B isotopes has been detected), show that the NIRIM-2 defect is the Ni_i-B, or possibly Ni_i-Al, complex. However, there are other preferred candidates as will be shown shortly.

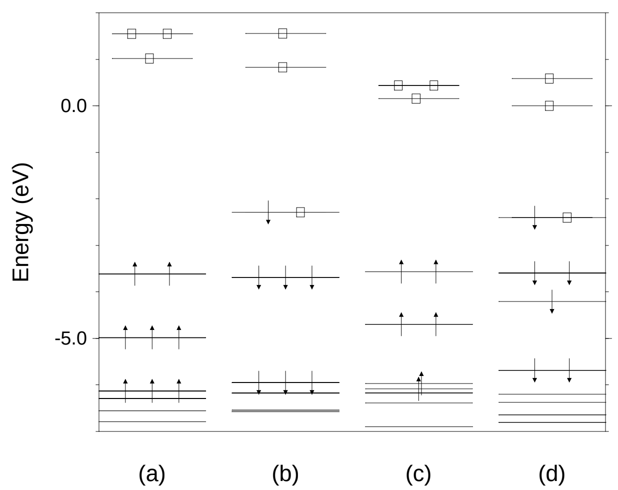

Fig. 2: A plot of the electronic structure (Kohn-Sham eigenvalues) of the two interstitial Ni defects examined in this work. (a) and (b) correspond to the Ni_i^+ spin-up and spin-down electronic levels respectively, with the arrows signifying filled states and the boxes empty states. Similarly, (c) and (d) correspond to Ni_i^+-B^-. The levels in (a,b) have been shifted downwards by 4 eV to bring the valence band tops into coincidence. The lines with two (three) arrows or boxes represent e (t_2) states. Only levels in the region of the band-gap are plotted.

Substitutional Ni^-. The cluster containing the substitutional defect, Ni_s^-, was relaxed with an effective spin of S=3/2 with the innermost 17 atoms being allowed to move. The relaxed structure showed that Ni remained on site with four nearest-neighbours at 1.89 Å and the twelve next-nearest neighbours at 2.58 Å. The pseudo-wavefunctions associated with the filled $t_2^{\uparrow}$ states show nodal surfaces between Ni and neighbouring C atoms although it seems that these wave-functions are neither strongly localised on Ni nor its C neighbours in contrast with the vacancy [2] and Ludwig and Woodbury [1] models. The electronic levels are shown in Fig. 3 (a,b). The highest occupied level is $t_2^{\uparrow\uparrow\uparrow}$, as expected. Table 1 gives optical transitions around 1.7 and 3.1 eV. The 2.51 eV optical line has been correlated with this EPR centre, as quoted in Ref. [6].

The same cluster was then relaxed with effective spin of S=1/2. The total energy for this structure was some 1.03 eV *higher* than that with S=3/2. Thus the S=3/2 configuration is found to be the more stable, in agreement with experiment.

The Ni_s^--N_s^+ complex. The relaxed structure for the S=1/2 defect had C_{3v} symmetry with the Ni-N bond length of 1.92 Å and the three Ni-C bond lengths at 2.07 Å. The N atom has moved slightly ($\sim$ 0.15 Å) towards the T_d site. The presence of the N atom splits the triply degenerate $t_2^{\uparrow}$-level of the Ni_s^- defect into an occupied $a_1^{\uparrow}$-level 1.4 eV below an $e^{\uparrow}$-level occupied by one hole as shown schematically in Fig. 3 (c). The lowest energy allowed optical transitions are listed in Table 1, and one at 1.4 eV could account for the 1.693 eV transition found by Lawson *et al* [6] in annealed diamonds containing Ni and N.

The same cluster when relaxed with an effective spin of S=3/2 has an energy 0.8 eV greater than that with S=1/2. This implies there is an interesting transition in S when N atoms are brought progressively closer to Ni_s^-.

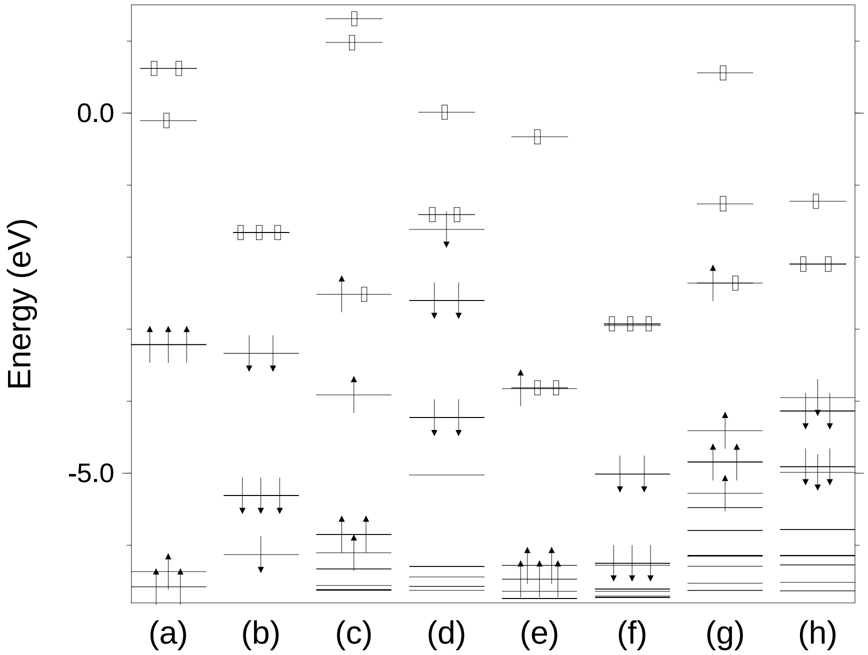

Fig. 3: The electronic structure of the four Ni_s defects. (a) and (b) correspond to the Ni_s^-, (c) and (d) to $Ni_s^-N_s^+$, (e) and (f) to Ni_s^+, and (g) and (h) to Ni_s^+-B^-. The levels have been shifted to bring the valence band tops into coincidence. Only levels in the region of the band-gap are plotted and the notation is the same as in Fig. 2.

Substitutional Ni^+. In diamonds where [N_s] is low, or compensated by B, one might expect Ni_s^- to be converted to Ni_s^+ with S=1/2. Ni_s would then act as both a donor and acceptor. To investigate this structure, Ni_s^+ was displaced from the T_d site along [111] by $\sim$ 0.4 Å. Upon relaxation, it returned to the T_d site, with the Ni-C nearest neighbours at 1.94 Å: an expansion of 0.12 Å from the negatively charged centre. This shows that the defect has almost T_d symmetry. The deep mid-gap $t_2^{\uparrow}$-level is now occupied by only one electron (Fig. 3 (e)). The location of these levels, far away from the bands, suggests that this charge state is stable. A weak Jahn-Teller distortion is now expected. The calculations indicate that the distortion is small, and thus it would only exist at low temperatures. If this leads to a trigonal defect, the t_2-level would split into an e and a_1-level although we are at present undecided which would be lower. Spin-orbit interaction would have to be included in a precise analysis.

Optical lines are expected (Table 1) around 2 and 2.5 eV. We believe that this defect is NIRIM-1. We note that in B rich diamonds, when Ni_s^{++} might be formed, the $t_2^{\uparrow}$-level would be empty leading to an non-magnetic defect – as observed – which contrasts with Ni_i^{++} with

S=1 as discussed above.

The Ni_s^+-B_s^- complex. Interaction between Ni_s^+ and B_s^- in low-N material would be expected to lead to a stable trigonal defect somewhat analogous with Ni_i^+-B_s^-. Both the Ni and B atoms were found to move along $\langle 111 \rangle$ resulting in a long B-Ni length of 2.32 Å. The three Ni-C bonds were 2.11 Å, and the Ni next-nearest neighbour-shell occurred at 2.51-2.56 Å. The energy levels are shown in Fig. 3 (g,h) and it can be seen that the t_2-levels of Ni_s^+ in Fig. 3 (e,f) have split into an e state lying below a_1. A single electron occupies the $e^\uparrow$ state, which then lies above an a_1-level. Of the possible optical transitions given in Table 1, the $e^\uparrow \rightarrow a_1^\uparrow$ (1.1 eV) has the lowest energy. Again, the e-level wavefunctions are nodal at the B site and hence strong hyperfine interactions with B are not expected. Zero-point motion contributions to the excitation energy, modified by different B-isotopes, would be present as the a_1-wavefunctions overlap B. Some splitting of the 1.1 eV line would then be expected from these different isotopes and this would be in addition to the spin-orbit splitting of the e-level. However, the B-isotopic splitting may be extremely small and not detectable as for example the absence of fine structure in the 856 meV PL line in C_i in silicon discussed elsewhere [10]. We believe that the complex is a strong candidate for the NIRIM-2 defect, as well as the 1.40 eV optical centre.

Discussion

The most noteworthy feature of these calculations is that whereas isolated Ni_i and Ni_s impurities have a small number of possible optical transitions, in general, when these impurities are complexed with donors and acceptors the T_d symmetry is lost and C_{3v} symmetries emerge. This change in symmetry splits the t_2-levels by $\approx$ 1 eV and produces a larger number of transitions at smaller energies. The six defects investigated should lead to about 20 optical lines. Now, experiment only identifies about five optically active Ni centres, which suggests that the transitions identified here have either low intensity, or only one class of Ni defects exist. As the only defect for which there is convincing evidence is Ni_s^-, one wonders whether all Ni related optical and EPR defects are simply different charge states of Ni_s and Ni_s complexed with other impurities. We note that all the optical features due to Ni are confined to octahedral growth sectors of diamond [11] which also suggests that these centres are incorporated as substitutional defects at the growing (111) surfaces.

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