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Microscopic Structure of Nickel-Dopant Centers in Diamond

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We present a theoretical investigation on the properties of interstitial nickel and its related complexes in diamond. The atomic configurations, symmetries, spins, and energetics of interstitial nickel, nickel-boron and nickel-vacancy complexes were investigated by a total energy *ab initio* methodology. Those results are used to explain certain electrically active centers, commonly found in synthetic diamond.

Keywords: Interstitial nickel; Diamond; Total energy *ab initio* methodology

I. INTRODUCTION

Macroscopic diamond samples have been synthesized by high pressure-high temperature methods, with transition metals such as Ni, Fe or Co or their alloys, serving as solvent catalysts. However, those metals end up incorporated in the resulting material, which may generate electrically active centers. While synthetic diamond has been used for mechanical applications, those impurities affected only marginally those applications. More recently, carbon based materials have been considered for new applications, such as electronic devices, for example in radiation detectors. In such cases, active centers may compromise the device performance, so it is important to understand the role played by those impurities.

Of all the transition metals used as catalysts, only nickel has been unambiguously identified in the resulting diamond. Therefore, the nickel-related active centers have received the greatest attention. Isolated substitutional nickel in diamond in the negative charge state (Ni_s^-) was identified by electron paramagnetic resonance (EPR) with spin $S=3/2$ [1]. Two other major centers, related to interstitial nickel, have also been detected in diamond [2]. The NIRIM-1 center was identified with a spin 1/2 and trigonal symmetry at very low temperatures, which switches to a tetrahedral one at higher temperatures. This center was tentatively assigned to an isolated interstitial nickel in the positive charge state (Ni_i^+). The NIRIM-2 center presents a trigonal symmetry and a spin 1/2. This center carries considerable controversy over its microscopic structure, it was initially suggested to be formed by an interstitial nickel with a nearby impurity or vacancy [2]. Other active centers have been identified more recently. The NE4 center [3], the precursor to other NE active centers, displays a D_{3d} symmetry and spin 1/2. It was tentatively associated to an interstitial Ni sitting in the middle position of a divacancy in the negative charge state, with $(\text{VNiV})^-$ aligned along a $\langle 111 \rangle$ direction.

There is considerable controversy over the microscopic structure of Ni-related centers in diamond. Here, we carried out an *ab initio* investigation on those microscopic configurations suggested to explain such active centers in diamond. Our results allowed to build a microscopic model which could explain most of the experimental data, specially those related to the NIRIM and NE4 centers.

II. METHODOLOGY

We used the spin-polarized full-potential linearized augmented plane wave method [4]. The calculations were performed within the density functional theory in the generalized gradient approximation [5]. For the 54-atom reference supercell, we used a $2 \times 2 \times 2$ grid to sample the irreducible Brillouin zone. Convergence on total energy was achieved using 7.0/R parameter (number of plane waves describing the interstitial region), where $R=0.64 \text{ \AA}$ is the radius of all atomic spheres. Self-consistent interactions were performed until convergence on the total energy and the atomic forces of respectively 10^{-4} eV and 0.02 eV/\AA were achieved. This methodology has been successfully applied to a number of defects in semiconductors [6-8].

III. RESULT

The electronic structure of isolated interstitial nickel [9, 10] is presented in Fig. 1. In the neutral charge state, Ni_i^0 presents a closed shell configuration, but in the positive charge state, Ni_i^+ presents a large trigonal distortion and a spin $S=1/2$. The highest occupied level has a delocalized e representation, which came from the t_2 level from Ni_i^0 .

Such electronic structure can be compared to the structure of a complex formed by an interstitial nickel and a substitutional boron (Ni_iB_s). The complex in a neutral charge state is stable in C_{3v} symmetry with a spin $S=1/2$. The highest occupied level, with a non-bonding e representation, has a large nickel character but a small boron one, as characterized by the total charge of that level inside the respective atomic spheres. Comparing the structure of the $(\text{Ni}_i\text{B}_s)^0$ and Ni_i^+ centers, the character of the highest occupied levels is considerably distinct. For the pair, the electron populating such upper level is essentially nickel-like, while it is very delocalized in the case of the isolated Ni impurity.

The same complex in a positive charge state, $(\text{Ni}_i\text{B}_s)^+$, is stable in a C_{3v} symmetry and presents an effective spin $S=1$. The interstitial Ni atom relaxes in the trigonal axis, moving toward the boron atom. In terms of the electronic structure, the highest occupied level has a non-bonding e representation.

Table I summarizes the results for the centers, including recent results for substitutional nickel [9, 10]. The struc-

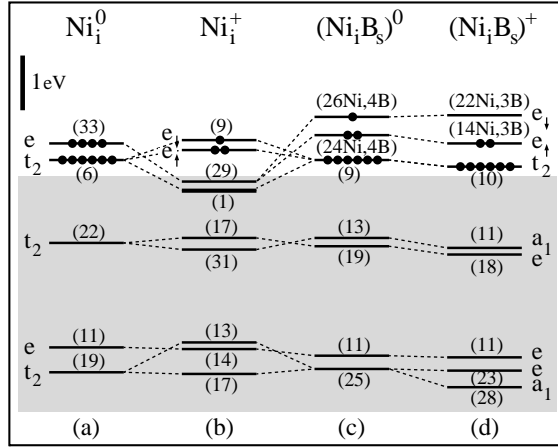


FIG. 1: 3d-related Ni energy levels in the gap region: (a) Ni_i^0 , (b) Ni_i^+ , (c) $(\text{Ni}_i\text{B}_s)^0$, and (d) $(\text{Ni}_i\text{B}_s)^+$. Levels with spin up and down are represented by \uparrow and \downarrow arrows, respectively. The number of filled circles gives the level occupation. The numbers in parenthesis represent the d -character percentage of charge inside the Ni atomic sphere. In the nickel-boron pairs, the p -character percentage of charge inside the B atomic sphere is also shown. Gray region represents the valence band.

TABLE I: Results for Ni-related centers in diamond: symmetry, multiplet ground state ($^{2S+1}\Gamma$), formation energy (E_F), and transition energy (E_t with relation to the valence band top). Here E_F is the Fermi energy.

Center	Sym.	Γ	$E_F(\text{eV})$	$E_t(\text{eV})$
Ni_s^+	C_{3v}	$^2\text{A}_1$	$5.9 + E_F$	$2.6(0/+)$
Ni_s^0	C_{3v}	^3E	8.5	
Ni_i^-	T_d	$^4\text{A}_2$	$11.5 - E_F$	$3.0(0/-)$
Ni_i^0	T_d	$^1\text{A}_1$	17.2	
Ni_i^+	C_{3v}	^2E	$16.3 + E_F$	$0.9(0/+)$
$(\text{Ni}_i\text{B}_s)^0$	C_{3v}	^2E	16.1	
$(\text{Ni}_i\text{B}_s)^+$	C_{3v}	^3A	$14.8 + E_F$	$1.3(0/+)$
$(\text{VNiv})^+$	D_{3d}	$^2\text{E}_u$	$5.2 + E_F$	$0.2(0/+)$
$(\text{VNiv})^0$	D_{3d}	$^3\text{A}_{2u}$	5.4	
$(\text{VNiv})^-$	D_{3d}	$^2\text{E}_u$	$6.2 - E_F$	$0.8(0/-)$

ture for the NIRIM-1 was initially suggested to be Ni_i^+ , with Ni_s^+ being ruled out [2]. However, our results show that both configurations could in fact explain the NIRIM-1 in terms of symmetry and spin. Our results favor the Ni_s^+ center, which is supported by recent experimental investigations [11]. The Ni_s^+ configuration has a very small trigonal distortion, so that there is a small total energy difference between the Ni_s^+ in T_d and C_{3v} symmetries. This small difference in energy between those two symmetries could explain the experimental observation of a symmetry transition at a very low temperature for the NIRIM-1 center [2].

Considering now the NIRIM-2 center, one of the proposed models was an interstitial nickel with a nearby vacancy [2].

Our calculations show that such configuration is unstable, the interstitial nickel relaxes toward the vacancy, with the final configuration being a substitutional nickel. On the other hand, our results for isolated Ni_i^+ are consistent with NIRIM-2 EPR data on symmetry, ground state multiplet, and spin. The $(\text{Ni}_i\text{B}_s)^0$ complex is also consistent with that EPR data. In terms of the charge distribution, the highest occupied level in the $(\text{Ni}_i\text{B}_s)^0$ pair is considerably more localized than that in the Ni_i^+ , favoring an EPR observation.

It has been recently proposed that NIRIM-2 should involve Ni_i with a next nearest neighboring boron atom [11]. The pair of a Ni_i with a nearest neighboring boron was ruled out based on the small experimental trigonal energy splitting ($\lambda \approx 55\text{meV}$) between the two excited multiplets. It was argued that an ionic interaction between two point charges (Ni_i^+ and B_s^-) as nearest neighbors in diamond would lead to a very large splitting ($\lambda \approx 0.5\text{eV}$), which would be inconsistent with the experimental value [11]. However, as it has been recently discussed [12], an ionic model, based on point charges, is not reliable to describe the interaction between a transition metal and a dopant in semiconductors. Therefore, the energy splitting should be much smaller than that suggested, and the results on the $(\text{Ni}_i\text{B}_s)^0$ pair would still be consistent with the NIRIM-2 center. Another center has been associated to nickel-boron pairs. The NOL1 [13] center, probably the same center as the NIRIM-5 center, has been found in heavily boron doped diamond. Our results for the $(\text{Ni}_i\text{B}_s)^+$ pair are fully consistent with this center on symmetry and spin.

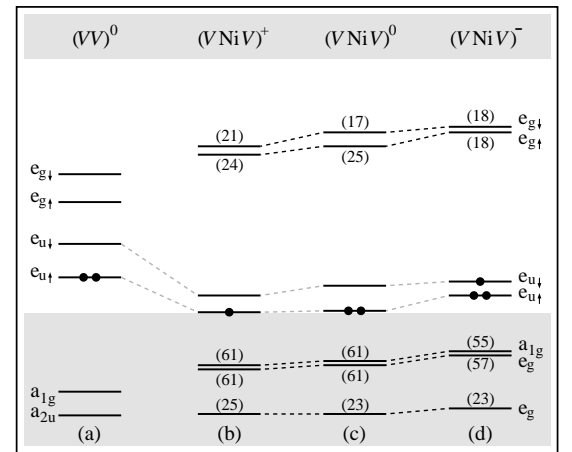


FIG. 2: 3d-related Ni levels near the diamond gap region for (a) $(\text{VV})^0$ (b) $(\text{VNiv})^+$, (c) $(\text{VNiv})^0$, and (d) $(\text{VNiv})^-$. Energy levels with spin up and down are represented by \uparrow and \downarrow arrows, respectively. The gap level occupations are given by the number of filled circles. The numbers in parenthesis represent the d -character percentage of charge inside the Ni atomic sphere.

Figure 2 presents the electronic structure of the nickel-divacancy (VNiv) complex, and the results are summarized in table I. In the negative charge state, the center has spin 1/2, which would be fully consistent with the experimental data for the NE4 center [3]. On the other hand, the electronic structure

of the center cannot be associated to a t_2^5 Ni electronic configuration, as suggested earlier [3]. Instead, our results show that the relevant electronic properties of this center should be associated with the divacancy-like orbitals, which appear in the bottom of the gap, while the Ni-related orbitals remain resonant in the valence band.

IV. SUMMARY

In summary, we performed an *ab-initio* investigation on the properties of nickel-related defects in diamond. Our results provide a consistent microscopic model for several active centers in diamond. Ni_i^+ or Ni_s^+ centers could explain the properties of the NIRIM-1 in terms of spin and symmetry. Our results suggest that Ni_s^+ is more likely for the NIRIM-1 cen-

ter, consistent with recent investigations [11, 14]. An isolated interstitial nickel in the positive charge state could explain the experimental results for the NIRIM-2 center. However, the $(\text{Ni}_i\text{B}_s)^0$ pair could also be the microscopic structure for NIRIM-2. Additionally, our results for the $(\text{Ni}_i\text{B}_s)^+$ pair are fully consistent with the experimental data for the NOL1 center.

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