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Substitutional nitrogen atom in diamond. A quantum mechanical investigation of the electronic and spectroscopic properties

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ABSTRACT

This paper reports the fully-relaxed lattice and electronic structures, vibrational spectra, and hyperfine coupling constants of the substitutional N_s defect in diamond, derived from B3LYP calculations constructed from *all-electron* Gaussian basis sets and based on periodic supercells. Mulliken analyses of the charge and spin distributions indicate that the defect comprises a single unpaired electron distributed very largely over both the negatively-charged substituted site and one of the four nearest-neighbour carbon sites, which relaxes away from the impurity. This leads to a local C_{3v} symmetry, with the nitrogen 'lone pair' lying along the C_3 axis and pointed towards the 'dangling' bond of the shifted carbon neighbour. The calculated band gap is 5.85 eV, within which a singly-occupied, majority spin donor band is found ~2.9 eV above the valence band, and an unoccupied, minority spin acceptor band ~0.9 eV below the conduction band. Atom-projected densities of states of the donor and acceptor levels show that, contrary to a widespread description, ~30% only of the donor band derives from nitrogen states *per se*, with the majority weight corresponding to states associated with the shifted carbon atom. The defect formation energy is estimated to be ~3.6 eV. The calculated IR spectrum of the impurity centre shows several features between 800 and 1400 cm^{-1}, all of which are absent in the perfect crystal, for symmetry reasons. These show substantial agreement with recent experimental observations. The calculated hyperfine constants related to the coupling of the unpaired electron spin to the N and C nuclei, for which the Fermi contact terms vary from over 200 MHz to less than 3 MHz, are generally in good agreement with the largest experimental values, both in terms of absolute magnitudes and site assignments. The agreement is less good for the smallest two values, for which the experimental assignments are less certain. The results lend support to previous suggestions that some of the weaker lines in the observed spectra, notably those below ~7 MHz, which are difficult to assign unambiguously, might result from the overlap of lines from different sites.

1. Introduction

Diamond, with its high melting point, chemical stability, wide band gap, high carrier mobility and optical transparency in the Infrared (IR), is an attractive candidate for application in numerous areas of technological importance, including high temperature diodes, microwave transistors, thermistors and radiation detectors [1,2]. Consequently, these extreme properties, which can often be related to the presence of intrinsic and extrinsic defects and can be incorporated in both natural and synthetic diamond despite the strength of the C-C bonding [3–8], have been the subject of widespread and sustained theoretical and experimental interest [5–18]. Of the many and varied experimental techniques that are available, IR and Raman spectroscopy have been shown to be particularly suited to the attempted characterization of the atomic nature of point-defects in diamond-like materials [6,7,12,16,17,19–25].

Nitrogen is the most common impurity in diamond, leading to numerous phases which are characterized by the content and atomic nature of the impurity. In type *Ib* diamond, isolated nitrogen atoms substitute single carbon atoms [26,27], giving the substitutional defect, N_S, also referred to as C centres; they are the simplest nitrogenous defect in diamond. However, pure natural *Ib* diamonds are extremely rare, for high geological temperatures and pressures

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promote aggregation, first to vicinal N_S pairs, known as A aggregates, which, at more extreme conditions, coalesce to form so-called B aggregates, in which four N_S surround a carbon vacancy. In addition, during B aggregation, a side reaction also leads to the formation of N_3 aggregates, in which three N_S impurities are bound to a carbon vacancy [28,29]. On the other hand, synthetic diamonds produced by CVD (carbon vapour deposition) and controlled HTHP (high temperature high pressure) grow generally as type *Ib*, but often, with minor amounts of other defects [30].

The single substitutional defect, N_S, leads to a distinctive IR spectrum with characteristic vibrational modes [31–38] at 1130 and 1344 cm^{-1}; it also gives rise to the P1 electron paramagnetic resonance (EPR) signal, which is how it was first discovered in 1959 [39]. Both the early EPR and subsequent ENDOR studies [39–43] have shown that the P1 centre has an effective spin of $S = \frac{1}{2}$, a C_{3v} symmetry with the nitrogen atom, N_S, displaced away from one of its four neighbours, and that most of the unpaired spin is located on just one of the carbon atoms neighbouring N_S. Correlations between the intensity of the 1130 cm^{-1} peak and the N_S content derived from EPR experiments have established that P1 and C centres are unambiguously the same defect [44,45].

The structure of the N_S defect has been confirmed by several *ab initio* calculations [47–50], which show that it consists of a single nitrogen atom bonded to three carbon neighbours. The nitrogen lone-pair orbital and that of the un-coupled 'dangling' bond electron of the furthermost carbon neighbour are directed towards each other forming a fourth, more extended N-C *bond*, which is calculated to be between 24% and 32% longer than the C-C bond in diamond. It is this chemical re-construction that is believed to drive the energy of the donor, namely the un-coupled electron, deep into the band gap, some 1.7 eV - 2.2 eV below the conduction band minimum according to photoconductivity [51] and optical spectra measurements [52].

However, it is important to recognise that neither of these sets of measurements can reveal the detailed electronic structure of the donor level. Clearly it is the result of nitrogen insertion into the diamond lattice, but may not be a nitrogen level *per se*. All previous calculations, whether finite cluster or periodic supercell, have been based on the simplest implementations of DFT, either LDA or PBE. However, these are known to describe poorly the exchange interaction, leading to appreciable underestimates of the band gap, which is precisely where the defect states are located.

Conversely, recent quantum-mechanical characterization of several point-defects in diamond [53–62] has shown a notable accuracy of hybrid functionals (which include in their formulation a certain percentage of *exact* exchange interaction) in predicting the electronic properties of these systems. Accordingly, the present paper reports new calculations of the charge and spin densities, band structure, IR and Raman frequencies and hyperfine coupling constant of the C centre (N_S) in diamond based on the energy-minimised atomic configuration of the defective lattice. The methodology comprises a combination of *all-electron* B3LYP electronic structure calculations for defective supercells containing up to 512 diamond units, and fully-analytic quantum mechanical methods for the *ab initio* evaluation of the IR and Raman spectra of solids.

2. Computational methods

For the most part, the DFT [63,64] calculations reported in this paper were based on the B3LYP global hybrid functional [65,66], as implemented in the CRYSTAL program [67]. However, for comparison, selected features of the electronic properties of the N_s defect have also been examined using other DFT formulations based on pure LDA [68,69] and PBE [70], and the global PBE0 [71] and range-separated HSE06 [72] functionals. Pople's standard 6-21G [73] *all-electron* basis sets of Gaussian type functions have been adopted for both carbon and nitrogen, except for values of 0.23 and 0.30 $Bohr^{-2}$ for the exponents of the outermost *sp* orbitals of the host and dopant atoms respectively. Again, for comparison and confirmation, two groups of additional basis sets have been examined. The first comprising, 6-21G, 6-31G and 6-31G*, was used to verify the N_s formation energy. The second, consisting of 6-31G-J* and 6-311G-J* bases [74], was employed for calculations of the electron-nuclear spin hyperfine coupling tensor (see below). These latter sets were designed with the explicit aim of creating small, but sufficiently accurate, basis sets for calculating spin coupling constants. They were derived from standard 6-31G and 6-311G bases by expanding the core functions followed by a new contraction of the valence functions [74].

The truncation criteria of the Coulomb and exchange infinite lattice series are controlled by five thresholds, T_i, which have been set to 8 (T_1-T_4) and 16 (T_5). The convergence threshold on energy for the self-consistent-field (SCF) procedure has been set to 10^{-8} hartree for structural optimizations, while the convergence threshold has been set to 10^{-10} hartree for frequency calculations.

The DFT exchange-correlation contribution and its gradient are evaluated by numerical integration over the unit cell volume. The generation of the integration grid points is based on an atomic partition method, originally proposed by Becke [75], in which the radial and angular points are obtained from Gauss-Legendre quadrature and Lebedev two-dimensional distributions respectively. The choice of a suitable grid is crucial both for numerical accuracy and cost consideration. In this study a pruned grid with 75 radial and 974 angular points has been used.

The long-established supercell approach is used to simulate different defect concentrations. Here cells containing 64, 128, 216 and 512 atoms have been considered, and indicated as S_{64}, S_{128}, S_{216} and S_{512} in the following. Reciprocal space sampling is based on a regular Pack-Monkhorst [76] sub-lattice grid centred at the Γ point (*i.e.* at the centre of the first Brillouin zone), leading to 4 (S_{64} and S_{128}) and 2 (S_{216} and S_{512}) sample points along each of the reciprocal lattice vectors, which corresponds to 13 and 4 **k**-points in the irreducible part of the Brillouin zone respectively, after point symmetry has been taken into account.

Harmonic phonon frequencies, ω_p at the Γ point are obtained from the diagonalization of the mass-weighted Hessian matrix of the second energy derivatives with respect to atomic displacements *u* [77–81].

$$W^{\Gamma}_{ai,bj} = \frac{H^0_{ai,bj}}{\sqrt{M_a M_b}} \quad \text{with} \quad H^0_{ai,bj} = \left(\frac{\partial^2 E}{\partial u^0_{ai} \partial u^0_{bj}}\right), \tag{1}$$

where atoms *a* and *b* (with atomic masses M_a and M_b) in the reference cell, **0**, are displaced along the *i*-th and *j*-th Cartesian directions, respectively. Integrated intensities for IR absorption $\mathscr{I}_p$ are computed for each mode *p* from the mass-weighted effective-mode Born-charge vector $\vec{Z}_p$ [82,83] by means of the CPHF/KS relationship [84,85].

$$\mathscr{I}_p \propto \left|\vec{Z}_p\right|^2. \tag{2}$$

The relative Raman intensities of the peaks are computed analytically via a similar scheme [86,87].

The coupling between the spin of the unpaired electron(s) (**S**) and the system of the nuclear spins (**I**) is described through the spin Hamiltonian: