Density Functional Studies of Muonium in Diamond: The Mux Centre

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Abstract

Diamond is potentially an important wide band-gap semiconductor because of its high intrinsic carrier mobility, high thermal conductivity and hardness. Hydrogen is a significant electrically active impurity in CVD diamond, but its properties are not well understood. Muonium is chemically a light isotope of hydrogen so that the μSR technique can provide useful characterisation for the state H atoms in a crystalline material. We present the results of a computational investigation to identify a μSR centre labelled Mux which has a large isotropic hyperfine interaction, less than axial symmetry, and is possibly associated with nitrogen defects. Density functional calculations were used to study the geometries, electronic structures, electrical levels and hyperfine interaction of hydrogen and muonium in a range of sites.

Keywords: Diamond, Density functional theory, electronic structures

1.   Introduction

In the past decade, the quality of single-crystal diamond grown from the gas phase has reached levels suitable for electronics [1]. However, the incorporation of hydrogen present in the growth gas leads to electrically active defects [2,3] so there is a clear need to improve the understanding the structure and properties of H-containing point defects in diamond. A pseudo-isotope of hydrogen called muonium is made up from a positive muon and an electron. The muon has same spin as proton, but about one ninth the mass, and about three times the nuclear magnetic moment. Muon-spin-relaxation μSR) experiments which detect the interaction between unpaired electron spin and the muon spin are sensitive probes of structure, and have been highly successful in determining the properties of H in a wide range of materials. For pure diamond, two μSR centres labelled normal and anomalous muonium relate to the tetrahedral interstitial site (MuT) and bond centred site (MuBC), respectively. The former exhibits an entirely isotropic hyperfine interaction (3711 ± 21MHz), whereas MuBC is comprised from a combination of a small isotropic term, and an anisotropic term aligned along the [111] direction A_s = -205.7, A_p = 186.9 [4]. At low temperature, both MuT and MuBC are observed, but the amplitude of MuBC increases between 350 and 800 K, explained by an activated transitions from MuT to a thermodynamically more stable MuBC. In addition to hydrogen, a common impurity, especially in natural diamond, is nitrogen. During heat-treatment above around 1600 ℃ nitrogen forms aggregates, of which nearest-neighbour pairs (A-centres) and N_4 surrounding a vacant site (B-centres) are particularly stable. In material containing such aggregates a new muonium centre is seen, but as its structure is unknown, it has been labelled MuX [5]. This muonium has less than axial symmetry, but a large isotropic hyperfine interaction indicative of a non chemically-bonded muonium centre: the μSR spectra are fitted to hyperfine parameters of A_s = 4158 ± 1500 MHz and A_p = 248 ± 13 MHz. Note the large experimental error bar for As. In this paper, we present the results of density functional simulations to test the experimental hypothesis.

2.   Method

First-principles density functional theory within the generalized gradient approximation [6] calculations are carried out using the AIMPRO code [7, 8]. Wave functions are expanded in atom-centred Gaussian basis functions (22, 40 and 16 functions for C, N and H atoms, respectively), and the charge-density fitted to a plane-wave basis with maximum kinetic energy of 300 Ha. The optimised structures for muonium and hydrogen in diamond are obtained by relaxing all atoms in supercells comprised from 64 or 216 host sites (simple-cubic lattice with lattice vectors of 2a0 or 3a0).   To obtain total energies, the Brillouin-zone is sampled using the Monkhorst-Pack scheme [9] generally with a uniform mesh of $2\times2\times2$ special k-points. Core-electrons are eliminated by using norm-conserving pseudo potentials [10] and hyperfine interactions obtained by reconstructing the all-electron wave functions in the core region [11, 12]. Diffusion barriers have been obtained by using the climbing nudged elastic band formalism [13]. Relative eneries are obtained using the calculated formation energies [14]

$$E^f = E^t - \sum_i \mu_i + q(E_v + \mu_e) + \chi$$

Where E^t the calculated total energy, μ_i and μ_e is are the chemical potentials of the atoms and electrons, respectively, E_v is the energy of valence band top, q is the charge state, and χ is the correction term due to the periodic boundary condition [15].

3.   Results

Muonium in pure diamond

To confirm the accuracy of the computational scheme we have first analysed the properties of muonium in the MuT and MuBC configurations. We find that the T-site is 1.25 eV higher in energy than the bond-centred site, but that the reaction T→BC is activated by 0.6 eV. These values are consistent with previous theory and experiment [4, 16]. The calculated hyperfine tensors for the two sites are listed in Table 1.

Table I: Comparison of experimental and theoretical work for hyperfine tensors of MuT and MuBC (MHz)

	Mu_T		Mu_{BC}	
	A_s (MHz)	f	A_s (MHz)	A_p(MHz)
This study	3960	0.89	−271	235
Ref. 17	3347	0.75	-	-
Ref. 18	-	-	−233	204
Experiment [4]	3711	0.831	−205.7	186.9

* f is the ratio of the isotropic hyperfine interaction for the defect to that for muonium in vacuum

Although there 7% error in value for MuT, qualitatively the differences between the two sites where the muonium is non-bonded (Mu_T) and chemically interacting (Mu_{BC}) is very clear, and the error bars are typical of hyperfine calculations [19]. We view the analysis of the A-tensors for muoumium to validate our method

Muonium in N-containing diamond

We have simulated the two suggested5 systems for MuX. The structures of the A- and B-centres are shown schematically in Fig. 1 and Fig.2. Both configurations are stable because all atoms are chemically satisfied: all C and N atoms are tetrahedrally bonded to four and three other atoms, respectively.
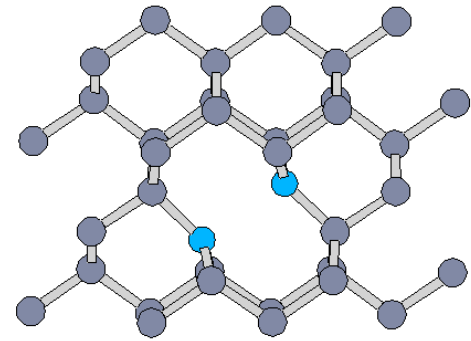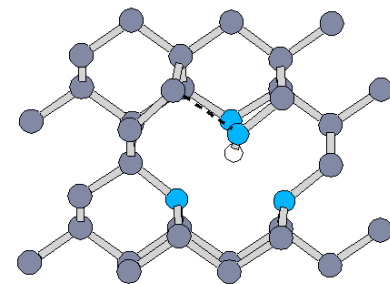

(a) A-centre in diamond
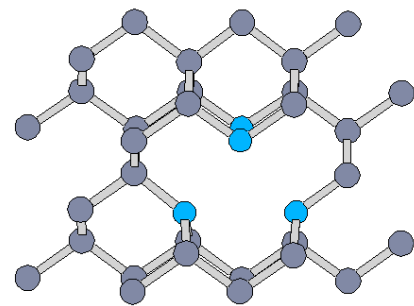
(b) B-centre in diamond,
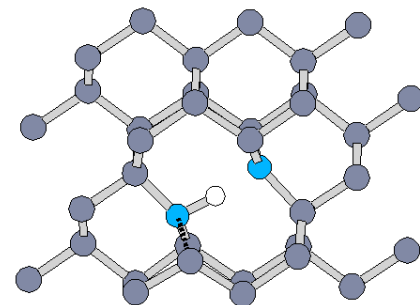
(c) Muonium in A-centre in diamond

(d) Muonium in B-centre in diamond.

Figure 1: Schematics showing the calculated structures of (a) A-centre in diamond, (b) B-centre in diamond, (c) muonium in A-centre in diamond, (d) muonium in B-centre in diamond. Vertical and horizontal directions are [001] and [110] respectively. The gray, blue and

white colour are carbon and nitrogen atoms and muonium, respectively. The broken lines represent broken bonds.

4.   Discussion

The hyperfine-tensors for complexes of muonium with A- and B-centres mean that these centres are most probably not responsible for MuX. However, there are a number of ways that the calculation must be viewed. First is that the calculations relate to a static structure, whereas the experiment involves the motion of the constituents. Indeed, it has been suggests that some of the error in the estimate of the hyperfine-tensors for anomolous muonium in pure diamond arise from the zero-point motion of the very light muon along the axis of the C--C bond [18,20,21]. We might ask the question as to if motional effects for either of the complexes can result in agreement with the MuX parameters. It seems unlikely since even in the case of MuBC the effect of including motional averaging is a perturbation, whereas for either of the two N-containing complexes with muonium, the isotropic term must increase by two orders of magnitude to match the measured values of MuX. μSR A second possibility, given the large uncertainty in the experimental parameters, is that is resolving the muonium annihilation events in a region not directly within the N-aggregates, but in an approximately tetrahedral cage in the immediate vicinity of them. However, the perturbation to the hyperfine-tensors of MuT even in the T-sites adjacent to the A- and B-centres is very small, and the binding energies in these chemically unreacted sites are also very small, so this interpretation seems unlikely to be correct. A final possibility that we will discuss is that muonium is tunnelling rapidly between sites around the N-aggregates. Indeed, such effects are thought to be present in the case of muonium in Zn-doped GaAs [22], but if this were the case in N-containing diamond, it is not obvious why the resulting hyperfine-tensor would be non-axial given the high symmetry of the two nitrogen aggregates involved. There remains the possibility that the MuX centre is not associated with the N-aggregates directly. In fact there are two good candidates for sites in material containing aggregated N. In such diamond there is evidence for nano-cavities and planar self-interstitial aggregates, both of which have open regions to trap the mobile muonium that would result in isotropic components to the hyperfine-interaction, consistent with the measured values for MuX. Of these, perhaps the more favourable option would be the self-interstitial precipitate, as this has a reasonably regular structure that would yield a non-axial tensor.Calculations investigating these possibilities are underway.

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