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Abstract
Different charged forms of substitutional oxygen in diamond are examined
using *ab initio* plane-wave pseudopotential calculations. The results show that
two defect levels are associated with substitutional oxygen and that the charged
form of the defect depends sensitively on the Fermi level. One of the defect
states lies well in the energy gap and the other is located near the conduction
band edge. The positively charged form of the oxygen defect is suggested to be
responsible for an optical absorption band occurring at 2.6 eV. It is shown that
oxygen in the lattice vacancy exhibits an amphoteric behaviour in diamond.

1. Introduction

Of the many defects in diamond, nitrogen [1, 2] and boron [3] are the main chemical elements
now well identified as being associated with a variety of complexes. Nitrogen as a simple
substitutional defect forms a deep level at 1.9 eV [4, 5] below the conduction band edge and
boron gives a shallower level at 0.365 eV above the edge of the valence band [6, 7]. Whilst
the defect levels associated with both B and N are now well established, neither defects have
levels conveniently located near the bulk band edges that offer the potential to make diamond an
efficient electronic semiconductor. For this reason the properties of a variety of other chemical
defects in diamond are now being investigated [8–10].

The optical spectra of defects in diamond are often characterized by strong features
involving a zero-phonon line and related sidebands. Often the degeneracy of states associated
with such transitions leads to strong Jahn–Teller effects. Because of the localized nature
of such defects the electronic interaction with the diamond host is relatively weak and the
optical behaviour more characteristic of a molecular-like system. The vacancy in diamond is
probably the most well known defect that exhibits dynamic Jahn–Teller features and, notably,
the negatively charged vacancy has a zero-phonon structure in which the electronic transition
involves a_1 and t_2 one-electron states [11, 12]. This is observed in the characteristic optical
spectrum—often referred to as the ND1 band—as equally spaced sharp phonon replicas that
can be described through a simple vibronic model from which a Huang–Rhys factor, S, is
derived. In the case of the ND1 band, $S \simeq 1.5$ [13].

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On the other hand, the optical absorption of defects can cover quite a broad energy range suggesting significant interaction with the lattice. The optical absorption of nitrogen is one such transition involving both a localized (ground) state and a delocalized (excited) state. Some time ago, Collins and Mohammed [14] reported a unique optical feature of brown gem-quality diamond. This spectrum consists of a broad featureless absorption band peaking at 2.6 eV. Luminescence of the centre, on the other hand, occurred at 2.721 eV with a well defined sharp zero-phonon structure and related phonon sidebands separated by 34 meV and a Huang–Rhys factor lying in the range $6.4 < S < 8.5$. This feature is not unlike that associated with the ND1 band in diamond that is associated with the negatively charged vacancy and characteristic of a transition to a one-electron non-degenerate (a_1) state. The defect responsible for the 2.6 eV broad absorption and 2.721 eV relatively sharp emission was uncertain.

As has been shown from previous defect calculations on diamond [8, 9] and many other materials [15], the defect energy level is very much dependent upon the location of the Fermi energy in the host material. Unlike the case for several semiconductors, a precise location of the Fermi level in diamond is difficult to engineer, but in the case of type-IIB diamond the Fermi level is located near the edge of the valence band due to the presence of B.In view of this, the material can be regarded as p-type. With type I diamond, which contains N, the Fermi level lies nearer the conduction band, but N as a simple point defect is quite deep and thus is not a feasible defect to use for n-type conductivity.

In this paper we shall investigate the properties of a simple substitutional oxygen defect in the diamond lattice. On the basis of the analysis presented here, we argue that O located at the vacancy in diamond is an amphoteric defect with a vacancy-type character. Our findings for the positively charged form of the defect show that an energy level structure emerges that is not dissimilar to that of the negative vacancy and has a similar energy level structure. For this reason we argue that the defect observed optically by Collins and Mohammed [14] may be associated with positively charged oxygen.

2. Computational analysis

The present work uses soft pseudopotentials generated through the method proposed by Troullier and Martins [16] with plane waves of cut-off 64 Ryd. Four special supercell k-points [17] have been used to obtain the charge density with electronic interactions evaluated using the local density approximation [18]. Throughout the present work a cubic supercell consisting of 64 atoms was used and all atoms in the supercell were allowed to relax self-consistently. We have considered neutral and negatively and positively charged forms of the defect, the latter being modelled by adding or removing an electron from the 64-atom supercell. As we shall see, the size of the supercell is justified by the highly localized lattice distortion about the O defect.

2.1. Computational results

In figure 1 we show the defect-related band structure of the oxygen defects in diamond as compared with a similar calculation for the bulk material. We note that the conduction band minima of bulk diamond occur in the region $\Gamma < k < X$ of the supercell, a point that has been alluded to in a recent publication [19]. All charged forms of O are associated with a deep non-degenerate a_1 state situated near the middle of the energy gap in diamond, but we also see the emergence of other (degenerate) states lying nearer the conduction band edge. The location of the lower a_1 state remains at nearly the same energy—about the centre of the bulk energy gap—for all charged forms of oxygen, unlike the higher-energy states. In the case of the O
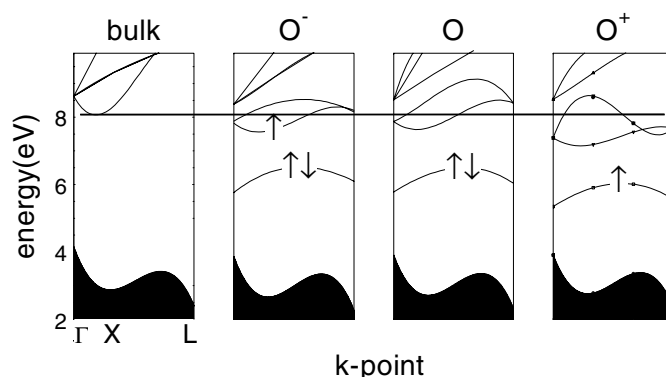
Figure 1. Electronic band structure of bulk diamond and for O defects in diamond. Arrows denote electrons.

Table 1. Defect energy levels relative to the valence band edges (eV) obtained from a tight-binding fit. (In the case of O^-, the t_2 level is slightly split.) The LDA-calculated bulk energy band gap is 4.5 eV as compared with the experimental energy gap of 5.5 eV.

Defect	$E(a_1)$	$E(t_2)$	ΔE
O^{2+}	1.18	3.36	2.18
O^+	1.50	3.50	2.00
O	1.96	4.13	2.17
O^-	1.98	~ 3.87	1.89

and O^- defects these states marginally overlap with the bulk conduction band edges, but with O^+ the states are noticeably lowered in energy, becoming slightly deeper in the energy gap.

Using a second-neighbour tight-binding fit [20] to the energy levels, we are able to estimate the positions of the defect energy levels, and these values are given in table 1.

Even though dispersion of the excited state is substantially changed with ionization of the centre, the state always remains degenerate at the Γ point of the supercell (except in the case of the negatively charged state) where essentially it is a threefold-degenerate (t_2-related) defect level. In absorption, the transition will reflect the delocalized excited degenerate state and therefore be broadened. In contrast, in emission, the transition will reflect the more localized character of the ground state. As can be seen from table 1 the energy of the t_2 state of O^+ is deeper than the t_2 level of O (by about 0.6 eV). Transitions between the a_1 and t_2 states of O^+ will therefore be between levels that are more localized than those associated with O or even O^-. For this reason we suggest that the transition observed by Collins and Mohammed [14] is associated with a transition of the O^+ defect.

In order to understand the electronic energy level structure it is revealing to consider electronic changes occurring at the O defect when the centre is ionized—i.e. the difference electronic structure between O and O^+. First there is a significant outward relaxation about the O ion with a small related compression of distances between the first and second C atoms from the defect. In table 2 we give the nature of the relaxation. We found little evidence of any non-symmetric relaxation for either O or O^+, as occurs for N in diamond or as exhibited by O in other materials such as Si, but there is some slight indication of an asymmetric relaxation for O^- because of Jahn–Teller effects. This is not unexpected because the localized a_1 state will, to first order, not be subject to any deformation. In figure 2 we show the charge density for each of the O and O^+ centres. Subtle changes are occurring at the core of the O atom but,
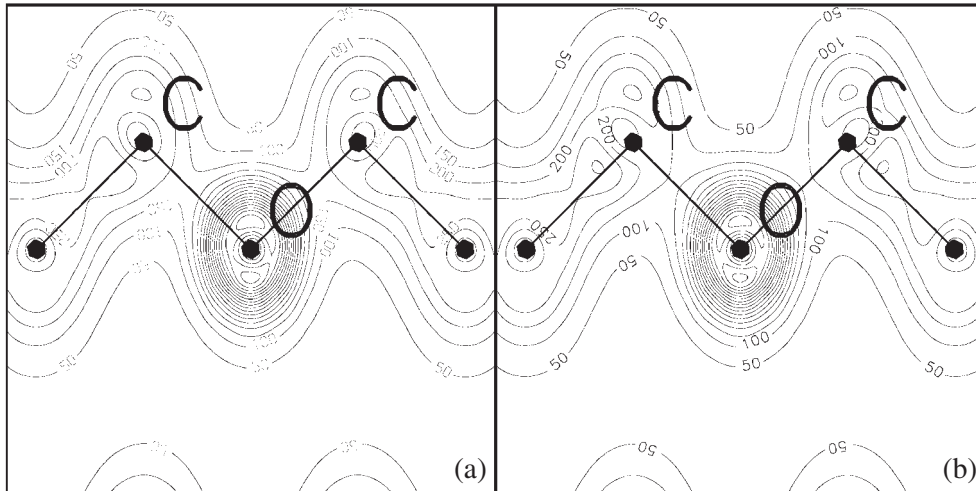
Figure 2. Electron-density distributions of (a) O and (b) O^+ in diamond. The units are *me* $Bohr^{-3}$.

Table 2. The lattice relaxation and range of the Fermi level (measured relative to the top of the valence band) where the defect is most probable. Other charged states such as O^- have not been considered.

| Defect	d_{O-C} (Å)	d^1_{C-C} (Å)	d^2_{C-C} (Å)	Fermi level (eV)
O^{2+}	1.66	1.51	1.54	0–1.39
O^+	1.69	1.50	1.54	1.39–1.97
O	1.72	1.50	1.53	1.97–2.89
O^-	1.74	1.49	1.53	> 2.89

in the main, there is a slight reduction in charge distribution from O to O^+. Less charge is observed between C and O atoms than between C atoms, indicative of a weaker C–O chemical bonding with respect to that of C–C bonds. This would suggest that the defect exhibits some kind of vacancy character with defect states associated with the C-atom dangling bonds. This feature is probably associated with the a_1 defect level.

2.2. Defect formation energies

We have considered the energy of formation of the oxygen defects, which is defined as [15]:

$$E_f = E(C_{63}O) - 63\mu_C - \mu_O + q\mu_e$$

where $E(C_{63}O)$ is the total energy of the supercell with one atom replaced by the O defect, μ_C the chemical potential of C (here taken from a calculation for diamond) and μ_O the chemical potential of the O atom. Here we have obtained a value for μ_O calculated using a recently reported stable structure for a solid-state molecular form of oxygen [21, 22]. The final term in the expression for E_f is included to accommodate charged defects (like O^+ or O^-) and represents the energy needed to obtain charge from some background potential. This term is necessary to maintain charge neutrality of the above expression for E_f, as in calculations of charged forms of the defect, electrons are either added or removed from the supercell. The value of μ_e can vary in the range $0 \leqslant \mu_e \leqslant E_g$, where E_g is the energy gap, depending upon the nature of the host material, but can be calculated implicitly from the calculated Fermi
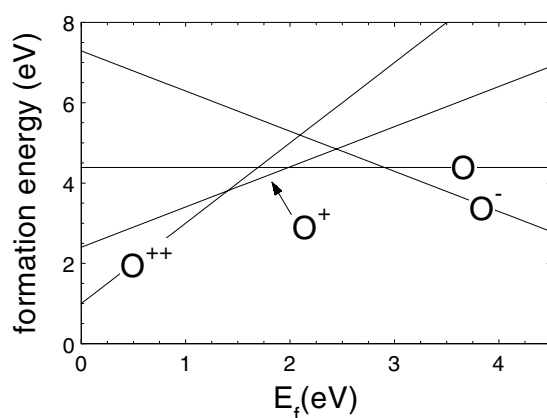
Figure 3. Formation energies of charged states of substitutional O in diamond. The energy gap of diamond is 5.5 eV.

energy of the defect system relative to the energy of the valence band maximum [15]. The calculated band gap is 4.5 eV compared to 5.5 eV from experiment. It is well known that the LDA severely underestimates the band-gap energy for supercell calculations. Since the states corresponding to the more localized a_1 and less localized t_2 levels have non-zero overlaps with the conduction band states, the difference between the a_1 and t_2 levels should be somewhat larger than the calculated ones found in table 1. The a_1 and t_2 levels in the band gap are occupied in some charge states of the oxygen defect. Since the positions of those levels are not accurate due to the method used, this uncertainty should be taken into account in the formation energies as well. The results for the formation energies in the different charge states are shown in figure 3. The formation energy of oxygen changes substantially with the Fermi energy, as shown. In table 2 we show the range of values for the Fermi level in which a specific charge state of O is the most stable. These values compare quite favourably with the results of some similar calculations reported earlier [8].

2.3. A defect molecule model

The highly localized nature of the mid-gap level associated with substitutional O is rather surprising. As discussed earlier, the reason for this is that the O atom bonds relatively weakly to the carbon dangling bonds in the vacancy, and thus exhibits a feature characteristic of a vacancy. It is well known that the isolated C vacancy gives rise to defect levels of a_1 and t_2 [11] with the t_2 defect level lying energetically above the a_1 level. Oxygen has outer valence states of s and p atomic character. In figure 4 we show schematically how such states hydbridize in such a way that it leads to a defect level ordering consistent with the results of *ab initio* calculations presented above. The lower bonded states formed between (i) the vacancy a_1 and O 2s orbitals and (ii) the vacancy t_2 states and O 2p orbitals are both completely occupied. The anti-bonding a_1^* and t_2^* states will be occupied by one to three electrons for O^+, O and O^- respectively. (In the case of O^-, the symmetry is slightly reduced to C_{2v} resulting in the small split of the t_2^* level.) Results of a calculation for the O^{2+} defect—for which the defect molecule model would predict a t_2 level even lower in energy that is completely filled—is entirely consistent with results of the defect molecule model. The O^{2+} defect is therefore electrically inert. The calculated formation energies are also consistent with this prediction.
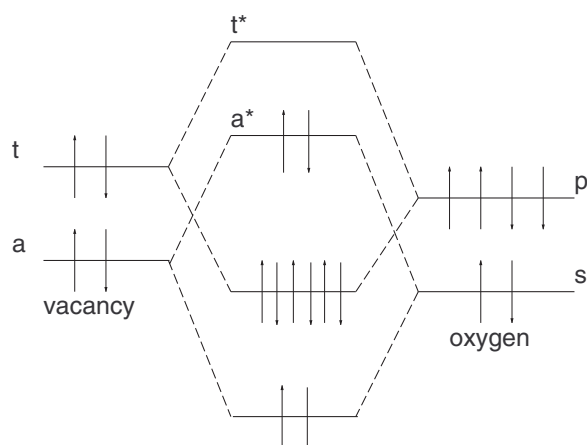
Figure 4. The defect molecule model for the defect levels of the neutral O defect in diamond.

3. Conclusions

We have used *ab initio* plane-wave computational modelling on various forms of the substitutional O in diamond. In general O gives rise to two defect-related energy states in the band gap—one a non-degenerate a_1 state lying near the middle of the energy gap and the other a threefold-degenerate t_2 state located close to the conduction band edges. The latter t_2 state is strongly affected when the O defect becomes ionized, and then in the positively charged form a defect level emerges that is clear of the conduction band. We suggest that electronic transitions between the a_1 and t_2 states of the positively charged O^+ defect may be responsible for the optical features found at about 2.6 eV observed in diamond as reported by Collins and Mohammed [14]. The calculated value for the emission energy of the O^+ defect is $\sim$2 eV less than the observed 2.6 eV. But as we have stated earlier, the LDA approximation significantly underestimates the band-gap energies and thus will undoubtedly underestimate transition energies. This will be especially true here, as the excited state of O^+ is only marginally localized.

There is an outward relaxation of the lattice for each of the charge states of the O defect, but this has only a small effect on the electronic properties of the defect.

We have predicted regions in which various charge states of the O defect will be most probable. This shows a rather strong dependence on the Fermi level in the material. Only when the Fermi level lies around the middle of the energy gap will either O^+ or O^{2+} be observed by photoluminescence. The nature of nitrogen doping in the diamond sample used by Collins and Mohammed [14] indeed implies a relatively low Fermi level and is thus consistent with the predictions made here. In contrast, the O^- defect has occupied levels lying very near the conduction band edge and only appears stable when the Fermi level is high in the material. This means that oxygen located at a C vacancy in diamond has very much an amphoteric character and thus can act as an electron trap in diamond. It is unlikely that, in itself, it will give rise to n-type conductivity. However, the possibility that O can form combinations with other defects such as N to produce n-type conductivity in diamond cannot be excluded.

Acknowledgments

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