The divacancy in silicon and diamond

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(August 4, 1999)

Abstract

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Abstract

First-principles studies of the divacancy (V_2) in both silicon and diamond are reported. We demonstrate that the contrasting experimental spin-density localisation of both systems can be explained through the one-electron pictures arising from opposing distortions.

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The removal of two neighbouring atoms from the diamond structure results in a defect with D_{3d} symmetry (see Fig. 1). A linear combination of atomic orbitals (LCAO) approach shows that the six dangling bonds of the divacancy give rise to four electronic levels in D_{3d} – two doublets, e_u and e_g (see Fig. 2) and two singlets, a_{1g} and a_{1u} which are lower in energy. In the neutral charge state the singlets are filled and two electrons occupy the lower doublet, e_u. The one-electron configuration $a_{1g}^2\, a_{1u}^2\, e_u^2\, e_g^0$ gives rise to three multiplets: $^3A_{2g}$, $^1A_{1g}$ and ^1E_g. The $S = 1$ state, $^3A_{2g}$, is orbitally non-degenerate and hence no Jahn-Teller distortion is expected. If the divacancy has spin 0, however, then a Jahn-Teller distortion is expected to lower the ground state symmetry and split the one-electron levels, e_u and e_g.

The silicon divacancy is observed by electron paramagnetic resonance (EPR) in two charge states [1]. The $S = 1/2$ spectra labelled G6 and G7 arise from V_2^+ and V_2^- respectively. The neutral charge state of the silicon divacancy is not observed by EPR, presumably because it possesses zero spin. Both G6 and G7 were found to possess C_{2h} symmetry below 40 K. Above this temperature the signals undergo motional broadening and narrowing effects resulting from thermally activated reorientations of the defect between three equivalent Jahn-Teller distortions. Above 110 K, the effective symmetry arising from the rapid reorientation was observed to be trigonal. The spin-density is found to be localised largely ($\sim 60\%$) on the two atoms in the defect mirror plane.

Watkins $et\ al$ [1] explain the low symmetry structure and spin-density results in terms of a strong 'pairing' distortion. Two pairs of dangling bonds may be reconstructed to produce a defect with C_{2h} symmetry. The LCAO method shows that the e_u and e_g doublets split under the pairing distortion as shown in Fig. 2(d). Two of the resultant singlet levels, b_u and a_g are localised on the mirror plane atoms, whereas the b_g and a_u wavefunctions are nodal on the mirror plane. Therefore, since the positive charge state has electronic configuration $b_u^1\, a_u^0$, the unpaired electron occupies an orbital which has amplitude on the mirror plane, consistent with experiment.

For V_2^-, a small pairing distortion would give rise to the electronic filling $b_u^2\, a_u^1$. In this case the unpaired electron occupies an orbital which is nodal in the mirror plane. In order

to explain the observed spin-density localisation, Watkins suggested that the Jahn-Teller distortion is strong enough to cause cross-over of the a_g and a_u levels thus giving $b_u^2 \, a_g^1$.

An alternative explanation for the spin-density localisation results of V_2^- has arisen from LDF supercell studies of Saito $et \, al$ [2]. A distortion which is inverse to the pairing distortion (see Fig. 2(b)) gives rise to a different one-electron ordering. Here, an outward displacement of four equivalent atoms leads to five-fold co-ordination with three strong covalent back-bonds and a pair of "resonant bonds" across the divacancy. A modest distortion of this type results in the electronic filling $a_u^2 \, b_u^1$. The unpaired electron then occupies an orbital with amplitude on the mirror plane consistent with experiment. Watkins points out [3], however, that only the pairing distortion appears consistent with stress alignment measurements. The application of compressive stress along $[01\bar{1}]$ lifts the degeneracy of the three Jahn-Teller distortion directions. One of the distortion directions is observed to be enhanced at the expense of the other two. Although the pairing model appears consistent with this observation, it is unclear why such an effect should arise from the resonant-bonding structure.

Further large-scale LDF super-cell calculations [4] have also found that the resonant-bonding structure to be stable. However, the study finds a new low symmetry structure is lowest in energy.

The R4/W6 EPR centre observed in irradiated diamond is attributed to the neutral charge state of the divacancy. The centre possesses effective spin 1 and so has a non-degenerate ground state, ${}^3A_{2g}$. It is then intriguing that the ground state of the defect also has C_{2h} symmetry, even though no simple Jahn-Teller effect can be responsible.

Hyperfine measurements [5] have shown that, in contrast to the divacancy in silicon, the diamond divacancy has very little spin-density ($< 2\%$) localised on the mirror plane atoms. This observation may be explained through the one-electron picture only by the electronic configuration $a_u^1 \, b_g^1$ or $b_g^1 \, a_u^1$.

LDF theory (AIMPRO [6]) has been employed in this study using large, hydrogen terminated silicon (diamond) clusters of composition $Si_{146}H_{98}$ ($C_{96}H_{78}$).The wave-function basis consisted of independent s and p Gaussian orbitals with four different exponents, sited at

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each Si (C) site. A fixed linear combination of two Gaussian orbitals was sited on the terminating H atoms. In addition, a Gaussian s and p orbital was placed at each Si–Si (C–C) bond centre. The charge density was fitted with four independent Gaussian functions with different widths on each atom and three on the terminating H atoms. One extra Gaussian function was placed at each bond centre. All atoms were optimised using a conjugate gradient method. The total energy of each stable cluster was calculated and the character of each Kohn-Sham level introduced into the gap was determined.

V_2^+, V_2^0 and V_2^- in silicon were optimised with symmetry constrained to D_{3d}. An inward breathing motion of atoms resulted in a lengthening of Si–Si bonds around the divacancy so that the optimised distances, $l_{ab} = l_{ac} = l_{bc}$ (see Fig. 2 (c) for atom labelling) were reduced from the ideal value of 3.83 Å. Structures are reported in table I.

The distorted structures were investigated using two different initial structures corresponding to distortions of the pairing and resonant bonding types. During relaxation, symmetry was constrained to C_{2h}. In silicon, no outward (resonant bonding) distortion was found to be stable in any charge state. Stable pairing structures, however were located for all charge states investigated.

In both the single negative and single positive charge states the pairing distortion is found to be sufficient to cross the a_g and a_u levels as shown in Fig 2 (e). The energy of the optical transition between the a_g and a_u levels for V_2^- was calculated using a transition state method [7] to be 0.4 eV in excellent agreement with the experimental value, 0.34 eV [8].

In diamond, the $S = 1$, D_{3d} defect was found to have four Kohn-Sham levels in the bandgap with two doublets, e_g and e_u lying above two singlet levels b_u and a_g. All six atoms surrounding the divacancy relaxed outwards from their ideal positions by about 0.17 Å during optimisation.

The pairing distortion was found to be unstable in diamond, spontaneously relaxing to a D_{3d} structure. An outward distortion was located with energy 0.1 eV higher than that of the D_{3d} structure. In this distortion the b singlet levels cross giving b_u higher in energy than b_g (Fig. 2(a)). This results in the unpaired electrons occupying orbitals with nodes on

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the mirror plane. The angles made by the back-bonded atoms to each of the four atoms out of the mirror plane were determined to be 115.4°, 115.9°, 118.5° giving an average angle of 116.6° in reasonable agreement with experiment ($\sim 115°$). The distances between the atoms of the defect were found to be $l_{ac} = l_{bc} = 2.87$ Å and $l_{bc} = 2.68$ Å as compared with $l_{ac} = l_{ab} = l_{bc} = 2.75$ Å for the relaxed D_{3d} defect.

Although care must be taken, particularly in the case of diamond, where many electron effects are greater, the observed distortion of the spin $S = 1$ divacancy in diamond may be understood by consideration of the one-electron picture. In D_{3d} (Fig. 2 (c)) the e_u doublet is occupied by two electrons with parallel spins. When a modest distortion to lower symmetry occurs (Fig. 2 (b) or (d)) the combined one-electron energy of the two electrons is expected, to first order, to remain constant, but the distortion is disallowed because of the energy cost from increased strain around the defect. However, our calculations demonstrate that a larger distortion causes cross-over of the one-electron levels. This means, for example, that an outward distortion to C_{2h} symmetry can cause the b_g level to fall below the b_u level (Fig. 2 (a)). Hence it is apparent that the sum of the one-electron energies of the unpaired electrons is now reduced in the distortion. If this reduction exceeds the strain energy, then the distortion will be stable. Although this pseudo–Jahn-Teller effect holds equally for the pairing case, this distortion involves a larger movement of atoms from their ideal positions. We find that the associated strain energy is prohibitively large. However, an outward distortion may be expected, *a priori*, to be favourable in diamond due to the capability for sp^2 hybridization of carbon.

To conclude, we have successfully modelled the distortions required to explain the experimental observations for the divacancy in silicon and diamond. Calculations support the rebonding-by-pairs model for the divacancy in silicon for *both* positive and negative charge states. The spin-density in both cases is localised predominantly on the two silicon atoms in the mirror plane of the defect, in agreement with EPR studies. The calculated optical transition of V_2^- in silicon, which is a good measure of the magnitude of the distortion is in excellent agreement with experiment. The outward distortions previously reported are

found to be unstable and may arise because the volume of the unit cells were kept constant or from limitations in unit cell or basis size. In diamond, an outward distortion can account for the observed spin-density measurements.

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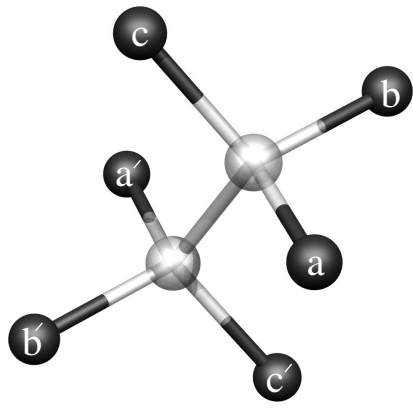[8] J. H. Svensson, B. G. Svensson and B. Monemar, Phys. Rev. B **38**, 4192 (1988).

TABLES

TABLE I. Distances (Å) between atoms surrounding the divacancy for the relaxed D_{3d} and C_{2h} structures in silicon and diamond. Distances are given with reference to Fig. 1.

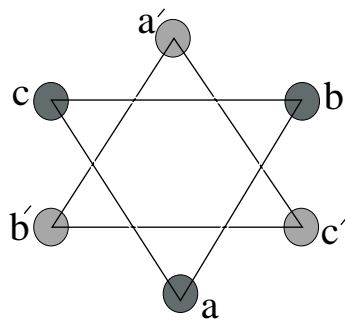| | SILICON | | | | DIAMOND | | | |
| | D_{3d} | C_{2h} | | | D_{3d} | C_{2h} | | |
Charge state	$l_{ab} = l_{ac} = l_{bc}$	l_{ab}	l_{ac}	l_{bc}	$l_{ab} = l_{ac} = l_{bc}$	l_{ab}	l_{ac}	l_{bc}
V_2^+	3.77	3.92	3.92	2.94	$\cdots$	$\cdots$	$\cdots$	$\cdots$
V_2^0	3.71	3.78	3.78	2.92	2.75	2.87	2.87	2.68
V_2^-	3.66	3.71	3.71	2.76	$\cdots$	$\cdots$	$\cdots$	$\cdots$

FIG. 1. (a) Schematic of the ideal divacancy in silicon or diamond. The atoms are labelled following the notation used by Watkins and Corbett [1]. (b) We summarise the structure of the divacancy with a view down the principal [111] axis.

FIG. 2. The effect of symmetry lowering distortions to C_{2h} on the one-electron levels of the ideal, D_{3d} divacancy. For clarity, circles indicate the orbitals with finite amplitude on the defect mirror plane. (a) & (b): A large (a) and small (b) resonant bonding, 'outward' distortion. The four equivalent atoms move out in pairs so that $l_{ac} = l_{ab} < l_{bc}$ and $l_{a'c'} = l_{a'b'} < l_{b'c'}$. (c) The D_{3d} structure. (d) & (e): A small (d) and large (e) pairing distortion. A bond is formed between the two atom pairs b, c, and b', c' such that the distances $l_{ac} = l_{ab} > l_{bc}$ and $l_{a'c'} = l_{a'b'} > l_{b'c'}$.

(a)

(b)

$$a_g$$

$$b_g$$ $$e_g$$

$$b_u$$ $$e_u$$

$$a_u$$

$$b_g$$

$$a_g$$

$$a_u$$

$$b_u$$

(a)　　　　(b)　　　　(c)　　　　(d)　　　　(e)