THE STRUCTURE AND MOTION OF THE SELF-INTERSTITIAL IN DIAMOND

ALISON MAINWOOD

Physics Department, King's College, Strand, London, England

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F. P. LARKINS† and A. M. STONEHAM

Theoretical Physics Division, AERE Harwell, Didcot, Oxon OX11 ORA, England

Abstract—We have made self-consistent semi-empirical molecular orbital calculations for various possible self-interstitial geometries in diamond, both with and without lattice distortion. Total energies are obtained, not merely the sum of one-electron eigenvalues. The results show that the (100) split interstitial has the lowest formation energy, not the cubic, hexagonal or bond-centred forms favour previously.

The nature of the interstitial does not support the local heating model of enhanced diffusion in the presence of recombination or ionisation. A Bourgoin–Corbett mechanism involving negative hexagonal and neutral split interstitials is possible, but the apparent stability of the negative hexagonal interstitial may be an artefact of the calculation. We suggest a local excitation model is appropriate in fourfold-coordinated semiconductors.

1. INTRODUCTION

The apparently athermal motion of the silicon interstitial[1] is one of the most striking results in the radiation damage of semiconductors. Explanations vary in detail, but normally invoke free carriers present from ionisation, rather than some fortuitously-small activation energy. Ionisation- and recombination-enhanced phenomena are not uncommon, including diffusion in semiconductors[1, 2], semiconductor device degradation[3], recrystallisation[4], catalyst efficiency[5] and photochemical damage in ionic crystals[6]. However, the precise mechanisms involved in interstitial motion depend on the form of the interstitial. Rather little has been established unambiguously by experiment. Thus we have made detailed calculations on possible interstitials in diamond. Parts of this work will be discussed elsewhere; the present paper is concerned with possible diffusion mechanisms in both diamond and in related materials like silicon.

2. THEORETICAL METHODS

Our calculations use an approximate molecular-orbital method to study clusters of carbon atoms with and without interstitials. We have chosen the CNDO (Complete Neglect of Differential Overlap) method which, like others of this type, combines simplicity with physical sense[7]. In essence, the matrix elements in the Hartree–Fock–Roothaan equations are approximated systematically in terms of three semi-empirical physical parameters: orbital exponents (ξ), electronegativities (ϵ) and bonding parameters (β). Given these parameters, the CNDO program obtains self-consistent solutions analogous to Hartree–Fock solutions. The results list one-electron energies, the total energy, wave-functions and Mulliken charges. All our calculations have used the Harwell MOSES code[8], which handles a range of semi-empirical methods; it includes greatly improved numerical methods, plus options like periodic boundary conditions.

The CNDO method has been used in several very successful studies of condensed-matter problems[9,10]. There are three critical factors. First, how does one choose the CNDO parameters? The standard lists, usually based on organic molecule studies, are unsatisfactory. The present parameters were taken from Harker and Larkins' work[11] on the band structure of diamond using periodic boundary conditions. The values $\xi =$ 1.765 au^{-1}, $\epsilon = 7.0(s)$, $5.5(p)$ eV and $\beta = -10.2$ eV give good results for the equilibrium spacing, cohesive energy and the width and structure of the valence band, as well as other satisfactory qualitative features. Secondly, which cluster should be used? It must be large enough that the interstitial is sensibly distant from the surface, and the surface itself must be treated properly. It is especially important to make sure that there is no surface state close to the Fermi energy. The present calculations used up to 38 atoms, with up to an additional 44 effective atoms saturating the dangling bonds on the surface. The third critical factor is the local lattice distortion. One can, of course, guess sensible qualitative motions of the near neighbours, and minimise the total energy for each type of displacement. But the motions of further neighbours may be important too, and cause complexity at least. We have used previous results using valence-bond forces[12] to relate the motions of more distant neighbours to those of the first neighbours.

3. THE INTERSTITIAL CONFIGURATION

Six different types of interstitial in diamond were considered (Fig. 1). These were the tetrahedral (T), hexagonal (H) and bond-centred (B) sites, plus three

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†Permanent address: Chemistry Dept., Monash University, Clayton, Victoria, Australia.
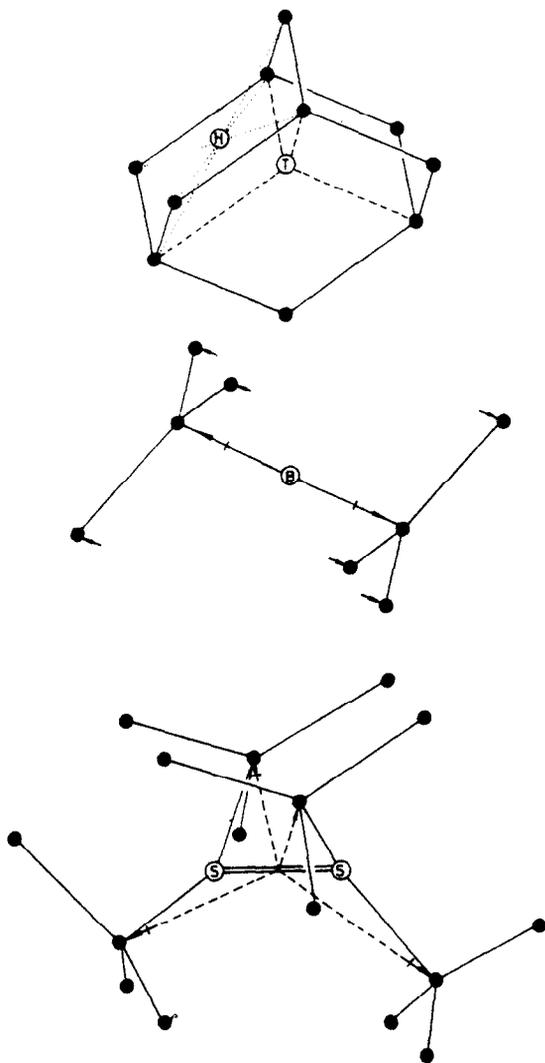
Fig. 1. Interstitial geometries: the tetrahedral (T), hexagonal (H), bond-centre (B) and (100) split forms are shown, together with the important lattice relaxations.

split interstitials in which two atoms are associated with a single lattice site: the ⟨100⟩ split form in its spin singlet (S) and triplet (S') states, and the ⟨100⟩ form (S₁₁₀). Both relaxed and unrelaxed clusters were considered. For each type of interstitial calculations were made for a cluster centred on the interstitial site, and, for each such cluster, calculations were made for each type of interstitial which could be put sensibly clear of the surface.

The conclusions are both qualitatively unambiguous and reasonably consistent quantitatively. The most stable interstitial is the ⟨100⟩ split interstitial S. Its singlet state is lowest, the triplet state S' lying 1.7–1.8 eV higher. The hexagonal form H is the second most favoured form, about 1.5 eV above S. The ⟨100⟩ split interstitial (S₁₁₀), the tetrahedral (T) and the bond-centred (B) forms are all significantly higher in energy. Our results thus agree with work using the more approximate Extend Hückel Theory[13] which suggested that the ⟨100⟩ split interstitial is favoured, but we do not agree with the conclusion from Extended Hückel Theory that the bond-centred inter-

stitial is also favoured. Indeed, previous low energies for the bond-centre appear to be an artifact of Extended Hückel Theory, which works in terms of a sum of one-electron eigen-values, not a total energy. This double-counts electron–electron interactions and omits nuclear–nuclear interactions, with especially serious errors for the bond-centre geometry. There are no direct experimental observations of self-interstitials in diamond. However, experiments on several other systems, notably silicon[14], suggest ⟨100⟩ split interstitials are the common form. Split interstitials are, of course, well documented in both ionic crystals and metals[15].

The model also suggests sensible properties for the ⟨100⟩ split interstitial in diamond. The total energies show that the cluster containing S is stable relative to one with the extra atom at infinity by about 2.8 eV. The surface sites are, of course, stable relative to S, because of the substantial lattice cohesive energy gained by bringing an extra atom from infinity to the surface. The local lattice distortion is almost entirely symmetric, with the first neighbours moving outwards by around 19%. The two atoms constituting S are separated by 1.51 Å, close to the bulk C–C spacing, and the Mulliken charges indicate little charge transfer between them and their neighbours. The one-electron energies all lie close to the band edges, so distinctive optical absorption is unlikely. This suggests the R2 centre[16] is not in fact an isolated interstitial.

The vibrational frequencies for various local motions (not strictly normal modes) have also been estimated. For reference, the Raman energy for diamond is 165 meV. The internal vibration of S gives 180 meV, and the axial translational motion of the two atoms of S gives 127 meV, though this decreases through anharmonic terms at large amplitudes. The A₁ (breathing mode), T₂ (trigonal) and E (tetragonal) motions of the nearest neighbours let to energies 148, 115 and 178 meV respectively. Thus the internal vibrations and E modes may lead to weakly-localised modes; the translational motion gives rise neither to a local mode, nor to a resonance mode like that postulated in metals.

4. INTERSTITIAL DIFFUSION

Experiment suggests that the interstitial in diamond moves at low temperatures[17, 18], with an estimated activation energy of 1.3 eV[18]. Neither the charge state nor the atomic process is established, and there is no evidence of ionisation or recombination enhanced motion. We note that two of the more probable predicted diffusion paths give activation energies of the right order of magnitude. The more direct route—basically translation plus rotation—gives around 0.8 eV, whereas the less direct route via the hexagonal site gives around 1.5 eV.

Our results have implications for recombination or ionisation-enhanced motion in analogous crystals. Broadly, two main types of mechanism have been suggested (Fig. 2). The main difference depends on whether the recombination (or carrier capture) energy E_R is transferred to lattice vibrations (Local Heating Model)
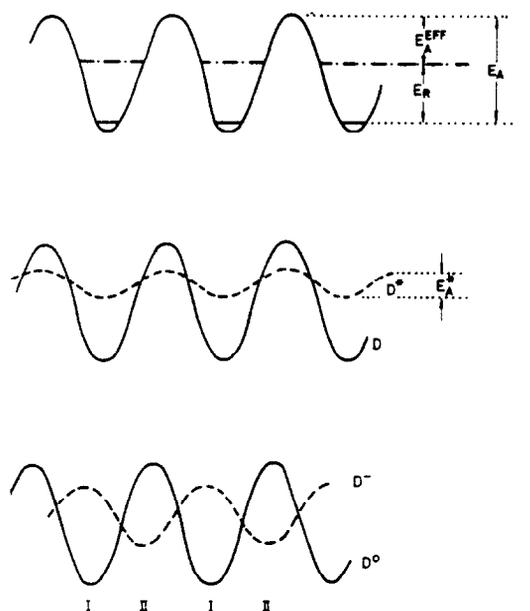
Fig. 2. Local heating and local excitation mechanisms. (a) Local heating; E_R is the recombination energy, and $E_A{}^{EFF}$ the effective activation energy; (b) Local excitation; The activation energy is lower in an excited electronic state D^*, i.e. $E_A^* < E_A$; (c) Bourgoin–Corbett model; The equilibrium configurations for the two charge states D^0 and D^- are distinct, and indicated by I, II respectively.

or whether it leads to an altered electronic state which alters the potential energy surfaces controlling motion (Local Excitation Model)[19].

In Local Heating Models the recombination energy is supposed to be converted to vibrational energy in the reaction coordinate. This model has been discussed recently[20]. It obviously requires a localised reaction mode which does not dissipate energy rapidly to other degrees of freedom. This presents no difficulty in molecules, for instance. But in solids this requires the reaction coordinate to be a genuinely localised mode or resonance mode, in weak contact with the other modes[21]. It is clear from our calculations that the reaction co-ordinate is not localised in this sense for the $\langle 100 \rangle$ split interstitial in diamond. Further, and contrary to the known situation in metals, it seems mostly unlikely that suitably local reaction modes will exist in other tetrahedral semiconductors like silicon or GaAs.

Local Excitation Models exist in many forms. It is well known that one finds different diffusion rates when one alters the charge state or electronic state of the defect[19]. Other well-documented cases include the photochemical production of defects in alkali halides[6, 10], where there is a small, possibly zero, activation energy[10]. We have not yet been able to look at the energy surfaces in excited states, and so it is not clear if

the recombination energy will excite suitable states for athermal motion. One does expect low energy excitations of the double bond of the split interstitial, though, for diamond, even this energy may be quite high. Silicon or germanium may be more suitable. One special case of a Local Excitation Model is the Bourgoin–Corbett suggestion[22]. The essential element is that the interstitial has a different configuration in different charge states. Successive alternate capture of electrons and holes takes the interstitial athermally from one site to the next. Our calculations are inconsistent with all but one possibility, namely a mechanism based on negative hexagonal and neutral split interstitials. We are not satisfied with the results for the negative interstitials, primarily because the extra electron charge localises on the outside of the cluster and not near the interstitial. Further calculations may resolve this point.

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