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Radiation Damage and Defects in Semiconductors

Radiation Damage and Defects in Semiconductors

Proceedings of the international conference
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Physics and the United States Air Force
held at the University of Reading
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Foreword

The topics covered at this Conference were all related to the processes of displacement of atoms from their normal sites in semiconductors by particle irradiation. Interest ranged from the stability of simple defects to the processes of conversion to the amorphous state. We owe our thanks to Dr J E Whitehouse who was the Organizing Secretary of the Conference for his work there and as Editor of the Proceedings for this invaluable record.

E W J MITCHELL
Chairman

18 October 1972

Preface

To many this volume will be a diary of events for the three days 19–21 July 1972. To many others it is a series of papers dealing with defects in semiconductors all conveniently collected in one place. The former are those who participated in the International Conference on Defects in Semiconductors held at the J J Thomson Physical Laboratory of the University of Reading. The latter group are those who acquire this volume for its value as a statement of the present position. It is now impossible to convey to the second group so much of the proceedings and particularly those insights given in conversation. Feeling that formalized and edited 'discussion' at the end of papers contributes little in this respect and considerably delays publication, we have omitted even this. Nevertheless we still hope that nonparticipants will read the papers in the spirit in which they were given, that is often to show where research was going rather than where it has reached.

To those that were there the greatest joy must surely have been to be present during the free exchange of views and criticism by theoreticians. Much of this is recorded in the contribution of Professor Coulson who made an all-too-brief appearance at the conference for the panel discussion on theoretical aspects of defects. We look forward to our problems receiving his attention on future occasions.

The organizers had specifically requested that all the reviews deal with techniques or phenomena without regard to any particular material. The broad overview so obtained was largely responsible for the great popular appeal of the conference and the flood of applications. Capacity audiences for all speakers was the rule and standing in the aisles appeared to heighten rather than dull enthusiasm.

Certain topics dealt with here might equally well appear in the proceedings of other specialist conferences, for instance, on ion implantation. We were very much alive to this possibility when planning the conference and emphasized that contributions must have a clear connection to radiation damage. The result has been reports from these allied fields which are indispensable to our present understanding of radiation damage.

The conference was the seventh in the series started at Gatlinburg in 1959 and was organized on the initiative of Professor Mitchell in conjunction with the Institute of Physics. The total enrolment was greater than 200 scientists from 19 countries. My own tasks first as Secretary to the Organizing Committee and later as Honorary Editor of the Proceedings have been made easier, indeed only possible, by expert help willingly given. These helpers are large in number and maybe will forgive me if I do not list their names but rather give their affiliations: staff of The Institute of Physics Meetings Office, staff of The Institute of Physics Publishing Office and members of the J J Thomson Physical Laboratory. To paraphrase my own comment at the end of the conference I hope the next organizers receive as much eager help. On behalf of all the participants I gratefully acknowledge the financial assistance provided by the United States Air Force which benefited us all.

J J Thomson Physical Laboratory,
University of Reading
October 1972

J E WHITEHOUSE
Secretary

Contents

Session 8: Radiation damage in III-V compounds

Session 9: Radiation damage in tellurium and II–VI compounds

Session 10: Recent techniques of defect characterization

Mechanisms of defect production†

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Abstract. Recent theoretical work on the configuration of the interstitial argues that the self-interstitial in diamond and silicon is an interstitialcy configuration rather than the tetrahedral or hexagonal configuration. We argue here that these results imply a theoretical estimate of the adiabatic displacement energy which is about one half earlier estimates, which we also argue is in better accord with experiment. We discuss the interatomic potential in a covalent semiconductor and the prospects for dynamic damage calculations in these materials. We present calculations on diamond and on silicon which suggest that the Frenkel pair are created as charged defects, for example, I^+ and V^-, giving rise to a coulombic contribution to the displacement energy. The coulombic term is isotropic as is, to first order, the static lattice displacement energy, in agreement with the experiments of Brown and Augustyniak. We briefly survey our recent work on ionization-enhanced diffusion (IED) mechanisms and note that IED can markedly affect the type of defects observed; for example, these mechanisms can account for the athermal, long range motion observed in low temperature damage in Si and Ge, as well as anomalous effects in more ionic systems and in ion implantation. We argue that IED may also be a factor in the so called ionization damage in semiconductors.

There have been a number of reviews of mechanisms of defect production and of defect production rates (Seitz and Koehler 1956, Bäuerlein 1962, Mitchell 1965, Corbett 1966, Sosin and Bauer 1969). For that reason we will not attempt here a comprehensive review in this limited space but will review the situation in semiconductors in the light of recent developments. It is useful to contrast the relatively primitive situation in semiconductors with that in metals where our state of understanding is quite advanced because there exist extensive calculations (primarily numerical computer modelling) closely coordinated with experiment. In metals the conduction and valence electrons are generally treated as providing the cohesive energy, but are otherwise neglected in defect calculations. The lattice is modelled by repulsive spheres held together by the cohesive energy, the interatomic repulsion being described by an isotropic, two-body potential, for example, a Born–Mayer potential. This approach has yielded a number of calculations (Bennemann 1961, Seeger *et al.* 1962, Johnson and Brown 1962, Johnson 1964) which give a good picture of the configurations of the defects and their migration energies, as well as several calculations (Gibson *et al.* 1960, Erginsoy *et al.* 1964) in which the dynamics of radiation damage events are followed by keeping track of the motion of approximately 1000 atoms; these latter calculations have arrived at estimates of the displacement damage threshold and its anisotropy against crystallographic orientation.

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In semiconductors, of course, the valence electrons cannot be ignored. There have been two semiquantitative treatments of the displacement process in semiconductors. Kohn (1954) considered that there were two contributions to the displacement energy, E_d. The first is the potential energy of pushing a substitutional atom into an interstitial site. The second is the bond-breaking energy; he assumed that creating an interstitial required breaking four sp^3 bonds. Kohn estimated the displacement energy in Ge as approximately 15 eV. He also argued that if a nearest neighbour atom is in the [111] direction from a lattice atom, it would be easier to displace the atom in the $[\bar{1}\bar{1}\bar{1}]$ direction, that is, between its three other neighbours, than in the [111] direction; thus he concluded that the displacement threshold would be anisotropic. Bäuerlein (1959, 1962, 1963) considered three contributions to E_d: the repulsive potential energy term, a strain energy term and the bond-breaking energy; he argued that the first two were negligible and that the last was dominant. He argued that the single bond energy is one half the total bond energy (E_B) per atom, hence the displacement energy is approximately $2E_B$. He took as E_B the heat of sublimation corrected for the fact that atoms sublime in the (s^2p^2) configuration rather than (sp^3); he used the total binding energy since he believed that the electron would not undergo the (sp^3) transition during the time of the displacement. Thus he added the sublimation energy (for Si approximately 107 kcal $mole^{-1}$ or 4·6 eV) to the s–p promotion energy (73 kcal $mole^{-1}$ or 3·2 eV) giving E_B approximately 7·8 eV or E_d approximately 15·6 eV. This value is in accord with experiment which gives approximately 13 eV (Loferski and Rappaport 1955a, 1958, 1959, Vavilov *et al.* 1960, Flicker *et al.* 1962, Novak 1963). His value for Ge (15·3 eV) is also close to experiment, approximately 15 eV (Klontz and Lark–Horovitz 1952, Loferski and Rappaport 1955b, Vavilov *et al.* 1956, 1958, Smirnov and Glazunov 1959, Brown and Augustyniak 1959, Chen and MacKay 1968), but for diamond ($\sim$24 eV) is quite low as compared with experiment ($\sim$80 eV) (Clark *et al.* 1961), more in accord with the approximate 30 eV value found for graphite (Eggen 1950, Lucas and Mitchell 1964, Iwata and Nihara 1966, Montet 1967). When we compare this with the metals, the rough agreement between the Kohn–Bäuerlein estimates and experiment is a problem; their estimates are adiabatic, while in metals it was found that E_d was several times the adiabatic interstitial formation energy, the rest of the energy being phonons created in the act of displacement. Clearly dynamic calculations in semiconductors, such as have been done in metals, would be desirable.

The barrier to carrying out such calculations is the treatment of the electronic contribution to the bonding. Whereas this bonding could be ignored with relative impunity in metals, it is clearly vital in semiconductors. In fact from organic chemistry we know that there is not one interatomic potential between two carbon atoms but several depending on what the electrons do; thus for a C–C single bond, that is, a σ bond between the carbons, the equilibrium distance is approximately 1·54 Å, for a C=C bond, that is, an additional π bond between them, the distance is about 1·33 Å and for a C≡C bond, that is, a σ and two π bonds, it is about 1·20 Å.

Recent calculations (Watkins *et al.* 1971, Weigel *et al.* to be published) using molecular orbital techniques to study the properties of the interstitial shed some light on our problem. As a starting point, those calculations have used the extended Hückel theory (Hoffman 1963), a simple, non selfconsistent, semiempirical, one electron, linear combination of atomic orbitals molecular orbital theory. As these authors, and others, have indicated the extended Hückel theory has both its strengths and limitations. Messmer and Watkins (to be published) emphasized that this

approach not only provides a practical computational scheme but has special utility as a survey tool which supplies insight and guidance in areas where neither experimental or theoretical information exists; we also take this view and hold that both the interstitial calculations and displacement mechanism discussion, which we will give

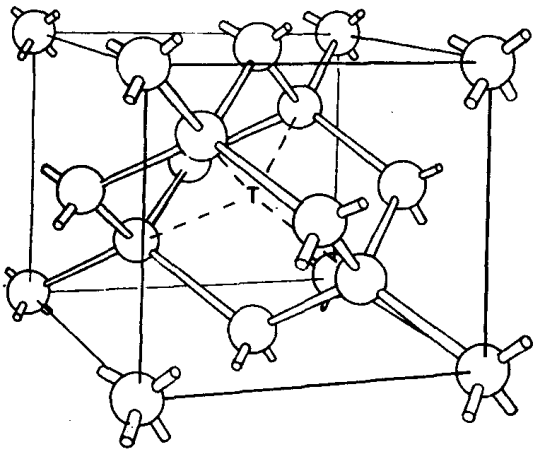

Figure 1. The tetrahedral (T) interstitial site in the diamond lattice with the four nearest neighbours indicated.

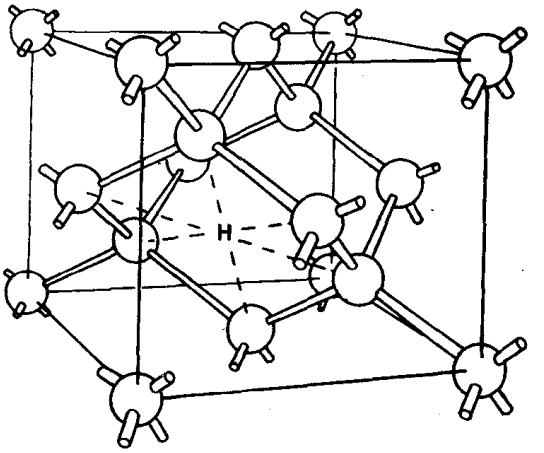

Figure 2. The so called hexagonal (H) interstitial site with the six nearest neighbours indicated. The H site is at the centre of the puckered ring formed by these six neighbours.

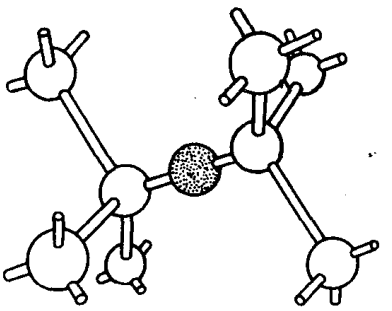

Figure 3. The bond-centred (B) interstitial configuration in which the interstitial is between two neighbouring atoms on substitutional sites.

shortly, provide insights that transcend the limitations of the extended Hückel theory and point out many features which must be included in a proper treatment.

The interstitial calculations indicate that the lowest energy interstitial configuration is not one in the tetrahedral (T) site (figure 1) nor the hexagonal (H) site (figure 2) as had been commonly supposed, but is either a bond-centre (B) configuration (figure 3) or a split interstitial (figure 4) configuration (interstitialcy) such as are

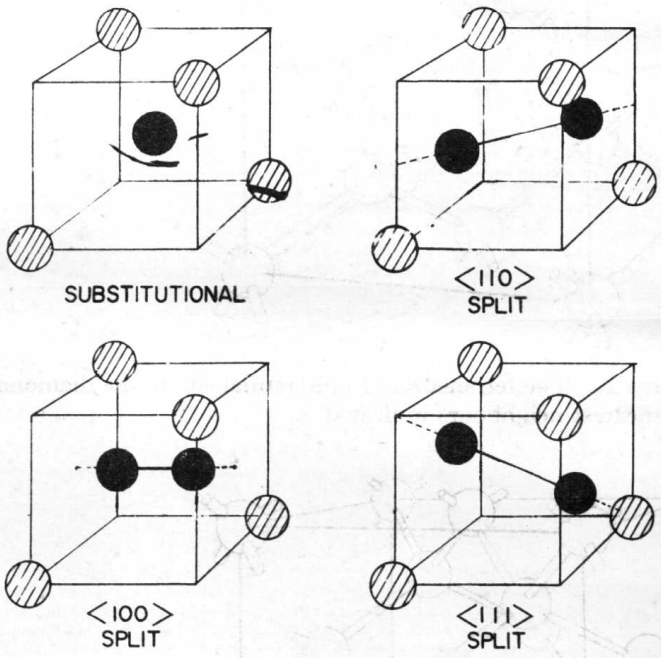

Figure 4. The principal split interstitial configurations in the diamond lattice. In a split configuration two atoms are equally displayed from a substitutional site.

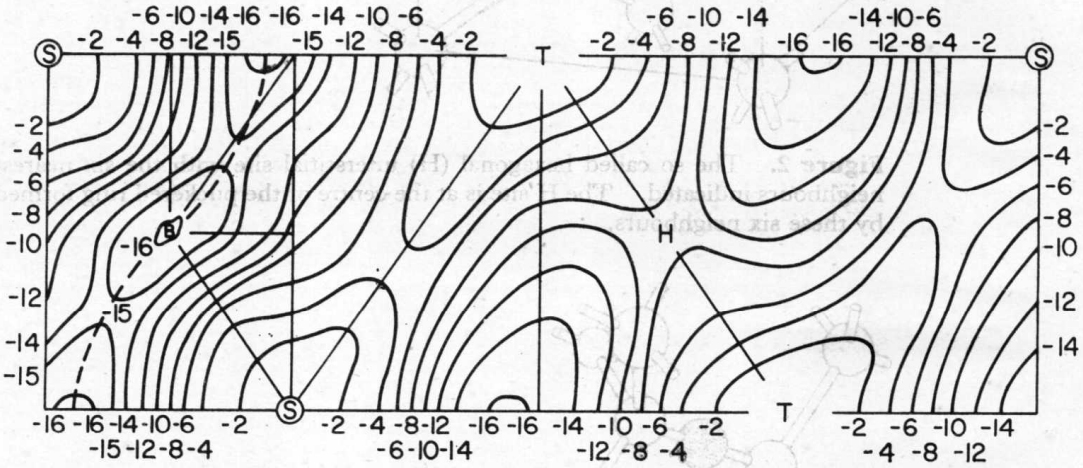

Figure 5. Potential energy contours in a (110) plane for an interstitial carbon atom in a rigid diamond lattice, that is, no lattice relaxations are permitted, hence split configurations are not included in this plot. The energies are expressed in eV with the tetrahedral (T) site chosen as the energy origin.

thought to occur in metals and ionic crystals. The first step in the calculations was to calculate the interstitial energy in a static lattice, that is, allowing no motion of the substitutional (S) lattice atoms. Figure 5 shows the potential energy contours obtained for diamond in a portion of the {110} plane. As can be seen the H site is 9·1 eV lower in energy than the T site and the B site 16·1 eV lower! In addition a minimum in a ⟨100⟩ direction from an S site can be seen; this minimum is as close as the static lattice can come to a split ⟨100⟩ interstitial. Further calculations which we will not present here, but which include relaxation of a lattice atom to form the split interstitials shown in figure 4 and relaxation of neighbouring atoms, indicate that the split ⟨100⟩ interstitial is lower in energy than the bond-centred interstitial by approximately 2 eV and that both of these are substantially lower than the T or H interstitials, even when relaxations are included. Similar results are found for silicon although there the computations are not completed.

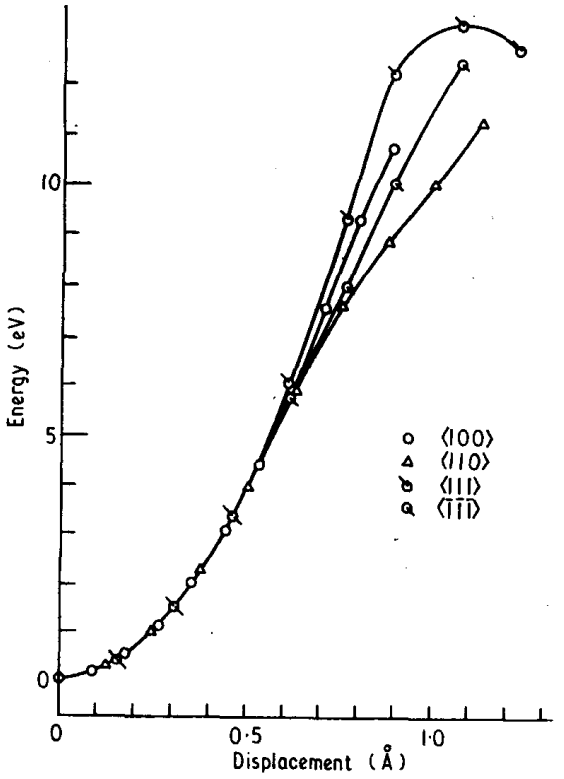

Figure 6. Potential energy for the displacement of a carbon lattice atom (the central one in a rigid 35 carbon atom cluster) in various directions.

These interstitial calculations argue that Kohn and Bäuerlein erred in discussing the displacement process by choosing the wrong interstitial configuration. Figure 5 also emphasizes the importance of electronic bonding in the displacement process since the figure shows the potential energy that an interstitial, remote from a vacancy, would experience for low energy collisions with a static lattice; that is, figure 5 applies to the collision of a carbon atom *with the diamond lattice* (not just with isolated carbon atoms). The actual displacement in the static lattice can be modelled as well. For this we use a cluster of 35 atoms and displace the central atom in the major crystallographic directions *vis-à-vis* the fixed, remaining atoms in the cluster; the corresponding potential energy curves are shown in figures 6 and 7 for diamond and

silicon respectively. We see that the potential well that binds the substitutional atom is quite isotropic; for energies above the minimum as high as 10 eV, in this static lattice, the difference in energy between going along a ⟨111⟩ towards an atom or away from an atom is less than 2 eV in diamond, that is, there is *not* an 'easy' way out of the potential well. We note in the curves for the ⟨111⟩ motion, that is, towards an atom, that the energy *drops* for small atom–atom separations; this is an artifact of the extended Hückel calculations, and a more sophisticated computational approach would be required to get the energy here for small separations. We argue, however,

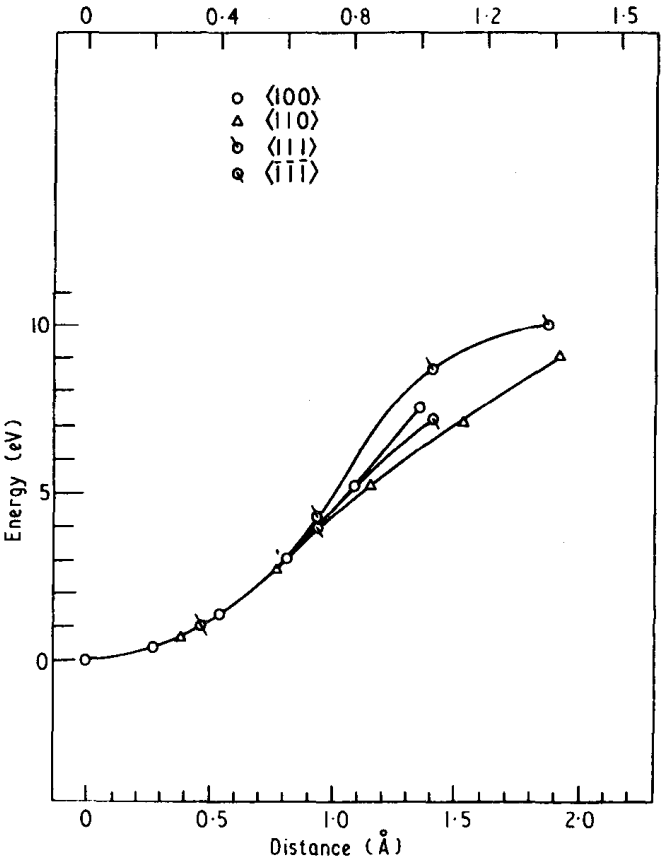

Figure 7. Potential energy for the displacement of a silicon lattice atom (the central one in a rigid 35 silicon atom cluster) in various directions.

that for small separations (and high excitation energies) the rest of the lattice becomes less important and we have essentially an atom–atom collision. While this is probably correct there does not seem to be experimental information in this energy range which establishes this energy independently. In figures 8 and 9 we show a comparison of the ⟨111⟩ data for diamond and silicon, respectively, with the potential energy given by the Thomas–Fermi potential (Slater 1960) fitted only in energy but with no adjusted distance parameter. Channelling measurements and calculations, which require potentials at somewhat higher energies, have used a number of potentials, including the Thomas–Fermi one, with a variety of parameters. Recognizing that there is some uncertainty in the potential energies extrapolated into this energy range we would argue from figures 8 and 9 that the energies obtained from the extended Hückel theory are consistent with the channelling potentials.

Continuing the trajectories of the displaced atom in the otherwise static diamond lattice beyond the displacements shown in figure 6 gives 'barriers' for displacement of 16 eV along the ⟨110⟩, 21·5 eV for ⟨$\overline{1}\overline{1}\overline{1}$⟩ and 22 eV for ⟨100⟩. We do *not* believe these are to be construed as displacement energies though. We believe the more likely damage production mechanism involves collision in the nonstatic lattice which result in the low energy, interstitial configurations and avoid the higher energy T and H configurations. Dynamic calculations, or at least semidynamic, that is, allowing relaxations and replacements, will be required to establish the actual mechanisms, however.

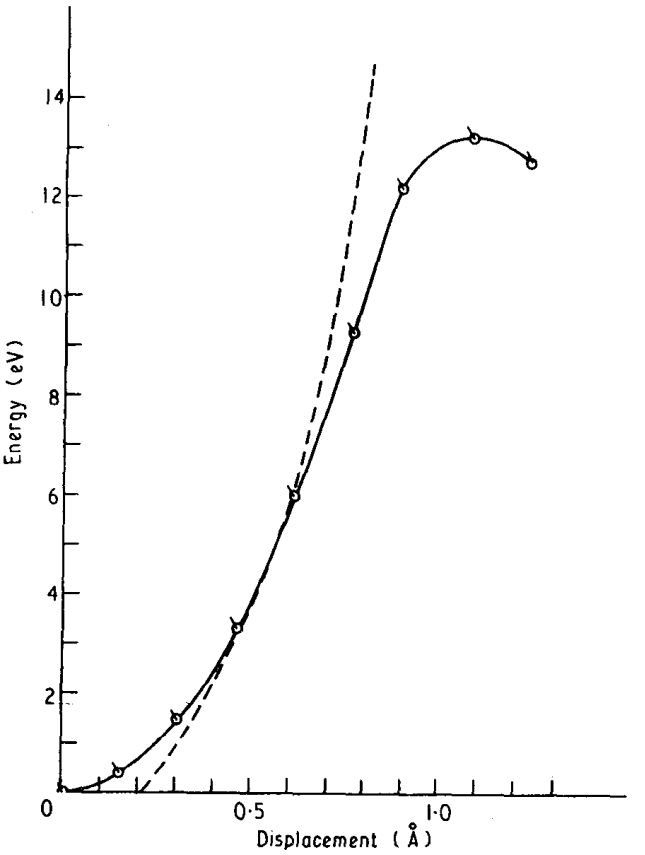

Figure 8. The ⟨111⟩ potential energy curve in figure 6 fitted to the Thomas-Fermi potential for carbon.

In the spirit of the Kohn–Bäuerlein arguments we can estimate the threshold for this type of displacement mechanism. For simplicity we look only at the 'bond' energy. Both the T and H interstitials involve four broken bonds for the neutral interstitial; following Bäuerlein this would imply an adiabatic displacement energy of approximately 16 eV for Si, that is, four volts per bond. The bond-centred interstitial has, roughly speaking, sp bonding to the two adjacent neighbours with its additional two electrons in p-orbitals. The split ⟨100⟩ configuration is more involved since it has two atoms in the configuration; in a normal substitutional lattice site both these atoms would have 4 sp^3 bonds; in the split-⟨100⟩ configuration they each have 3 sp^2 bonds to neighbours and one nonbonding p-electron. If we make the approximation that the sp, sp^2 and sp^3 bonds (and their mixtures) have the same bond energy

(see Mulliken 1951) and that the electrons not involved in σ bonds are equivalent, then intercomparison is easy, since the B and split $\langle 100 \rangle$ configurations would have the same energy (whereas extended Hückel calculations say the latter is about 2 eV lower) and T and H would be the same (whereas extended Hückel theory says the latter is several eV lower). Both B and split $\langle 100 \rangle$ involve two broken bonds; T and H involve four. Thus where Bäuerlein obtains for T (and H) an E_d approximately

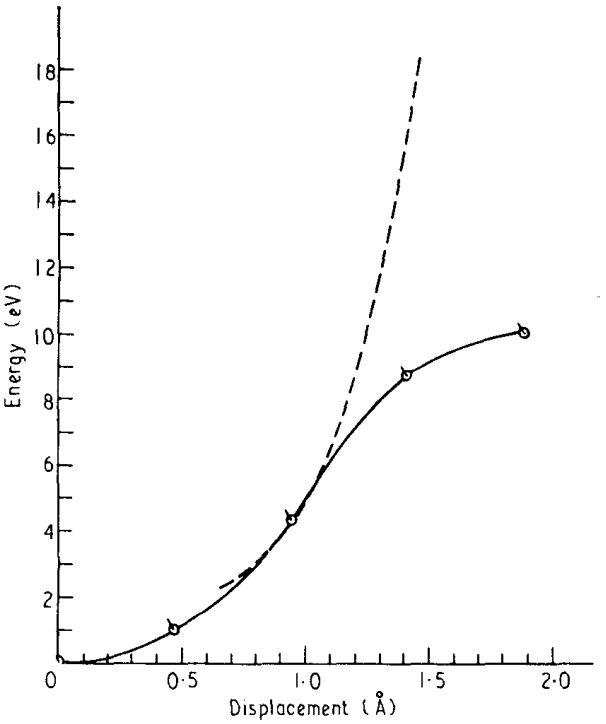

Figure 9. The $\langle 111 \rangle$ potential energy curve in figure 7 fitted to the Thomas–Fermi potential for silicon.

equal to 16 eV, we would get for the adiabatic displacement energy for B and split $\langle 100 \rangle$, an E_d of approximately 8 eV for silicon. This is now well below experiment allowing for some loss of energy in the definitely nonadiabatic displacement process. Dynamic calculations will be required to establish the extent of the nonadiabaticity and validate the view presented here.

But the calculations shown in figures 6–9 indicate more. In figures 10 and 11 we show for diamond and silicon, respectively, the electronic energy levels which appear in the vicinity of the forbidden gap as the central atom of the static 35-atom cluster is displaced, that is, as an interstitial atom is created leaving behind a vacancy. As can be seen, a set of levels of A_1, B_1 and B_2 symmetry (C_{2V} point group) come into the forbidden gap from both the valence and conduction bands. Mulliken charge population analysis on these levels shows the upper set to be associated with the displaced atom (the interstitial) while the lower set is associated with the vacancy left behind. Extended Hückel studies of the isolated interstitial at T and of the isolated vacancy show that both have T_2 levels (T_d point group); as the symmetry is lowered by the presence of the other defect the T_2 level splits into just these A_1, B_1 and B_2 levels.