Lattice distortion near vacancies in diamond and silicon—I

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MS. received 7th August 1970

Abstract. A dynamical relaxation procedure, coupled with a valence force potential, has been used to calculate the distortion around point defects in a diamond-type crystal. The method has been applied to the vacancy in diamond and silicon. We have calculated the response of the lattice to symmetrized forces on the nearest neighbours to the vacancy. The results can be used in estimates of point defect properties which depend on lattice distortion, including the Jahn–Teller effect, and formation energies. The ratios of the atomic displacements under uniform external stresses for the perfect lattice and for the lattice with a vacancy are also determined. These ratios are important in the analysis of stress splitting data. The most striking feature of the results is that the effective frequencies (effective force constants) obtained are considerably smaller than those estimated previously.

1. Introduction

Many of the measurable properties of point defects are sensitive to the distortion of the host lattice by the defect. These properties include the order and detailed positions of the electronic energy levels, as well as the formation and migration energies. In this paper we discuss the distortion of diamond and silicon lattices by point defects. Although we shall concentrate on the neutral vacancy, the results can be used rather directly for substitutional defects in these lattices.

Previous estimates of the lattice distortion from point defects in the diamond structure have made very restrictive assumptions (Swalin 1961, Scholz and Seeger 1965, Seeger and Swanson 1968, Hasiguti 1968). These authors have been principally concerned with the effects of distortion on formation and migration energies of vacancies. Their estimates assume that both the elastic properties of the perfect lattice and the forces which result from rebonding of the electrons at the vacancy may be adequately represented by a central pairwise interaction between the atoms. Schmid *et al.* (1968) went slightly beyond this form, including some bond-bending terms. A generalized Morse-type function was used, and the same function used to represent the perfect crystal properties and the local rebonding at the defect. However, the central interaction is not adequate. Smith (1948) has shown from dynamical matrix theory that first neighbour noncentral forces, as well as central forces, are necessary to predict the second order elastic constants for diamond structure crystals. Also, it is unreasonable to suppose that the same potential function describes both the rebonding at the vacancy and the interaction between the atoms of the perfect crystal.

In the dynamic relaxation method we use a valence force potential to describe the interaction between the atoms in the perfect crystal, and we estimate the lattice distortion from forces of various symmetries applied to the atoms nearest to the defect. Two basic assumptions are made. First, we assume that the distortions are sufficiently small so that the harmonic approximation is valid. The dynamical method is not restricted to this approximation; the limiting factor is the interatomic potential, which is determined from harmonic lattice properties. There is no available potential suitable for discussing anharmonic properties accurately. We emphasize that all treatments of distortion of which we are aware

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are also strictly limited to the harmonic approximation, although this restriction is rarely explicit. Second, we assume that the distortions are produced by forces on the nearest neighbours to the defect. The forces result from the electronic re-organization which occurs in the creation of the defect. Our calculations for the neutral vacancy estimate these forces in two different ways, described in the following paper. With these two basic assumptions, we have estimated the distortion near neutral vacancies in diamond and silicon. We have also made more complete estimates of the vacancy formation energies in these crystals.

The general basis of the method is developed in the next two sections. The method is then applied to the specific problem of the neutral vacancy.

2. Dynamic model for the defect lattice

The method used to determine the configuration of the atoms surrounding a point defect in the crystal is an adaptation of the computer simulated techniques developed by Bullough and Perrin (1968) using a discrete atom model. They used such a model to study the nucleation and growth of interstitial loops in α-iron. Since the diamond-type lattice may be considered to be composed of two interpenetrating fcc sublattices, it is convenient to establish within the computer an array which consists of a large parallelepiped of discrete interacting atoms which belong to one of the two sublattices. We have used a parallelepiped containing 686 'atoms' and placed the point defect, in our case a vacancy, at the centre of this array of atoms. It is a good approximation to hold the atoms near the boundary of this assembly fixed. These atoms are sufficiently far from the point defect such that this constraint does not influence the configuration of the atoms near the vacancy. We checked this point in one case by using an assembly with over 2000 atoms and found no differences in the relaxed configuration of the atoms nearest the defect.

The energy of the assembly of atoms in the perfect crystal was evaluated using a prescribed interaction between the atoms. A defect was then introduced into the system. In general, one may either remove an atom or atoms so as to create a vacancy or assembly of vacancies, or alternatively introduce extra atoms into interstitial positions. The computer program was developed to handle all these possibilities, although we have only considered the single vacancy so far. The total energy of the system including the defect may now be re-evaluated.

In most systems the removal or addition of an extra atom causes the atoms in the vicinity of the disturbance to experience a net force and so they move to minimize the total energy of the system again. By integrating the classical equations of motion for the complete set of interacting atoms the new atomic configuration around the vacancy may be found. It is possible to write

$$\ddot{x}_\alpha^i(t) = m^{-1} F^i(x^i(t), x^j(t), \ldots, x^n(t)) \tag{2.1}$$

where $x_\alpha^i(t)$ ($\alpha = 1, 2, 3$) are the cartesian components of the position vector $x^i(t)$ for atom i, at time t, relative to a fixed laboratory system of axes. F_α^i is the net force on atom i in the direction x_α and depends upon the position of the other atoms $j \ldots n$, at a particular time t, which are interacting with atom i. For a system with central forces only this equation reduces to a sum of component terms which are each a function of the distance between atom i and one of the other atoms. However, when noncentral terms are included such a decomposition is not so readily available. We may also write

$$F_\alpha^i(t) = -\frac{\partial \Phi}{\partial x_\alpha^i(t)} \tag{2.2}$$

where Φ is the expression for the total potential energy of the system with n interacting particles.

We solve the set of differential equations by numerical integration, writing

$$\ddot{x}_\alpha^i(t) = (\Delta t)^{-1}\{V_\alpha^i(t + \Delta t/2) - V_\alpha^i(t - \Delta t/2)\}$$
$$= m^{-1}F_\alpha^{-1}(x^i(t), x^j(t), \ldots, x^n(t))$$

and

$$V_\alpha^i(t + \Delta t/2) = (\Delta t)^{-1}\{x_\alpha^i(t + \Delta t) - x_\alpha^i(t)\}.$$

Thus from the configuration and velocity distribution after time t (the latter strictly after time $(t - \Delta t/2)$) the coordinates and velocity of each atom at a subsequent time are

$$V_\alpha^i(t + \Delta t/2) = V_\alpha^i(t - \Delta t/2) + \Delta t(m^{-1}) F_\alpha^i(x^i(t), \ldots, x^n(t)) \tag{2.3}$$

$$x_\alpha^i(t + \Delta t) = x_\alpha^i(t) + \Delta t V_\alpha^i(t + \Delta t/2). \tag{2.4}$$

While holding the atoms near the boundary fixed, each atom in the assembly is considered in turn and the force on it due to neighbouring atoms evaluated. From the difference equations (2.3) and (2.4) the mean velocity and hence new position of each atom after the current time step is determined. After the velocity and position of each atom is updated a norm proportional to the kinetic energy of the lattice is evaluated and the process considered for the next time step. Using a suitable choice of time step the kinetic energy passes through a maximum value after a few complete iterations. At this point the atoms are brought to rest and the iterations restarted. This dynamic procedure ensures very rapid convergence to the absolute minimum in total potential energy. This method also has the advantage that metastable configurations can usually be avoided and the true stable configuration found.

It is a useful dynamic method for our purposes which permits us to overcome many of the inadequacies of previous approaches.

3. Potential interaction between atoms

Valence crystals have strongly directional covalent bonding between nearest neighbour atoms, with much weaker interactions between an atom and its second neighbours. To predict the properties of the diamond-type crystal satisfactorily it is necessary to use a function which includes noncentral as well as central force terms. Fortunately, potential relationships for diamond and silicon which have many of the desired characteristics have been determined by McMurry and co-workers (McMurry *et al.* 1967, Solbrig 1968, private communication from McMurry).

These workers have expressed the potential energy of the diamond-type crystal in terms of valence coordinates which involve changes in bond lengths and bond angles. For the diamond crystal a valence force potential expression was derived which yields calculated phonon dispersion relations in extremely good agreement with experimental data obtained by Warren *et al.* (1965, 1967). The elastic stiffness constants calculated using the potential relation agreed very well with the data obtained by McSkimin and Bond (1957) using an ultrasonic method, while the Raman frequency obtained by Robertson *et al.* (1934) was used as a fitting parameter. Recently, a preliminary set of valence force constants for the silicon crystal have been obtained (Solbrig 1968, private communication from McMurry). The fit to the phonon dispersion curves obtained by Dolling (1963) and Palevsky *et al.* (1959) is not as good as for diamond, but is sufficiently accurate for our purposes. We have also made preliminary calculations for silicon using the valence force potentials of Singh and Doyal (1970). These results agree quite well with those based on Solbrig's values.

The expression for the total deformation energy, Φ, for a system of n interacting particles may be presented in terms of the valence force coordinates as follows:

$$\Phi = \sum_{i=1}^{n} \Phi_i$$

where Φ_i is the potential energy contribution associated with each atom in the array. Now

$$\Phi_i = \tfrac{1}{4} F_r \sum_{j=1}^{4} (\Delta r_{ij})^2 + \sum_{j=1}^{3} \sum_{k=j+1}^{4} \{\tfrac{1}{2} r_0^2 F_\theta (\Delta \theta_{jik})^2$$

$$+ f_{rr} \Delta r_{ij} \Delta r_{ik} + r_0 f_{r\theta} (\Delta r_{ij} \Delta \theta_{jik} + \Delta r_{ik} \Delta \theta_{jik})\} \tag{3.1}$$

where the terms represent contributions to the potential energy arising from the various spring constants. The change in bond length between nearest neighbour atoms i and j from the equilibrium internuclear distance r_0 is Δr_{ij}. The change in bond angle between atoms j, i and k, where i is the atom at the apex, is $\Delta \theta_{jik}$. The force constants are defined as follows: F_r is a bond stretching constant for nearest neighbour atoms i and j; F_θ is an angular rigidity constant for the angle θ_{jik}; f_{rr} is an interaction constant for a bond pair, such that j and k are nearest neighbours to i; $f_{r\theta}$ is an interaction constant for the bond ij which forms an arm of the angle θ_{jik}. Table 1 shows the values of these force constants for the diamond and silicon crystals.

Table 1. Valence force constants for the diamond and silicon crystal

Force constant	Diamond	Silicon
F_r	24·8220†	9·2697
F_θ	2·2360	0·1838
f_{rr}	0·8571	0·1684
$f_{r\theta}$	1·7497	0·2495

† All constants in units of eV Å^{-2}.

In the expression for Φ_i we have neglected the terms containing $f_{\theta\theta}$ and $f_{\theta\theta*}$, because in general the energy contribution from these terms will be small. To include such terms leads to a complicated expression for the force on each atom. It is important to note that this function effectively gives us the *deformation* potential energy, since for the perfect crystal configuration Φ is zero.

The force acting on the atom i in the x_α direction ($\alpha = 1, 2, 3$) at time t is as given in equation (2.2). We may also write this equation as

$$F_\alpha^i(t) = \frac{\partial \sum_{i=1}^{n} \Phi_{ii}}{\partial x_\alpha^i(t)}. \tag{3.2}$$

It should be noted that terms other than Φ_i are functions of $x_\alpha^i(t)$. The expression for the force on a particular atom involves the knowledge of the derivatives of Δr_{ij}, $\Delta \theta_{jik}$ and $\Delta \theta_{iji}$ with respect to $x_\alpha^i(t)$. For the radial term we have

$$\frac{\partial \Delta r_{ij}}{\partial x_\alpha^i} = \frac{x_\alpha^i - x_\alpha^j}{r_{ij}} \tag{3.3}$$

where the terms are as defined previously. Note that we have abbreviated the symbol $x_\alpha^i(t)$ to x_α^i for convenience. To get the angular terms we use direction cosines to express $\cos \theta_{jik}$ as

$$\cos \theta_{jik} = \sum_{\alpha=1}^{3} \frac{(x_\alpha^j - x_\alpha^i)(x_\alpha^k - x_\alpha^i)}{r_{ij} r_{ik}}. \tag{3.4}$$

Now

$$\cos \theta_{jik} = \cos \theta_{jik}^0 \cos \Delta \theta_{jik} - \sin \theta_{jik}^0 \sin \Delta \theta_{jik}.$$

For the perfect diamond-type lattice at equilibrium

$$\cos \theta_{jik}^{0} = -\tfrac{1}{3} \qquad \sin \theta_{jik}^{0} = \frac{2\sqrt{2}}{3}.$$

Since we assume that the displacements of the atoms are sufficiently small that the harmonic approximation is valid, we may write

$$\cos \Delta \theta_{jik} \simeq 1 \qquad \sin \Delta \theta_{jik} \simeq \Delta \theta_{jik}.$$

Hence

$$\cos \theta_{jik} \simeq -\tfrac{1}{3} - \frac{2\sqrt{2}}{3} \Delta \theta_{jik}. \tag{3.5}$$

By use of equations (3.4) and (3.5) we obtain

$$\frac{\partial \Delta \theta_{jik}}{\partial x_{\alpha}^{i}} = \frac{3}{2\sqrt{2}} \left[\left\{ \frac{(x_{\alpha}^{i} - x_{\alpha}^{k})}{r_{ik}^{2}} + \frac{(x_{\alpha}^{i} - x_{\alpha}^{j})}{r_{ij}^{2}} \right\} \cos \theta_{jik} \frac{(x_{\alpha}^{i} - x_{\alpha}^{k}) + (x_{\alpha}^{i} - x_{\alpha}^{j})}{r_{ij} r_{ik}} \right] \tag{3.6}$$

and

$$\frac{\partial \Delta \theta_{ijl}}{\partial x_{\alpha}^{i}} = \frac{3}{2\sqrt{2}} \left\{ \frac{(x_{\alpha}^{j} - x_{\alpha}^{i})}{r_{ij} r_{jl}} - \frac{(x_{\alpha}^{j} - x_{\alpha}^{i})}{r_{jj}^{2}} \cos \theta_{ijl} \right\}. \tag{3.7}$$

It is through terms like $\partial \Delta \theta_{ijl}/\partial x_{\alpha}^{i}$ that the force on atom i depends upon the position of its second nearest neighbours.

There still remains a difficulty in applying this potential function to our problem. The valence force function is essentially an equilibrium potential; if we break a bond or remove an atom from the crystal no relaxation of the lattice occurs unless we allow rebonding of the electrons. While at first sight this may seem surprising it is perhaps reasonable. In saturated hydrocarbons the average carbon–carbon single bond length is $1\cdot537 \pm 0\cdot005$ Å compared with $1\cdot544$ Å in the diamond crystal (Sutton 1965). If we argue that the single bond in saturated hydrocarbons is fully relaxed, then the 'tension' in the C—C bond in diamond should be very small, since ΔR is $0\cdot007$ Å. Consequently the relaxation of surrounding atoms on breaking a bond should be small. This is, of course, a very simple-minded argument and ignores the effect of electron re-arrangement which may result in a change in the state of hybridization of the atoms nearest the defect. However, the success of the valence force function in predicting the physical properties of diamond suggests that it is a reasonable argument. A similar argument may be used to justify the use of a valence force potential description of the interactions between atoms in the silicon lattice. In crystalline silicon the Si–Si bond length is $2\cdot35$ Å compared with $2\cdot32 \pm 0\cdot02$ Å in such compounds as Si_2H_6 and Si_2Cl_6 (Sutton 1965). It is likely that the valence force potential will be less accurate for silicon than for diamond, but it should be adequate for our purposes, and is in any case better founded than the potentials used by other workers.

It follows that any distortion of the lattice in the vicinity of an isolated vacancy results from the rebonding of the vacancy electrons. It now remains to determine the equilibrium configuration of the lattice which results on application of external forces F_{α} of appropriate point symmetry and to estimate these electronic forces.

4. Linear response of the lattice

4.1. *General outline*

If the four nearest neighbours to the vacancy, denoted A, B, C and D, have cartesian coordinates $(\bar{1}, 1, 1)$, $(1, \bar{1}, 1)$, $(1, 1, \bar{1})$ and $(\bar{1}, \bar{1}, \bar{1})$ in the undistorted crystal, displacement of these atoms may be described in terms of 12 normal coordinates (Lannoo and Stoneham 1968). Three of these coordinates represent translations and three rotations. These are of

Table 2. Equilibrium position of atoms surrounding a single vacancy at $(0, 0, 0)$ in the diamond crystal after relaxation for applied forces of appropriate symmetry

Atom	Initial configuration	Relaxed configuration		
		$E(\epsilon)$ symmetry	$T_2(\xi)$ symmetry	A_1 symmetry
A	$(\bar{1}, 1, 1)$†	$(-1\cdot0, 1\cdot025, 0\cdot975)$	$(-1\cdot0, 1\cdot033, 1\cdot033)$	$(-1\cdot029, 1\cdot029, 1\cdot029)$
B	$(1, 1, 1)$	$(1\cdot0, -1\cdot025, 0\cdot975)$	$(1\cdot0, -0\cdot967, 0\cdot967)$	$(1\cdot029, -1\cdot029, 1\cdot029)$
C	$(1, 1, \bar{1})$	$(1\cdot0, 1\cdot025, -0\cdot975)$	$(1\cdot0, 0\cdot967, -0\cdot967)$	$(1\cdot029, 1\cdot029, -1\cdot029)$
D	$(\bar{1}, \bar{1}, \bar{1})$	$(-1\cdot0, -1\cdot025, -0\cdot975)$	$(-1\cdot0, -1\cdot034, -1\cdot034)$	$(-1\cdot029, -1\cdot029, -1\cdot029)$
A′	$(2, 2, 0)$	$(-2\cdot007, 2\cdot014, -0\cdot008)$	$(-2\cdot00, 2\cdot006, 0\cdot005)$	$(-2\cdot008, 2\cdot008, 0\cdot0)$
A″	$(0, 2, 2)$	$(0\cdot0, 2\cdot007, 1\cdot993)$	$(0\cdot014, 2\cdot016, 2\cdot016)$	$(0\cdot0, 2\cdot008, 2\cdot008)$
A‴	$(2, 0, 2)$	$(-1\cdot993, 0\cdot008, 1\cdot986)$	$(-2\cdot00, 0\cdot005, 2\cdot006)$	$(-2\cdot008, 0\cdot0, 2\cdot008)$
B′	$(2, 2, 0)$	$(2\cdot007, -2\cdot014, -0\cdot008)$	$(2\cdot00, -1\cdot993, -0\cdot005)$	$(2\cdot008, -2\cdot008, 0\cdot0)$
B″	$(0, \bar{2}, 2)$	$(0\cdot0, -2\cdot007, 1\cdot993)$	$(0\cdot013, -1\cdot984, 1\cdot984)$	$(0\cdot0, -2\cdot008, 2\cdot008)$
B‴	$(2, 0, 2)$	$(1993, -0\cdot008, 1\cdot985)$	$(2\cdot00, 0\cdot005, 1\cdot993)$	$(2\cdot008, 0\cdot0, 2\cdot008)$
C′	$(2, 2, 0)$	$(2\cdot007, 2\cdot014, -0\cdot008)$	$(2\cdot00, 1\cdot993, 0\cdot005)$	$(2\cdot008, 2\cdot008, 0\cdot0)$
C″	$(2, 0, \bar{2})$	$(1\cdot993, 0\cdot008, -1\cdot985)$	$(2\cdot00, -0\cdot005, -1\cdot993)$	$(2\cdot008, 0\cdot0, -2\cdot008)$
C‴	$(0, 2, \bar{2})$	$(0\cdot0, 2\cdot007, -1\cdot993)$	$(0\cdot013, 1\cdot984, -1\cdot984)$	$(0\cdot0, 2\cdot008, -2\cdot008)$
D′	$(\bar{2}, \bar{2}, 0)$	$(-2\cdot007, -2\cdot015, 0\cdot008)$	$(-2\cdot00, -2\cdot007, -0\cdot005)$	$(-2\cdot008, -2\cdot008, 0\cdot0)$
D″	$(\bar{2}, 0, \bar{2})$	$(-1\cdot992, -0\cdot008, -1\cdot985)$	$(-2\cdot00, 0\cdot005, -2\cdot007)$	$(-2\cdot008, 0\cdot0, -2\cdot008)$
D‴	$(0, \bar{2}, \bar{2})$	$(0\cdot0, -2\cdot007, -1\cdot993)$	$(0\cdot0, -2\cdot016, -2\cdot016)$	$(0\cdot0, -2\cdot008, -2\cdot008)$

† In units of $a/4$ where a is the cell constant.
Applied Force, $F_\alpha = 1$ eV Å^{-1}.

no interest to us in the present problem. The six remaining normal coordinates are given in the Appendix in terms of the displacements X_α, Y_α, Z_α (α = A, B, C, D) of the atoms. The Q_a mode is the 'breathing' or symmetrical mode of symmetry A_1. The normal coordinates Q_ϵ and Q_θ are E modes which describe the tetragonal distortion of the atoms surrounding the vacancy, while the Q_ξ, Q_η and Q_ζ modes belong to the T_2 representation of the T_d group and result in a trigonal distortion of the defect system.

The energy change associated with the lattice for a particular distortion, Q_α, of the vacancy may be represented within the harmonic approximation by writing

$$\Delta E(Q_\alpha) = - F_\alpha Q_\alpha + \tfrac{1}{2} M \omega_\alpha^2 Q_\alpha^2. \qquad (4.1)$$

The second term is the quasi-elastic potential energy term which represents the change in the total potential energy of the system when the atoms move to a new static equilibrium configuration with the nearest neighbours held fixed at a distortion Q_α. The mass of the atom is M and ω_α is the effective or response frequency of the lattice for the α mode.

We now seek the displacement Q_α in response to a small force F_α. These forces are symmetrized, so a given force F_α does not produce any distortion of different symmetry $Q_{\beta \neq \alpha}$. We shall describe the linear response, $\partial Q_\alpha / \partial F_\alpha$, in terms of the effective frequency, ω_α, of (4.1). In the harmonic approximation we can then determine the displacements due to the forces caused by rebonding, even when the forces depend strongly on the Q_α.

The energy change of the whole system under a set of constant forces, F_α, is, by (4.1)

$$\Delta E \equiv \sum_\alpha \Delta E(Q_\alpha) = - \sum_\alpha F_\alpha Q_\alpha + \sum_\alpha \tfrac{1}{2} M \omega_\alpha^2 Q_\alpha^2. \qquad (4.2)$$

The static equilibrium distortion is given by

$$\frac{\partial E}{\partial Q_\alpha} = - F_\alpha + M \omega_\alpha^2 Q_\alpha = 0 \qquad (4.3)$$

so that the linear response may be written

$$\frac{\partial Q_\alpha}{\partial F_\alpha} = \frac{1}{M \omega_\alpha^2} \qquad (4.4)$$

and the corresponding relaxation energy is

$$\Delta E(Q_\alpha) = - \frac{F_\alpha^2}{2 M \omega_\alpha^2}. \qquad (4.5)$$

The linear response, described by ω_α, may be evaluated for any given model of lattice dynamics. Once known, the ω_α may be used for other detailed microscopic models of the rebonding near a vacancy, or even for other neutral substitutional defects. We have used the dynamic relaxation method of § 2 and the valence force function of § 3 to estimate frequencies ω_α for the various symmetries. Only three calculations are necessary, corresponding to the A, E and T_2 symmetry distortions. In addition to giving the ω_α, the relaxation program also enables us to determine the equilibrium displacements of more distant neighbours of the defect when the nearest neighbour distortion is given by Q_A, Q_E and Q_T. Further, we may use the relaxation method to find the effect of the vacancy on the displacements produced by an external homogeneous stress. Many experiments on defects investigate the shifts of spectral lines under external stress. In interpreting the results it is usual to assume that the atoms in the crystal with a defect are displaced by the external stress by the same amount that they would move in a perfect crystal. This assumption is not generally valid. We may estimate the error by finding the displacements Q_α per unit external uniform stress for both the perfect lattice and for the lattice with a vacancy.

4.2. *Results for the valence force potential*

The equilibrium positions of the first and second neighbours to a vacancy before and

Table 3. Equilibrium position of the atoms surrounding a single vacancy at (0, 0, 0) in the silicon crystal after relaxation for applied forces of appropriate symmetry

Atom	Initial configuration	Relaxed configuration		
		$E(\epsilon)$ symmetry	$T_2(\xi)$ symmetry	A_1 symmetry
A	$(\bar{1}, 1, 1)$	$(-1\cdot0, 1\cdot10, 0\cdot90)$†	$(-1\cdot0, 1\cdot14, 1\cdot14)$	$(-1\cdot12, 1\cdot12, 1\cdot12)$
B	$(1, \bar{1}, 1)$	$(1\cdot0, -1\cdot10, 0\cdot90)$	$(1\cdot0, -0\cdot87, 0\cdot87)$	$(1\cdot12, -1\cdot12, 1\cdot12)$
C	$(1, 1, \bar{1})$	$(1\cdot0, 1\cdot10, -0\cdot90)$	$(1\cdot0, 0\cdot87, -0\cdot87)$	$(1\cdot12, 1\cdot12, -1\cdot12)$
D	$(\bar{1}, \bar{1}, \bar{1})$	$(-1\cdot0, -1\cdot10, -0\cdot90)$	$(-1\cdot0, -1\cdot14, -1\cdot14)$	$(-1\cdot12, -1\cdot12, -1\cdot12)$
A′	$(\bar{2}, 2, 0)$	$(-2\cdot05, 2\cdot07, -0\cdot05)$	$(-2\cdot00, 2\cdot02, 0\cdot0)$	$(-2\cdot04, 2\cdot03, -0\cdot02)$
A″	$(0, 2, 2)$	$(0\cdot0, 2\cdot02, 1\cdot98)$	$(0\cdot10, 2\cdot07, 2\cdot07)$	$(0\cdot02, 2\cdot03, 2\cdot04)$
A‴	$(\bar{2}, 0, 2)$	$(-1\cdot95, 0\cdot05, 1\cdot93)$	$(-2\cdot00, 0\cdot0, 2\cdot02)$	$(-2\cdot04, -0\cdot02, 2\cdot03)$
B′	$(2, \bar{2}, 0)$	$(2\cdot06, -2\cdot07, -0\cdot05)$	$(1\cdot99, -1\cdot97, 0\cdot0)$	$(2\cdot03, -2\cdot04, -0\cdot02)$
B″	$(0, \bar{2}, 2)$	$(0\cdot0, -2\cdot02, 1\cdot98)$	$(0\cdot10, -1\cdot92, 1\cdot92)$	$(-0\cdot02, -2\cdot04, 2\cdot03)$
B‴	$(2, 0, 2)$	$(1\cdot95, -0\cdot06, 1\cdot93)$	$(1\cdot99, 0\cdot0, 1\cdot97)$	$(2\cdot03, 0\cdot02, 2\cdot04)$
C′	$(2, 2, 0)$	$(2\cdot06, 2\cdot07, 0\cdot05)$	$(1\cdot99, 1\cdot97, 0\cdot0)$	$(2\cdot04, 2\cdot03, 0\cdot02)$
C″	$(2, 0, \bar{2})$	$(1\cdot95, 0\cdot05, -1\cdot93)$	$(1\cdot99, 0\cdot0, -1\cdot97)$	$(2\cdot03, -0\cdot02, -2\cdot04)$
C‴	$(0, 2, \bar{2})$	$(0\cdot0, 2\cdot02, -1\cdot98)$	$(0\cdot10, 1\cdot92, -1\cdot92)$	$(-0\cdot02, 2\cdot03, -2\cdot04)$
D′	$(\bar{2}, \bar{2}, 0)$	$(-2\cdot06, -2\cdot07, 0\cdot04)$	$(-2\cdot00, -2\cdot02, 0\cdot0)$	$(-2\cdot04, -2\cdot04, 0\cdot02)$
D″	$(\bar{2}, 0, 2)$	$(-1\cdot94, -0\cdot05, -1\cdot92)$	$(-2\cdot00, 0\cdot0, -2\cdot02)$	$(-2\cdot04, 0\cdot02, -2\cdot04)$
D‴	$(0, 2, 2)$	$(0\cdot0, -2\cdot02, -1\cdot98)$	$(0\cdot10, -2\cdot07, -2\cdot07)$	$(0\cdot02, -2\cdot04, -2\cdot04)$

† In units of $a/4$ where a is the cell constant.
Applied Force, $F_a = 0\cdot5$ eV Å^{-1}.

after the application of symmetrized forces F_α are given in tables 2 and 3. Table 2 gives the results for diamond with forces F_ε, F_ξ and F_a taking the value 1eV Å^{-1}. Table 3 gives the corresponding results for silicon, but with the forces reduced by 0·5 because of the greater deformability of the silicon lattice.

Table 4. Effective response frequencies associated with the nearest neighbour atoms to the vacancy in the diamond-type lattice for distortion modes of certain symmetries

Frequency	Diamond crystal	Silicon crystal
ω_a	$0\cdot95 \times 10^{14}$†	$0\cdot18 \times 10^{14}$
ω_E	$1\cdot13 \times 10^{14}$	$0\cdot21 \times 10^{14}$
ω_T	$0\cdot98 \times 10^{14}$	$0\cdot18 \times 10^{14}$
Raman frequency	$2\cdot49 \times 10^{14}$	$0\cdot985 \times 10^{14}$

† All frequencies in rad s^{-1}.

From these displacements and the atomic mass we may obtain the various effective frequencies. They are given in table 4. The values used by previous workers used one of two approximations. Friedel *et al.* (1967) assumed that the frequencies should be close to the Raman frequencies

$$\text{Diamond} \qquad \omega_R = 2\cdot49 \cdot 10^{14} \text{ rad s}^{-1}$$

$$\text{Silicon} \qquad \omega_R = 0\cdot985 \cdot 10^{14} \text{ rad s}^{-1}.$$

Lidiard and Stoneham (1967) estimated frequencies from a simple model which used central forces between nearest neighbours and assumed only the nearest neighbours to the vacancy moved. The simple model gives (after correction of a small numerical error)

$$\text{Diamond} \qquad \omega_E = 2\cdot02 \cdot 10^{14} \text{ rad s}^{-1}$$

$$\text{Silicon} \qquad \omega_E = 0\cdot825 \cdot 10^{14} \text{ rad s}^{-1}$$

and $\omega_E/\omega_T = \sqrt{2} \simeq 1\cdot41$. Elkin and Watkins (1968) have also used a similar model for a different defect. There is poor agreement between these figures and the values in table 4. Also the ratio ω_E/ω_T is only 1·15 for diamond and 1·17 for silicon. Since the frequencies are smaller than on any of these simple models, the lattice distorts more easily than the simple treatments suggest.

Finally, we determine the nearest neighbour displacements under a uniform external stress for the perfect lattice (Q_α^0) and for the lattice with a vacancy (Q_α^v). The ratios for silicon which are needed in the analysis of stress-splitting data, are

$$Q_a^v/Q_a^0 = 10\cdot6 \pm 1\cdot0$$

$$Q_\epsilon^v/Q_\epsilon^0 = 1\cdot4 \pm 0\cdot1$$

$$Q_\xi^v/Q_\xi^0 = 1\cdot8 \pm 0\cdot1$$

while for diamond

$$Q_a^v/Q_a^0 = 3\cdot2 \pm 0\cdot2$$

$$Q_\epsilon^v/Q_\epsilon^0 = 1\cdot5 \pm 0\cdot1$$

$$Q_\xi^v/Q_\xi^0 = 1\cdot9 \pm 0\cdot1$$

It is remarkable that these ratios are so large—especially for the A mode in silicon, and it is clear that it is a poor approximation to use the perfect lattice displacements. The large differences for the Q_a^v/Q_a^0 ratio in diamond and silicon indicate the greater relative

importance of the radial terms in the potential for silicon. This is also evident from table 1.

We are now able to calculate the extent of distortion for various estimates of electronic rebonding forces associated with the vacancy electrons. This is done in the following paper.

5. Conclusion

We have examined the linear response of the diamond and silicon lattices to symmetrized forces on the nearest neighbours to a particular site. The calculations have been made for both a perfect lattice and for a lattice with a neutral vacancy at the site. The results can be applied rather directly to estimate properties of defects which depend on the local lattice distortion. Such properties include the Jahn–Teller instability, the vacancy formation energy and the volume of solution of a defect: these features are discussed in detail in the following paper. Further, we have examined the distortion under a uniform external stress for both a perfect lattice and for a lattice with a neutral vacancy.

The most significant feature in our results is that the effective frequencies (or effective force constants), which measure the response of the lattice to the external forces, are much smaller than previous estimates. The lattice is much softer than previously assumed, and the distortion for a given force is correspondingly greater.

The reasons for this difference lie partly in the method of calculation. The previous results which can be compared most directly with ours are those of Lidiard and Stoneham (1967). In this earlier work it was assumed that all atoms except the nearest atoms to the vacancy were fixed. Effectively the frequencies which were obtained measure the response to forces applied suddenly, in a time much less than the periods of the lattice modes. Our present work allows all atoms to move, and we seek the static equilibrium configuration. Thus we calculate what is essentially the adiabatic response to the applied forces. The results which we have derived here are the ones appropriate to the defect properties discussed later. Physically the difference between the two sets of results means that it is very easy for the distant neighbours of the vacancy to adjust their positions so that the motion of the near neighbours is only slightly impeded. It is possible to give a specific example. The nearest neighbours to the vacancy respond to a totally symmetric force F_A by moving radially outward towards the centre of a triangle of next-nearest neighbours. The distance between the near neighbour and the next-nearest neighbours changes very little ($\simeq 6\%$ at most) even if the next neighbours are fixed. Thus very slight next-nearest neighbour motion can profoundly affect the strain energy. This is particularly true for silicon, where bond-bending forces are weak.

In addition to these changes of method there are also changes resulting from the different interatomic potential. The potential used here is considerably better than those used previously, in that it gives a good fit to phonon dispersion data. We have also verified that small changes in the potential leave the results largely unaffected.

Acknowledgments

Appendix. The normal coordinates for the vibrational modes of the tetrahedral group

The neighbours to the vacancy A, B, C, D have coordinates $(\bar{1}, 1, 1)$, $(1, \bar{1}, 1)$, $(1, 1, \bar{1})$ and $(\bar{1}, \bar{1}, \bar{1})$ respectively. Writing the x displacement of A as X_A, and so on, the Q_α are given below.

$$Q_a = \frac{1}{(12)^{1/2}} \{(-X_A + X_B + X_C - X_D) + (Y_A - Y_B + Y_C - Y_D) + (Z_A + Z_B - Z_C - Z_D)\} \subset A_1$$

$$Q_\theta = \frac{1}{(24)^{1/2}} \{2(-X_A + X_B + X_C - X_D) - (Y_A - Y_B + Y_C - Y_D) - (Z_A + Z_B - Z_C - Z_D)\} \subset E$$

$$Q_\epsilon = \frac{1}{\sqrt{8}} \{(Y_A - Y_B + Y_C - Y_D) - (Z_A + Z_B - Z_C - Z_D)\}$$

$$Q_\xi = \frac{1}{\sqrt{8}} \{(Y_A + Y_B - Y_C - Y_D) + (Z_A - Z_B + Z_C - Z_D)\}$$

$$Q_\eta = \frac{1}{\sqrt{8}} \{(X_A + X_B - X_C - X_D) + (-Z_A + Z_B + Z_C - Z_D)\} \Bigg\} \subset T_2$$

$$Q_\zeta = \frac{1}{\sqrt{8}} \{(X_A - X_B + X_C - X_D) + (-Y_A + Y_B + Y_C - Y_D)\}$$

References

BULLOUGH, R., and PERRIN, R. C., 1968, *Proc. R. Soc.* A, **305**, 541–52.

DOLLING, G., 1963, in *Inelastic Scattering of Neutrons in Solids and Liquids*, Vol. II (Vienna: I.A.E.A.) p. 37.

ELKIN, E. L., and WATKINS, G. D., 1968, *Phys. Rev.*, **174**, 881–97.

FRIEDEL, J., LANNOO, M., and LEMAN, G., 1967, *Phys. Rev.*, **164**, 1056–69.

HASIGUTI, R. R., 1968, *Int. Symp. on Lattice Defects in Semiconductors*, Ed. Hasiguti (Tokyo: University of Tokyo Press) pp. 131–7.

LANNOO, M., and STONEHAM, A. M., 1968, *J. Phys. Chem. Solids*, **29**, 1987–2000.

LIDIARD, A. B., and STONEHAM, A. M., 1967, *Science and Technology of Industrial Diamonds*, Vol. 1, Ed. J. Burls (London: Industrial Diamond Information Bureau), pp. 1–15.

MCMURRY, H. L., SOLBRIG, Jr. A. W., BOYTER, J. K., and NOBLE, C., 1967, *J. Phys. Chem. Solids*, **28**, 2359–68.

MCSKIMIN, H. J., and BOND, W. L., 1957, *Phys. Rev.*, **105**, 116–21.

PALEVSKY, H., HUGHES, D. J., KLEY, W., and TUNKELS, E., 1959, *Phys. Rev. Lett.*, **2**, 258–9.

ROBERTSON, R., FOX, J. J., and MARTIN, A. E., 1934, *Phil. Trans. R. Soc.* A, **232**, 463–533.

SCHMID, G., CHIK, K. P., and SEEGER, A., 1968, *Proc. Conf. Radiation Effects in Semiconductors, Santa Fe, 1967*, Ed. F. L. Vook (New York: Plenum Press), pp. 60–4.

SCHOLZ, A., and SEEGER, A., 1965, in *Radiation Damage in Semiconductors* (Paris: Dunod), pp. 315–38.

SEEGER, A., and SWANSON, M. L., 1968, *Int. Symp. on Lattice Defects in Semiconductors*, Ed. Hasiguti (Tokyo: University of Tokyo Press), pp. 93–127.

SINGH, B. D., and DOYAL, B., 1970, *Phys. Stat. Solidi*, **38**, 141–50.

SMITH, H. M., 1948, *Phil. Trans. R. Soc.* A, **241**, 105–45.

SUTTON, L. E. (Ed.), 1965, *J. Chem. Soc.*, Suppl. 18.

SWALIN, R. A., 1961, *J. Phys. Chem. Solids*, **18**, 290–6.

WARREN, J. L., WENZEL, R. G., and YARNELL, J. L., 1965, *Proc. Symp. Inelastic Scattering*, Vol. 1, (Vienna: I.A.E.A.), p.361.

WARREN, J. L., YARNELL, J. L., DOLLING, G., and COWLEY, R. A., 1967, *Phys. Rev.*, **158**, 805–8.

E2