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Lattice distortion near vacancies in diamond and silicon—II

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Abstract. Previous results (paper I), based on a dynamic relaxation procedure, coupled with a valence force potential function to represent the interaction between the atoms of the perfect crystal, have been used to calculate the distortion around point defects in a diamond-type crystal. The method has been applied to the isolated neutral vacancy in diamond and silicon for two alternative choices of rebonding forces for the vacancy electrons. In one case the electronic forces have been estimated from a detailed molecular orbital calculation, while in an alternative approach a generalized Morse-type potential relationship has been used. The formation energy of the neutral vacancy has also been calculated. For the vacancy in diamond values of 0·35 and 6·47 eV have been obtained using two alternative approximations to calculate the molecular orbital force terms, while with the Morse potential a value of −0·37 eV is obtained. The vacancy in silicon is estimated to have a formation energy of −38·8 eV using the molecular orbital parameters and −16·35 eV using the alternative method. The volume changes associated with the diamond-type system containing a vacancy are also calculated. The results suggest that one of the approximations used is not valid. Some of the possibilities are discussed.

1. Introduction

In this paper we calculate some of the measurable properties of point defects which depend on lattice distortion. These properties, including the relaxation volume change and formation energy of neutral vacancies in diamond structure lattices, are estimated using the two fundamental approximations described in the preceding article (Larkins and Stoneham 1971, to be referred to as I). The first approximation is the harmonic approximation for the lattice dynamics. The appropriate results for diamond and silicon and an analysis of the different interatomic potentials were given in I. The results are used here in this paper. The second approximation is the assumption that the distortion arises from forces on the nearest neighbours of the vacancy; the forces result from the local electronic reorganization which occurs in the creation of the defect. These forces are calculated using a detailed microscopic model in § 2.

These two approximations are used systematically, and the models chosen for both the lattice dynamics and for the defect electronic structure are the best currently available. It is therefore surprising that the distortion which results is, in some cases, extremely large, and suggests that one of the approximations is not valid. Some of the possibilities are discussed.

2. Calculation of rebonding forces between the vacancy electrons

To demonstrate the method we calculate the magnitude and symmetry of the rebonding forces using two alternative models. Firstly, we propose to use the results of a quantum mechanical calculation based upon the defect molecule method of Coulson and Kearsley (1957). Secondly, we consider the case where the rebonding of the four vacancy electrons is

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in terms of two noninteracting pairs such that a tetragonal distortion of the defect results. In this case, as in the studies by previous workers, the rebonding is described in terms of a generalized Morse potential whose parameters are deduced from the bulk properties of the crystal.

(i) *Molecular orbital method*

The electronic properties of the undistorted neutral vacancy in diamond and silicon have been determined by the method of Coulson and Kearsley (1957). The calculations (Larkins 1969) use atomic Hartree–Fock functions determined by Clementi (1965) to approximate the s and p orbitals on the atoms nearest the defect. Only the final results will be given here.

Two cases have been considered for diamond, with different values of the self-penetration integral, $P \equiv \langle a(1)|T_1 + V_{A1}|a(1)|\rangle$ described by Coulson and Kearsley. With $P = -7{\cdot}13$ eV, calculated directly, the ${}^3T_1$ electronic level is lowest in energy lying 0·31 eV below the ${}^1E$ level; for $P = -16{\cdot}42$ eV, the semi-empirical value it is 0·13 eV below this level. In both cases the order of these two levels is inverted compared with the findings of Coulson and Kearsley.

For the vacancy in silicon we consider here just the case where the value of the one-centre Coulomb integral, $\underset{\sim}{Q}$, is determined semi-empirically. With $\underset{\sim}{Q} = 8{\cdot}10$ eV, the lowest ${}^1E$ and ${}^3T_1$ electronic levels are grouped together within 0·2 eV of the ${}^5A_2$ ground state, with the ${}^1A_1$ and ${}^1T_2$ levels 1·15 eV and 1·52 eV above this level respectively. We shall see later that these two levels are particularly sensitive to the extent of symmetric distortion associated with the defect.

All electronic levels may be lowered in energy from interaction with the totally symmetric mode, $\underset{\sim}{Q}_a$. However, only degenerate levels can couple with the distortion modes of lower symmetry giving the Jahn–Teller effect. We may estimate the extent of symmetric relaxation, and hence energy lowering, associated with a particular electronic level described by a wave function ψ_k using equations (I.4.4.)† and (I.4.5) when we know the symmetric force term F_a

$$F_a = -\left(\frac{\partial}{\partial \underset{\sim}{Q}_a}\langle\psi_k|H_{\text{elec}}|\psi_k\rangle\right)_0 \tag{2.1}$$

F_a has been calculated by Larkins (1969). The only possible asymmetric distortion for a two-fold degenerate E level results from a coupling to E modes giving a tetragonal distortion of the centre (Öpik and Pryce 1957). The force term associated with this distortion is defined as

$$F_{EE} = -\left(\frac{\partial}{\partial \underset{\sim}{Q}_\theta}\langle\theta|H_{\text{elec}}|\theta\rangle\right)_0 \tag{2.2}$$

where $|\theta\rangle$ and $|\epsilon\rangle$ are the two electronic states of the E manifold. There are three possible tetragonal distortions which represent energy minima for the system; they have symmetry axes along the $\langle 100\rangle$, $\langle 010\rangle$ and $\langle 001\rangle$ directions. We consider just the $\langle 100\rangle$ configuration where $\underset{\sim}{Q}_\theta$ is given by (I.4.4) and $\underset{\sim}{Q}_\epsilon$ is zero. For a three-fold degenerate level with states $|\xi\rangle$, $|\eta\rangle$ and $|\zeta\rangle$ the formal results for the distortion are the same irrespective of whether we are considering electronic levels belong to the T_1 or T_2 irreducible representation. The T states may couple to either the E or T distortion modes such that either a tetragonal or trigonal distortion of the defect results. Mixed trigonal and tetragonal distortions do not occur for isolated levels, but only when there is accidental degeneracy (Stoneham and Lannoo 1969). There are four equivalent trigonal distortions with symmetry axes along the $\langle\bar{1},\bar{1},\bar{1}\rangle$, $\langle 1,1,\bar{1}\rangle$, $\langle 1,\bar{1},1\rangle$, and $\langle\bar{1},1,1\rangle$ directions and three of tetragonal symmetry as previously discussed. We consider just the tetragonal distortion for which $\underset{\sim}{Q}_\epsilon = 0$ and

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† Equations with the prefix I refer to the preceding article (Larkins and Stoneham 1971).

Q_θ is finite and the trigonal distortion where $Q_\xi = Q_\eta = Q_\zeta$. For these cases the force terms F_{TE} and F_{TT} are defined as follows:

$$F_{\mathrm{TE}} = -\frac{2}{\sqrt{3}}\left(\frac{\partial}{\partial Q_\epsilon}\langle\eta|H_{\mathrm{elec}}|\eta\rangle\right)_0 \tag{2.3}$$

and

$$F_{\mathrm{TT}} = -\frac{2}{3}\left(\frac{\partial}{\partial Q_\xi}\langle\eta|H_{\mathrm{elec}}|\zeta\rangle\right)_0. \tag{2.4}$$

Using equation (I.4.4) the values of the Q_α terms may be calculated. The energy lowering for the tetragonal distortion, $\Delta E(Q_\theta)$, is given by equation (I.4.5); for the trigonal distortion the energy lowering is given by three times an equivalent expression.

Table 1. Values of the force terms and the corresponding distortion and energy lowerings† for the two lowest levels of the neutral vacancy in diamond using the molecular orbital approach.

	F_{a} (eV Å^{-1})	Q_{a} (Å)	ΔE_{TA} (eV)	F_{TE} (eV Å^{-1})	Q_θ (Å)	ΔE_{TE} (eV)	F_{TT} (eV Å^{-1})	Q_ξ (Å)	ΔE_{TT} (eV)
^{3}T$_1$ Level									
Case 1	−12·17	−1·09	−6·60	−8·22	−0·51	−2·14	−5·58	−0·47	−3·90
Case 2	−11·97	−1·07	−6·37	−2·09	−0·13	−0·14	−3·53	−0·29	−1·56
^{1}E Level				F_{EE}		ΔE_{EE}			
Case 1	−10·97	−0·96	−5·18	−7·92	−0·50	−1·96			
Case 2	−12·13	−1·08	−6·56	−2·09	−0·13	−0·14			

† The energy lowerings given include both the electronic and elastic contributions.

The lowering in energy and the corresponding normal co-ordinates for the lowest ^{3}T$_1$ and ^{1}E levels of the vacancy system in diamond for the various force terms are given in table 1. The symmetric relaxation is the most important for both levels. In the two cases considered the ^{3}T$_1$ level is predicted to be the ground state of the system and to undergo a trigonal Jahn–Teller distortion. In case 1 the total lowering in energy of the system associated with the ^{3}T$_1$ ground state is 10·50 eV, while in case 2 it is 7·93 eV as the result of relaxation and distortion effects. From the values for the normal co-ordinates we may determine the co-ordinates of the atoms nearest the defect. At equilibrium, allowing for symmetric and trigonal distortion of the ^{3}T$_1$ level, the distances between the nearest neighbour atoms for case 1 are given by

$$\mathrm{AB} = \mathrm{AC} = \mathrm{BC} = 2{\cdot}10\,\text{Å}$$

$$\mathrm{AD} = \mathrm{BD} = \mathrm{CD} = 1{\cdot}33\,\text{Å}$$

while for case 2, AB = 1·94 Å and AD = 1·42 Å. These distances should be compared with the undistorted atom separations of 2·52 Å.

For the neutral vacancy in silicon a similar analysis can be carried out. The values for the symmetric force terms for the various lowest electronic levels are given in table 2. Using the value for ω_{a} given in table 4 of I to calculate distortion and lowering in energy for the system an unreasonably large value is obtained. The cause of this poor result is discussed in § 5.

When the electronic levels from the calculation for the undistorted vacancy in silicon are corrected for the symmetric relaxation energy contribution the ^{1}T$_2$ level becomes lowest in energy 2·43 eV below the ^{1}A$_1$ level. The order of these two levels does depend upon the value chosen for ω_{a}. The ^{1}T$_2$, but not the ^{1}A$_1$ level, may undergo a Jahn–Teller distortion. A detailed calculation shows that the trigonal distortion which results corresponds to an electronic energy lowering of 0·24 eV. As a result of these two distortions the ground state of the system has been lowered 48·45 eV and the electronic state has changed from a $^5A_2$ level to a $^1T_2$ level.

Table 2. Symmetric force terms and the corresponding energy lowerings and distortions associated with the lowest levels of the neutral vacancy in silicon for the case where $Q' = 8{\cdot}10$ eV.

		$\omega_a = 0{\cdot}18 \times 10^{14}$	
Electronic level (energy for $Q_a = 0$) (*eV*)	F_a (eV Å^{-1})	$\Delta E(Q_a)$† (eV)	Q_a (Å)
$^3T_1$ (−88·99)	−7·39	−28·89	−7·84
^1E (−88·89)	−7·57	−30·34	−8·03
$^5A_2$ (−89·05)	−7·87	−32·83	−8·37
$^1A_1$ (−87·90)	−9·55	−48·45	−10·17
$^1T_2$ (−87·53)	−9·70	−49·85	−10·29

† Electronic and elastic energy contributions.

(ii) *Morse potential method*

Here we assume that the four vacancy electrons rebond in pairs with negligible interaction between the pairs. A tetragonal distortion of the defect results. The pairwise rebonding may be described in terms of a generalized Morse potential of the form

$$U(r) = D\left[\frac{\alpha_2}{\alpha_1 - \alpha_2} \exp\{-\alpha_1(r - r_0)\} - \frac{\alpha_1}{\alpha_1 - \alpha_2} \exp\{-\alpha_2(r - r_0)\}\right] \tag{2.5}$$

where D is the bond dissociation energy, r_0 the equilibrium internuclear distance in the perfect crystal and α_1 and α_2 are parameters to be determined by the physical properties of the crystal. This is the approach which has been used by previous workers (Swalin 1961, Scholz and Seeger 1965, Seeger and Swanson 1968, Hasiguti 1968) who also used the same potential expression for interactions between the atoms of the perfect crystal. In all previous studies except that by Seeger and Swanson (1968) α_1 has been assumed to be equal to $2\alpha_2$ and α_2 determined from the compressibility of the crystal.

We have determined the value of D from the relation

$$D = \tfrac{1}{2}(E_S + E_P) \tag{2.6}$$

as suggested by Lidiard (1965) where E_S is the heat of sublimation at room temperature and E_P is the promotion energy for an electron from the s^2p^2 ground state of the isolated atom to the sp^3 valence state of that atom. Lidiard (private communication) has calculated E_P for the carbon, silicon and germanium atoms theoretically using Hartree–Fock functions for the s and p orbitals on the isolated atom. For the carbon atom E_P was estimated to be 7·46 eV which is in good agreement with the estimate of 7·545 eV obtained by Öpik (private communication to Lidiard) using the experimentally known energy values for the spectroscopic states and information obtained by extrapolation from data for isoelectric ions. For the silicon atom Lidiard obtained a value of 6·06 eV for E_P which is in good agreement with the extrapolated value of 6·22 eV obtained by Skinner and Pritchard (1953). We have chosen to use the values obtained by Lidiard as we can find no quantitative evidence to support the hypothesis of Voge (1936, 1948) that these values for E_P should be reduced in magnitude due to resonance with certain s^2p^2 configurations. The values for E_S are those used by Swalin (1961), Scholz and Seeger (1965) and Hasiguti (1968). Therefore we have

$$D_C = \tfrac{1}{2}(7{\cdot}22 + 7{\cdot}46) = 7{\cdot}34 \text{ eV}$$

$$D_{Si} = \tfrac{1}{2}(3{\cdot}66 + 6{\cdot}06) = 4{\cdot}86 \text{ eV}.$$

For diamond the parameters α_1 and α_2 for the Morse potential may be determined from the compressibility, β and the Grüneisen parameter, γ, because these quantities are essentially independent of temperature (Mitchell 1965, Berman and Thewlis 1955). However, for the silicon crystal γ is strongly temperature dependent and cannot be used in the determination of these parameters. In the expression for γ we use the semi-empirical relation, known as the Dugdale–MacDonald relation (Rice *et al.* 1958) rather than the expression derived by Slater (1939) as the former has been found by experience to give more reasonable agreement with experiment in many cases. By substitution of equation (2.5) in the appropriate expressions we obtain

$$\frac{1}{\beta} = D\alpha_1\alpha_2 \qquad (2.7a)$$

$$\gamma = \frac{\sqrt{3}a}{24}(\alpha_1 + \alpha_2) \qquad (2.7b)$$

where a is the cell constant for the crystal ($a = 3{\cdot}56$ Å (diamond), $a = 5{\cdot}43$ Å (silicon)). For the diamond crystal $1/\beta = 5{\cdot}448 \times 10^{12}$ dyn cm^{-2} (Mitchell 1965) and $\gamma = 1{\cdot}3$ (Berman and Thewlis 1955) such that

$$\alpha_1^{\mathrm{C}} = 3{\cdot}720\,\text{Å}^{-1} \qquad \alpha_2^{\mathrm{C}} = 1{\cdot}332\,\text{Å}^{-1}.$$

Because of the temperature dependence of γ for the silicon crystal we use only equation (2·7a) with $\alpha_1 = 2\alpha_2$ and $1/\beta = 9{\cdot}793 \times 10^{11}$ dyn cm^{-2} (McSkimin 1953). Hence we obtain

$$\alpha_2^{\mathrm{Si}} = 1{\cdot}01\,\text{Å}^{-1}.$$

We may now determine the tetragonal forces on the atoms nearest the defect, which are $\sqrt{8}\,a/4$ Å apart, from the relation

$$F = -\left.\frac{\mathrm{d}U(r)}{\mathrm{d}r}\right|_{r=\frac{\sqrt{8}a}{4}}. \qquad (2.8)$$

Hence, from equations (I.4.4) and (I.4.5) the extent of distortion and energy lowering corresponding to these forces may be determined. The results are shown in table 3 for the configuration where $Q_\epsilon = O$ corresponding to the case where the vacancy electron on atom A is bonding with the vacancy electron on atom B. The predicted lowering in energy due to the rebonding of the vacancy electrons in pairs using the Morse potential method is less than the energy lowering calculated when the rebonding was described within the molecular orbital formalism. We may also use our dynamic relaxation method to go beyond equation (2.8) and allow the forces to alter as the atoms move.

Table 3. Lattice distortion and energy lowering associated with the neutral single vacancy in a diamond-type crystal for tetragonal rebonding forces described by a Morse-type relation

Crystal	$F_{\mathrm{T}} = 4F$ (eV Å^{-1})	ΔE (eV)	Q_θ (Å)	Q_{a} (Å)
Diamond	−14·99	−9·05	−0·55	−1·09
Silicon	−6·78	−22·23	−3·04	−5·88

3. Volume change associated with vacancy relaxation

Using the continuum theory of lattice defects discussed by Eshelby (1956) the change in volume of a diamond-type crystal with a vacancy may be determined from the relation

$$\Delta V = \frac{r_0 F_{\mathrm{a}}}{3K} \qquad (3.1)$$

where K is the bulk modulus ($= 1/\beta$) for the crystal, r_0 is the nearest neighbour distance and F_a is the total symmetric force for the vacancy. Now the atomic volume is $8r_0^3/3\sqrt{3}$, so

$$\frac{\Delta V}{V} = \frac{\sqrt{3}}{8r_0^2 K} F_a. \tag{3.2}$$

Using the values for K and r_0 given previously we have for the diamond crystal

$$\frac{\Delta V}{V} = 2{\cdot}67 \,.\, 10^{-2} F_a$$

while for silicon

$$\frac{\Delta V}{V} = 6{\cdot}41 \,.\, 10^{-2} F_a$$

where F_a is eV Å^{-1}.

Using the values for F_a obtained by the molecular orbital method, we have for diamond

$$\frac{\Delta V}{V} = -0{\cdot}31 \qquad \text{(case 1, calculated } P \text{ integral)}$$

$$\frac{\Delta V}{V} = -0{\cdot}32 \qquad \text{(case 2, semi-empirical } P \text{ integral)}$$

while for silicon the change in volume from lattice relaxation is

$$\frac{\Delta V}{V} = -0{\cdot}61.$$

No experimental results are at present available.

4. Formation energy of the single vacancy

(i) *Molecular orbital approach*

It is now possible to make some estimate of the formation energy of the vacancy in the crystal. There are three contributions to this energy which must be considered.

First, the energy required to remove an atom from its perfect lattice site and place it on the surface of the crystal. This contribution to the energy is $2D$ where D is the bond dissociation energy. We note that $2D \equiv E_S + E_P$, from equation (2.6). Seeger and Chik (1968), Swalin (1961), Scholz and Seeger (1965) and Hasiguti (1968) omit the important promotion energy term.

Second, the difference in energy between the configuration in which the four vacancy electrons are in the ground state molecular orbital for the undistorted system, and a configuration where one electron is in each of the four hybridized orbitals with spins in a mutually random orientation. To calculate this difference we follow the method used by Coulson *et al.* (1963) for the vacancy in graphite. It is convenient to refer the energies of the two states to the energy of a third state in which the defect electrons are absent. Thus we consider the three states shown in figure 1: the reference state (I), the state II with one electron in each orbital and mutually uncorrelated spins, and state III with the electrons in their lowest electronic state. In all these cases we assume that the atoms are at their perfect lattice sites and that the electrons other than the defect electrons are in their perfect lattice states. $E_d \equiv E_{II} - E_{III}$ is then

$$E_d = (E_{II} - E_I) - (E_{III} - E_I). \tag{4.1}$$

The first term may be calculated following Coulson *et al.* (1963). Multiple exchange terms are important, especially for diamond, and we have always included them in full. For reference table 4 also includes the values with only single exchanges. The second term in $E_{\rm d}$ can be calculated directly in the defect molecule approach (Larkins 1969) and is also given in table 4. Analogous calculations have been made for the vacancy in germanium by Hwang and Watt (1968).

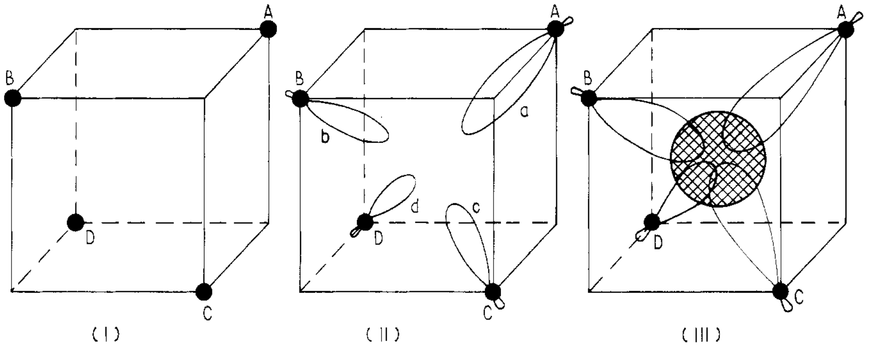

Figure 1. Various states of the vacancy system. (I), no vacancy electrons; (II), four vacancy electrons having mutually random spins; (III), four vacancy electrons in the ground state electronic level.

Third, the contribution to the formation energy is the lowering in energy of the system which results from a relaxation of the atoms near the defect. This contribution, designated $E_{\rm r}$, was calculated in the previous section. Therefore we have a formation energy

$$E_{\rm f} = 2D - E_{\rm d} - E_{\rm r}. \tag{4.2}$$

The results obtained are given in table 4.

Table 4. Values of terms contributing to the formation energy of the single vacancy in diamond and silicon using the molecular orbital approach

Crystal	$E_{\rm II} - E_{\rm I}$[a]	$E_{\rm II} - E_{\rm I}$[b]	$E_{\rm III} - E_{\rm I}$[c]	$E_{\rm d}$	$E_{\rm r}$	$2D$	$E_{\rm f}$
Diamond Case 1 $^3T_1$ level	−73·29[d]	−74·93	−78·76	3·83	10·50	14·68	0·35
Diamond Case 2 $^3T_1$ level	−114·41	−115·00	−115·28	0·28	7·93	14·68	6·47
Silicon Q = 8·10 eV	−88·81	−88·95	−89·05 ($^5A_2$)	0·10	48·45 ($^1A_1$)	9·72	

[a] single exchange only;
[b] multiple exchange terms included;
[c] from molecular orbital calculations (Larkins 1969);
[d] all energies in electron volts.

(ii) *Morse potential method*

It is again possible to use the expression (4.2) to determine the formation energy of the vacancy with this approach provided we redefine $E_{\rm d}$ as the difference in energy between the electrons in configuration II and a configuration with the electrons tetrahedrally bonded in pairs with the rebonding described by a Morse-type potential. Now this difference is equal to $-2U(r)$ where $U(r)$ is given by equation (2.z) for $r = (8/3)^{\frac{1}{2}}r_0$. For the diamond $E_{\rm d} = 6{\cdot}00$ eV while for silicon $E_{\rm d} = 3{\cdot}84$ eV. These values are very much larger than those given in table 4 and underline the difficulty of using a simple pairwise potential of these form. Using these values we obtain the following results for the formation energy:

$$E_f \text{ (diamond)} = -0{\cdot}37 \text{ eV}$$

$$E_f \text{ (silicon)} = -16{\cdot}35 \text{ eV}.$$

Preliminary calculations suggest that if we perform an explicit dynamic relaxation using the Morse potential relationships given above to describe the tetragonal rebonding forces slightly higher, but still negative, values are obtained for the formation energy of the isolated vacancy in diamond and silicon. Such calculations allow for the dependence of the forces on the nearest neighbour configuration.

5. Discussion of results including relation to experiment and previous calculations

In this paper we have used the dynamic relaxation procedure to calculate the distortion associated with the isolated single vacancy for two choices of rebonding forces. The results of paper I should be applicable to other point defects as well as alternative models for the force expressions describing the electronic reorganization. We have concentrated on the configuration of the atoms which are nearest the defect, but it is possible to determine the response of atoms far from the defect due to the applied forces. In this connection we have noted that fifth neighbours to the defect displace more than third or fourth neighbours for given forces on nearest neighbours. This characteristic of the diamond-type lattice agrees with the finding of Herman (1959) when calculating the vibrational spectrum of germanium.

In our calculation of the vacancy formation energy and of the relaxation volume per vacancy we believe that the values obtained from the molecular orbital method are the most reasonable. The serious limitation of the alternative Morse potential approach is that the potential curve is deduced from data near r_0, the equilibrium internuclear separation, and is then applied to the second nearest-neighbour distance. Further, the Morse potential approach neglects the interaction between the two pairs of vacancy electrons.

Unfortunately, there are no experimental estimates of the formation energy of the isolated vacancy in diamond. It now seems established that the formation energy for the isolated vacancy in graphite is around 7 eV (Henning 1965, Henson and Reynolds 1965, Simmons 1965), and it is possible that it is similar in magnitude in diamond. Such a value would be close to our prediction of 6·47 eV for case 2, although it is much larger than our other estimate. Previous estimates of 4·16 eV (Swalin 1961) and 5·79 eV (Scholz and Seeger 1965) used rather restricted relaxation procedures and pairwise interactions between all atoms; Bennemann's (1965) estimate of 3·68 eV was obtained from a band theory calculation for the unrelaxed vacancy.

The experimental value for the formation energy of the neutral vacancy in silicon is still subject to disagreement. Values of 4·73 eV, 4·88 eV and 5·14 eV have been reported by Ghoshtagore (1966), Wilcox and La Chapelle (1964) and Masters and Fairfield (1966) respectively. However, Watkins (1963) has deduced a lower value of around 3·5 to 4·0 eV. These may be compared with the theoretical estimates of Swalin (1961), Seeger and Swanson (1966), Scholz and Seeger (1965) and Bennemann (1965), using rather restricted models, which all lay in the range 2–3 eV. Our estimates using the effective frequencies of paper I and either of the sets of forces are unsatisfactory. Indeed, the formation energy has the wrong sign, and the lattice appears to be unstable against vacancy formation. This suggests that our analysis is incomplete (strictly we could have made a numerical error, but there are a number of checks which make this unlikely). There is, in fact, one obvious omission, even ignoring possible anharmonic terms. The electronic energy contains terms linear, quadratic and of higher order in the displacements. The quadratic terms (which may include cross-terms as $Q_a Q_\theta$) may be interpreted in two ways: as a displacement dependence of the forces, or as an extra term in the effective force constant. The problem, of course, is much more complicated, but is still soluble since there are no anharmonic terms. Calculations using such higher terms have already appeared for the F-centre in alkali halides (Stoneham and Bartram 1970). These quadratic terms are not easy to calculate, and probably need more accurate wavefunctions than we have at our disposal. However, to illustrate the effect of changing the effective force constants we have rederived the formation energy using the frequencies $\omega_a = \omega_E = \sqrt{2}\,\omega_T = 0{\cdot}825\,.10^{14}$ rad s^{-1} obtained by Lidiard and Stoneham. The formation energy for the silicon vacancy becomes 8·50 eV using the molecular orbital method and 4·71 eV with the Morse potential approach. These values are more in line with the experimental results. They tend to confirm the view, also supported by the volume-change results, that the effective forces are satisfactory. We note however, that the molecular orbital method as developed requires the atoms neighbouring the vacancy to be sp^3 hybridized. Any change in the hybridized state of these atoms would reduce the electronic force terms. Finally, we should emphasize another possibility. The phonon dispersion curves do not uniquely define the force constants (Slater 1958, Tewary, private communication) and it is possible that we have simply used incorrect interatomic forces in paper I. Intuitively, this possibility seems unlikely.

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