describes the nonparabolicity very well. None of this requires any statement about the number of electrons donated per Te atom. Weiner then makes the *assumption* that one Te atom donates one electron, and from this concludes that there are six electron ellipsoids. The point we wish to make is that there is no basis for this assumption. For example, it is known[30] that Sn, which along with Te is one row above Bi in the periodic system, produces three times the change in hole concentration that Pb does. (Pb is immediately to the left of Bi in the periodic system.) Then, the recent work of Brandt and Razumenko[31] shows that Pb only reduces the *electron* concentration by one electron per ellipsoid per 55 Pb atoms added. Moreover, if one just thinks a bit about what $\sim 10^{-2}\%$ Te in Bi does, one realizes that the "impurity band" width may well be of the order of the electron Fermi energy.[32] All this means that, at the least, it would be more prudent to use the existence of three ellipsoids to show that each two Te atoms add approximately one electron than to argue the other way.

[30] V. Heine, Proc. Phys. Soc. (London) **A69**, 505 (1956).
[31] N. B. Brandt and M. V. Razumenko, Soviet Phys.—JETP **12**, 198 (1961).

ACKNOWLEDGMENTS

We should like to acknowledge particularly helpful discussions with Dr. B. Lüthi and Dr. H. Thomas of this laboratory. We thank Dr. W. S. Boyle of Bell Telephone Laboratories for sending us a "first draft" of their review, and Dr. D. Weiner for making available a prepublication copy of his manuscript.

[32] Experiments on heavily doped germanium indicate that the band structure is not perturbed by large concentrations of impurities [cf. M. Pollak, Phys. Rev. **111**, 798 (1958)]. Presumably the situation is similar in bismuth, as Weiner's work suggests.

PHYSICAL REVIEW VOLUME 127, NUMBER 2 JULY 15, 1962

Point Defects in Copper*‡

R. A. JOHNSON† AND E. BROWN
Rensselaer Polytechnic Institute, Troy, New York

(Received March 12, 1962)

The atomic configurations and energies for point defects in copper have been studied theoretically using a classical model. The atoms near the defect are treated explicitly while the remainder of the crystal is treated as an elastic continuum with atoms imbedded in it. A Born-Mayer repulsive force law, Ae^{-ar}, is assumed to act between nearest neighbors. Vacancies, interstitials, di-vacancies, and di-interstitials have been considered. Configurations are found by choosing a starting configuration roughly approximating the situation under consideration, and an iterative process of successively adjusting the value of each variable occurring in the equation for energy such that the magnitude of the generalized force acting on it is minimized. The energy calculations include changes in bond energy in the discrete region, energy in the elastic field, and work done against cohesive forces, but neglect changes due to the redistribution of electrons. Various aspects of the model and method of calculation have been investigated, and the effects of electron redistribution are discussed. Predicted activation energies for motion of interstitials and vacancies are 0.05 and 0.43 eV, respectively. An upper limit of 0.26 eV has been found for the activation energy for migration of di-interstitials. The isolated interstitial has been thoroughly investigated, and eight well-defined equilibrium configurations have been found. Only one of these is stable, being the case in which two atoms are symmetrically split in the ⟨100⟩ direction about a vacant normal lattice site. The configuration in which the interstitial is located at a body center is found to be a local maximum, but the saddle point configuration for migration of interstitials is quite close to it.

INTRODUCTION

THE determination of atomic configurations and energies associated with point defects in metals has been the subject of a number of calculations.[1–11] The primary interest is in activation energies for motion and the associated atomic mechanisms. Therefore, metastable and saddle-point configurations must be investigated as well as the stable configuration. To a good approximation, the configurations may be determined by regarding the atomic coordinates classically (i.e., neglecting zero-point motions), but subject to forces which have essentially quantum mechanical

* Supported in part by the U. S. Atomic Energy Commission.
‡ This work is based on part of a dissertation to be submitted by Robert A. Johnson is partial fulfillment of the requirements for the degree of Doctor of Philosophy at Rensselaer Polytechnic Institute.
† Institute Fellow sponsored by International Business Machines Corporation.
[1] H. B. Huntington and F. Seitz, Phys. Rev. **61**, 315 (1942).
[2] H. B. Huntington, Phys. Rev. **91**, 1092 (1953).
[3] H. Kanzaki, J. Phys. Chem. Solids **2**, 24 (1957).
[4] C. Hall, J. Phys. Chem. Solids **3**, 210 (1957).
[5] L. Tewordt, Phys. Rev. **109**, 61 (1958).
[6] L. A. Girifalco and R. Streetman, J. Phys. Chem. Solids **4**, 182 (1958).
[7] R. A. Johnson, G. H. Goedecke, E. Brown, and H. B. Huntington, Bull. Am. Phys. Soc. **5**, 181 (1960).
[8] L. A. Girifalco and V. G. Weizer, J. Phys. Chem. Solids **12**, 260, (1960).
[9] A. Seeger and E. Mann, J. Phys. Chem. Solids **12**, 326, (1960).
[10] J. B. Gibson, A. N. Goland, M. Milgram, and G. H. Vineyard, Phys. Rev. **120**, 1229 (1960).
[11] K. H. Bennemann, Phys. Rev. **124**, 669 (1961); Z. Physik **165**, 445 (1961).

origins. Even with this approximation there remains a difficult many-body problem with relatively large uncertainties in the interactions.

In general, it is not sufficient to consider only the first few sets of atoms surrounding the defect, nor will elastic theory be valid in the immediate vicinity of the defect. Also, it had been assumed in early calculations that the lowest energy configurations would have the highest symmetry. This would effectively reduce the number of degrees of freedom to be considered. However, recent work by several investigators[7,10] has been discouraging in this respect, and there evidently is no clear way to simplify the problem by the use of symmetry. This difficulty arises primarily in the isolated interstitial problem, and we therefore have investigated this case in considerable detail. Furthermore, the problem of calculating the contribution to the energy from the redistribution of valence electrons has not been solved. Part of this term will cancel in the calculation of activation energies, but the residual uncertainty is not necessarily negligible. Experiments on low-temperature annealing of irradiated copper[12–14] indicate activation energies of the order of 0.1 eV, so that the contributions to the energy should be determined to at least this accuracy to be reliable.

It does not seem very likely that at present a calculation can be carried out with sufficient detail to give unequivocal answers to the mechanism of anneal in damaged material and to predict activation energies accurately, but the results of approximations are sufficient to shed light on some questions and provide insight into the problem in general.

Copper has generally been accepted as the "standard" for both experimental and theoretical research in this field. It is felt that focusing attention on one material and arriving at some understanding of its behavior will provide a base from which other materials can be approached more easily.

We have chosen a model in which the atoms near the defect are treated as classical particles, while the remainder of the metal (taken to be infinite) is treated as an elastic continuum with atoms imbedded in it. A Born-Mayer repulsive force law is assumed to act between nearest neighbors. This model is similar to that used by Tewordt.[5]

Isolated single defects, interstitial and vacancy, have been studied, and the activation energy for migration of these defects, as predicted by this model, have been determined, as well as the atomic mechanisms of diffusion. By the application of appropriate boundary conditions, the associated activation volumes have also been found. Preliminary results have been reported previously.[7]

[12] J. W. Corbett, R. B. Smith, and R. M. Walker, Phys. Rev. **114**, 1452 (1959).
[13] G. D. Magnuson, W. Palmer, and J. S. Koehler, Phys. Rev. **109**, 1990 (1958).
[14] A. V. Granato and T. G. Nilan, Phys. Rev. Letters **6**, 171 (1961).

Configurations are found by choosing a starting configuration roughly approximating the situation under consideration, and then successively adjusting the value of each variable occurring in the equation for energy such that the magnitude of the generalized force acting on it is minimized, and iterating this process many times. The energy in the crystal above that for a perfect crystal normally converges in the above process. Convergence is not ensured, but no difficulties have been encountered in this respect. The computations have been performed by high-speed computers.

THEORY

In our model, the atoms within a region containing the nearest hundred or so atoms to the defect, called region I, were considered as independent. The remaining atoms were treated as though they were imbedded in an elastic continuum. These atoms were further divided into regions II and III, where region II was composed of those atoms which have nearest neighbors in region I.

The static, isotropic, elastic equation is[15]

$$(\lambda+2\mu)\nabla(\nabla\cdot\mathbf{u})-\mu\nabla\times(\nabla\times\mathbf{u})=0, \tag{1}$$

where λ is Lamé's modulus and μ is the shear modulus. In the above, $\mathbf{u}$ defines the displacement field for an elastic continuum and is a function of $\mathbf{r}$. Thus $\mathbf{u}$ defines the displacement of each atom imbedded in the elastic continuum as a function of its position. There are an infinite number of solutions to this equation, and boundary conditions are needed to determine which are applicable to a given problem. The condition for large r is that the stresses approach zero. The boundary condition at the interface with region I cannot be so simply specified. An arbitrary solution of Eq. (1) satisfying the boundary condition at infinity can be expressed in terms of spherical harmonics. Only a few low harmonics appropriate to the symmetry under consideration were used. All terms were centered at the defect, and the total displacement vector is the vector sum of the displacements from the various terms. A term used in all cases is

$$\mathbf{u}_1=-C_1\nabla(1/r), \tag{2}$$

which gives rise to an expansion or contraction of the lattice. All other terms used distort the shape of the lattice, and were adjusted where necessary by adding or subtracting some $\mathbf{u}_1$ so that they give rise to no net volume change. The following terms were considered:

$$\mathbf{u}_2=C_2\nabla\left[\frac{1}{r^5}\left(\frac{x^4+y^4+z^4}{r^4}-\frac{3}{5}\right)\right], \tag{3a}$$

$$\mathbf{u}_3=C_3(1/r^4)\left[\tfrac{3}{2}(1-3\cos^2\theta)\mathbf{e}_r-3\cos\theta\sin\theta\mathbf{e}_\theta\right], \tag{3b}$$

$$\mathbf{u}_4=C_4(1/r^2)\left[-(11/6)(1-3\cos^2\theta)\mathbf{e}_r-\cos\theta\sin\theta\mathbf{e}_\theta\right], \tag{3c}$$

[15] A. E. H. Love, *The Mathematical Theory of Elasticity* (Dover Publications, Inc., New York, 1944), p. 249.

where the approximation $\lambda=2\mu$, values applicable to copper, has been made in $\mathbf{u}_4$. The term $\mathbf{u}_2$ has cubic symmetry, while $\mathbf{u}_3$ and $\mathbf{u}_4$ have cylindrical symmetry. Activation energies and region-I configurations were found to be insensitive to all terms except $\mathbf{u}_1$, so that in later calculations all other terms were neglected. The effect of $\mathbf{u}_1$ on the energy and the region-I configuration was relatively minor, but this term was retained since it can be used to find activation volumes. In the cases where two defects are in close proximity, region I consisted of the union of the two individual region I's. A $\mathbf{u}_1$ elastic term was centered at each defect, and the total displacement vector in the elastic region was the vector sum of the displacements from the two terms.

The interaction energy between two nearest-neighbor atoms i and j, a distance r_{ij} apart, was assumed to be a Born-Mayer repulsive potential with the form

$$\varphi_{ij}=A\exp[-\alpha(r_{ij}-r_0)/r_0], \tag{4}$$

where $A=0.053$ eV, $\alpha=13.9$, and r_0 is the perfect-lattice nearest-neighbor separation distance. Huntington[1,2] and Seitz[1] discuss the use of this potential, and the above values are taken from Huntington[2] as being applicable to copper. A further discussion may be found in Gibson *et al.*[10] who use the values $A=0.051$ eV, and $\alpha=13.0$. The present results were not found to be very sensitive to the choice of these parameters. The term "nearest neighbor" becomes ambiguous in a region where the periodicity of the lattice is lost. Care was exercised to insure that all bonds that gave an appreciable contribution to the energy were considered in each case. The cutoff distance for the interaction was normally taken to be about 1.7 or 1.8 half-lattice constants. In a face-centered cubic lattice, the nearest-neighbor distance is $\sqrt{2}$ half-lattice constants, and the next-nearest-neighbor distance is 2 half-lattice constants. The results were not found to be sensitive to the exact cutoff distance.

The force on atom i is given by

$$\begin{aligned}\mathbf{F}_i&=-(\partial E/\partial\mathbf{r}_i)\\&=-(\alpha/r_0)\textstyle\sum_j\varphi_{ij}\mathbf{r}_{ij}/r_{ij},\end{aligned} \tag{5}$$

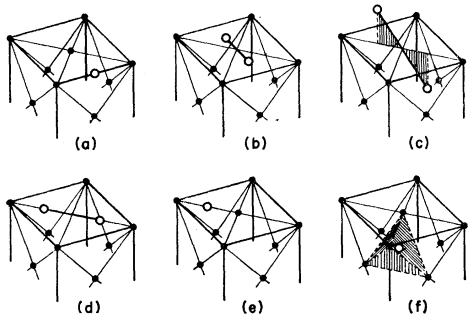


FIG. 1. Interstitial equilibrium configurations required by symmetry: (a) I_1, body-centered interstitial; (b) I_2, 100 split, or stable interstitial; (c) I_3, 111 split interstitial; (d) I_4, 110 split interstitial, or crowdion; (e) I_5, activated crowdion; and (f) I_6, tetrahedral interstitial.

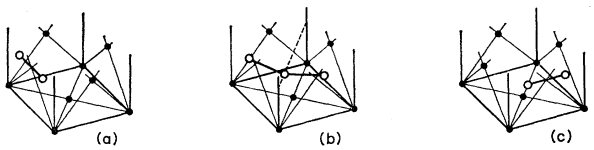


FIG. 2. The migration path for interstitials: (a) stable interstitial; (b) I_7, saddle-point configuration for migration; and (c) stable interstitial with axis perpendicular to the axis in (a).

where $\mathbf{r}_{ij}=\mathbf{r}_j-\mathbf{r}_i$, and atoms j are the nearest neighbors to atom i. The "force" on C_k is given by

$$\begin{aligned}F(C_k)&=-\partial E/\partial C_k\\&=(1/C_k)\textstyle\sum_i\mathbf{F}_i\cdot\mathbf{u}_k(\mathbf{r}_i),\end{aligned} \tag{6}$$

where atoms i are atoms in regions II and III. When an elastic continuum is displaced in accordance with solutions of the static elastic equation, each point remains in equilibrium. If elastic theory held exactly in our model, each atom in region III would always be in equilibrium, since it interacts only with atoms in the elastic region. Thus one would have $F_i=0$ for atoms i in region III. Elastic theory is sufficiently good that one can take this as an approximation, and thus have

$$F(C_k)=(1/C_k)\textstyle\sum_i\mathbf{F}_i\cdot\mathbf{u}_k(\mathbf{r}_i); \tag{7}$$

atoms i are in region II.

The process for finding energy minima and saddle points was as follows. Initial vector positions of each atom in region I and values of the elastic variables were chosen to be near a configuration of interest. Each coordinate of each atom in region I was varied in turn until the corresponding force component became zero. Then the value of C_1 was changed so that $F(C_1)$ was zero, and the same process repeated for all the elastic variables. Usually 10 to 20 such iterations were required for the energy and the configuration to converge sufficiently. For small displacements, both the position variables and the elastic variables are very nearly linear. Thus it is possible to find the force for a given variable at two positions and use linear extrapolation to the position where the force is zero.

Energy is calculated after each iteration using the formula

$$E=\textstyle\sum_a\varphi_{ij}-NA+\sum_bW_{ij}, \tag{8}$$

where the a summation is over bonds lying completely within regions I and II, N is the number of perfect lattice bonds included in this region before it was perturbed, and the b summation is over region II-region III bonds. The first two terms give the additional interaction energy within regions I and II, and the third term gives the work done by atoms in region II on atoms in region III. W_{ij} is found as follows:

$$dW_{ij}=-\mathbf{F}_{ij}\cdot d\mathbf{r}_i,$$

$$W_{ij}\approx\frac{\alpha A}{2r_0}\left[1+\exp\left(-\alpha\frac{r_{ij}-r_0}{r_0}\right)\right]\frac{\mathbf{r}_{ij,0}}{r_{ij,0}}\cdot(\mathbf{r}_i-\mathbf{r}_{i,0}).$$

In the above, the average value of $\mathbf{F}_{ij}$ was used, and the approximation made that $(\mathbf{r}_{ij}/r_{ij})\cdot(\mathbf{r}_i-\mathbf{r}_{i,0})=(\mathbf{r}_{ij,0}/r_{ij,0})\cdot(\mathbf{r}_i-\mathbf{r}_{i,0})$.

The elastic constraints implicitly provide a "pressure" which holds the lattice together against the repulsive Born-Mayer forces. This corresponds to the volume-dependent binding energy of the valence electrons, but does not take the details of the electronics energy into account.

Let $\Delta V'$ be the volume expansion of a hypothetical sphere around the defect.

$$\Delta V'=\int\int \mathbf{u}_1\cdot d\mathbf{S}$$
$$=2\pi C_1\Omega,$$

where Ω is the volume per atom in the perfect lattice. $\Delta V'$ is independent of the radius of the sphere. For a finite lattice, Eshelby[16] has shown that the boundary condition of zero stress at the surface of the lattice gives rise to an additional term in the volume expansion (the "image force" correction), which yields

$$\Delta V=\Delta V'[1+4\,\mu/(3\lambda+2\,\mu)].$$

For copper, $\lambda\approx 2\,\mu$, and thus

$$\Delta V=\tfrac{3}{2}\Delta V'$$
$$=3\pi C_1\Omega. \qquad (10)$$

RESULTS

There are six interstitial configurations which must be equilibrium configurations because of symmetry, only one of which is stable. They are denoted by the symbols I_1, I_2, $\cdots$ I_6, and are described as follows: I_1 (body-centered interstitial), one atom is located in the body center of a face-centered cubic cell [Fig. 1(a)]; I_2 (100 split interstitial), two atoms are symmetrically split in the ⟨100⟩ direction about a vacant normal lattice site [Fig. 1(b)]; I_3 (111 split interstitial), two atoms are symmetrically split in the ⟨111⟩ direction about a vacant normal lattice site [Fig. 1(c)]; I_4 (crowdion or 110 split interstitial), two atoms are symmetrically split in the ⟨110⟩ direction about a vacant normal lattice site [Fig. 1(d)]; I_5 (activated crowdion), one atom is located directly between two normal lattice sites [Fig. 1(e)]; and I_6 (tetrahedral interstitial) one atom is located at the center of the tetrahedron formed by four nearest-neighbor lattice sites [Fig. 1(f)]. In the three "split" cases, the atoms are approximately 1.2 a (a=half-lattice constant) apart. Our model gives rise to a number of additional equilibrium configurations. I_7 corresponds to an atom in the ⟨110⟩ direction from a body-centered position at a distance of 0.22 a from it [Fig. 2(b)], and I_8 to an atom in the ⟨111⟩ direction from a body-centered position at a distance of 0.17 a from it. There are many equivalent locations for the given sites. For the eight listed above, there are 42 equilibrium sites per atomic volume.

The 100 split interstitial I_2 was found to be the only stable configuration, and I_7 was found to be the energy saddle-point for migration of interstitials (see Table I). Gibson *et al.*[10] concur with this result. The predicted

TABLE I. List of equilibrium configurations. ΔV is given in units of Ω, the volume per atom of the perfect lattice.

	E (eV)	E above I_2 (eV)	C_1	ΔV (Ω)
I_1	4.223	0.084	0.261	2.46
I_2	4.139	0.000	0.233	2.20
I_3	4.613	0.474	0.259	2.44
I_4	4.588	0.449	0.252	2.37
I_5	4.840	0.701	0.273	2.57
I_6	4.729	0.590	0.274	2.58
I_7	4.186	0.047	0.232	2.19
I_8	4.212	0.073	0.246	2.32
V_1	−0.740		−0.051	−0.48
V_2	−0.313		−0.024	−0.23
DV_1	−1.527		−0.052, −0.052	
DI_1	7.675		0.225, 0.225	
DI_2	7.935		0.241, 0.241	

TABLE II. Defect migration

	Process	Activation energy (eV)	Activation volume
Vacancies	$V_1\rightarrow V_2\rightarrow V_1$	0.43	0.25Ω
Interstitials	$I_2\rightarrow I_7\rightarrow I_2$	0.05	−0.01Ω

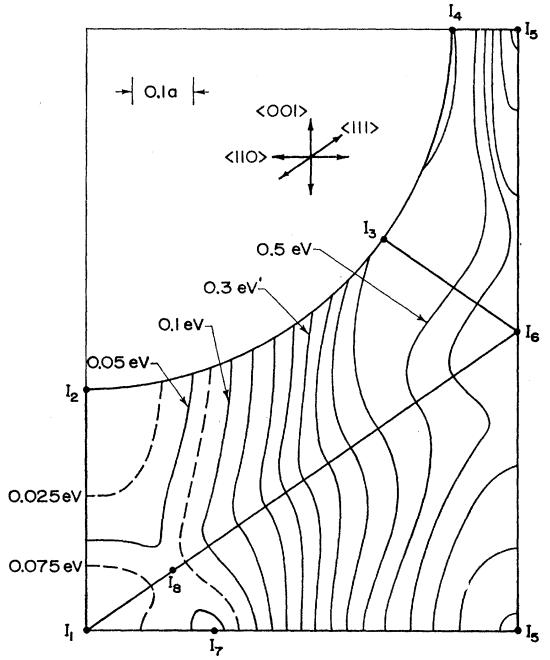


FIG. 3. Energy contours in a {110} plane passing through the body center.

[16] J. D. Eshelby, J. Appl. Phys. **25**, 255 (1954).

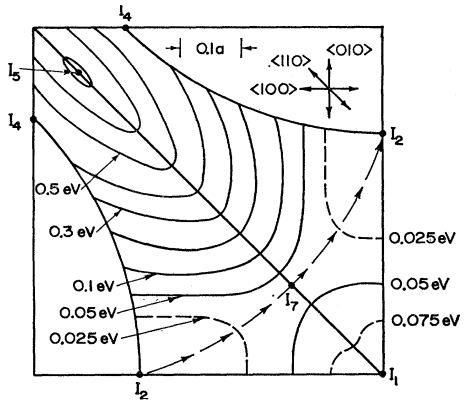


FIG. 4. Energy contours in a {100} plane passing through the body center.

activation energy for migration of interstitials is 0.05 eV, and the activation volume is negligible (Table II). The numerical results are listed in Table I. All these results were obtained using only $\mathbf{u}_1$ in the elastic regions. The variations caused by using other elastic terms and making other checks on the model will be discussed later. None of the results are significantly altered. The values of E listed in Table I are not formation energies, as no surface effects are considered. The differences in energy are the physically important values.

It was necessary to check for the possible existence of other equilibrium configurations. To accomplish this, configurations were defined by three coordinates and a three-dimensional plot was made of crystal energy vs configuration. In order to define the configurations by only three coordinates, the following two assumptions were made: (1) No two atoms approach closer than about 1.2 a; and (2) there is always one atom within a radius of 0.6 a from each normal lattice site. These assumptions have been fulfilled in each of our equilibrium configurations. The first is reasonable in view of the sharp increase in the Born-Mayer energy as distance decreases, and the second is reasonable in that too roomy a region would remain if it were not so. Space is divided into two regions; one includes the space inside spheres of radii 0.6 a about each lattice site, and the other includes the remainder of space. There is always one and only one atom in the latter region, which atom is called the interstitial. Thus, if the remaining atoms are at equilibrium positions consistent with the interstitial position, the crystal energy may be considered as a function of just the interstitial coordinates. If two atoms are on opposite ends of a sphere diagonal, each is considered half in and half out of the sphere. These are the "split" configurations. It is only necessary to consider energy contours outside the spheres, since if an interstitial enters a sphere, the atom which had been in that sphere leaves on the opposite side and becomes the interstitial. Although the computer was programmed to yield only equilibrium configurations and energies, it was possible to get estimates of energies for certain other configurations. The computer supplied the energy and configuration after each iteration, and after several iterations it was found that the convergence was smoothly monotonic for both energy and configuration coordinates. If a run was started far from equilibrium, after the first few iterations the configuration slowly stepped towards equilibrium, and the energy at each step was taken as an approximation to that which would be found if the interstitial were constrained at that position and the remaining atoms allowed to relax.

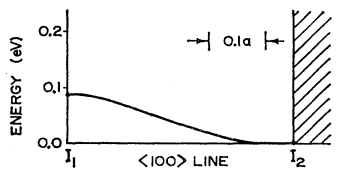


FIG. 5. Energy vs displacement along a ⟨100⟩ line passing through the body center. The curve is symmetric at I_1. The split configurations exist in pairs, so that the I_2 shown implies a complementary I_2 1.2a to the right of it.

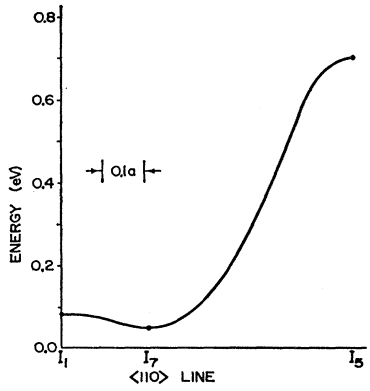


FIG. 6. Energy vs displacement along a ⟨110⟩ line passing through the body center. The curve is symmetric at I_1 and I_5.

The energy contours were found by interpolation and by symmetry considerations (e.g., the contours must be perpendicular to most axes of symmetry, must have threefold symmetry about the [111] axis, etc.). Although these contours are not to be taken as accurate, the general topological features would not be changed by small errors. They were plotted on clear plastic sheets which were then stacked, yielding an excellent three-dimensional picture. Unfortunately this model does not show up very well in two dimensions. The two most important planes are shown in Fig. 3 and Fig. 4. Figure 3, the {110} plane, contains all eight of the labeled points, and also a few of the less important points, but does not show the interstitial migration path. Figure 4, the {100} plane, shows the migration path, which is also seen pictorially in Fig. 2. Figures 5 through 8 are plots of the energy as one moves along certain symmetry lines. As mentioned, I_2, the 100 split interstitial, is the only minimum. I_1, the body-centered interstitial, is a local maximum; I_6, the tetrahedral interstitial is just barely a local maximum; and I_5, the

activated crowdion, is the maximum. I_3, I_4, I_7, I_8, and all others are saddle points. I_7 and I_8 are clearly shown to exist by the calculations. Other saddle points, which have not been labeled, exist by at most a few thousandths of an eV, and are not sharply defined by the calculation.

The vacancy problem does not contain the complexity of the interstitial. V_1 is the case where one atom is missing from a normal lattice site, and V_2 is the case where two atoms are missing from neighboring normal lattice sites, and an atom is located midway between these sites. As expected, the results of our calculations show that V_1 is the stable configuration, and V_2 is the saddle-point configuration for migration of vacancies (Table I). Only $\mathbf{u}_1$ was used in the elastic regions. The predicted activation energy for migration of vacancies is 0.43 eV, and the activation volume is one fourth of an atomic volume (Table II).

The surface effects cancel in forming a separated Frenkel pair, so that the formation energy for a Frenkel pair E_{Fp} is found by adding the stable configuration

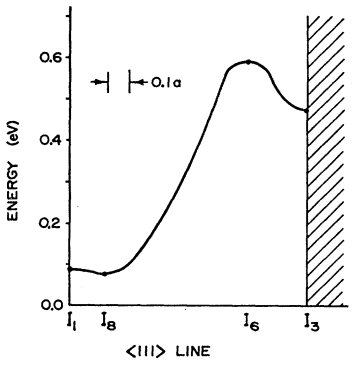


FIG. 7. Energy vs displacement along a ⟨111⟩ line passing through the body center. The curve is symmetric at I_1. The split configurations exist in pairs, so that the I_3 shown implies a complementary I_2 1.2a to the right of it.

energies $E(V_1)$ and $E(I_2)$;

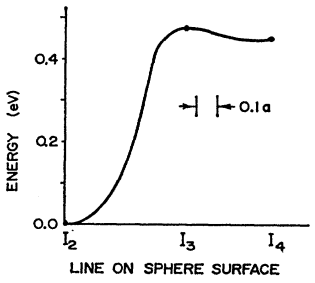
$$E_{\mathrm{Fp}}=3.40 \text{ eV}; \quad \Delta V=1.72\Omega.$$

The interaction of the elastic terms, which arises from the image force correction,[17] has been neglected.

A di-vacancy and two di-interstitial configurations have also been run, the results being listed in Table I. The di-vacancy considered is that of two neighboring lattice sites being vacant. The energy and volume change are very close to those for two separated vacancies. The first di-interstitial, DI_1, is the case where two 100 split interstitials are centered at neighboring lattice sites, such that if they are both split in the [100] direction, the line joining their centers is in the [011] direction [Fig. 9(a)]. DI_2 is the case where two interstitials are at neighboring body-centered sites [Fig. 9(b)]. DI_1 is lower in energy by 0.26 eV than

[17] J. D. Eshelby, Acta. Met. 3, 487 (1955).

FIG. 8. Energy vs distance along the line of intersection of a {110} lattice plane and the surface of the sphere which defines the split configurations.



DI_2. This should be an upper bound to the activation energy for migration of di-interstitials. Also, the di-interstitial binding energy (the energy difference between a di-interstitial and two separated single interstitials) was found to be 0.6 eV. The di-interstitial configurations were roughly a superposition of two single interstitial configurations (this was also found for close Frenkel pairs). A $\mathbf{u}_1$ elastic term was centered at each defect in both the di-vacancy and di-interstitial cases.

CHECKS ON THE MODEL

Since the model on which these calculations were based is not necessarily reliable, it was considered advisable to explore the sensitivity of the results to various changes. The following items were checked: (1) parameters in the Born-Mayer interaction, (2) use of elastic approximations, and (3) size of region I. In addition, a check on the consistency of the energy calculation was made.

The parameters used in the Born-Mayer potential were taken from Huntington[2] as being applicable to copper. A discussion of the use of this potential has also been given by Gibson *et al.*[10] Tewordt[5] performed his calculations with two sets of parameters, one of which is that given by Huntington. Bennemann[11] used the same potential, and also a Morse potential.

The sensitivity of the model to the choice of parameters was checked by calculating the activation energy for migration of vacancies for several different values. The results are shown in Fig. 10, where lines of constant energy are plotted as a function of A and α. The dashed line is the locus of values which give the correct compressibility. The energy and the volume expansion for a given case are rather sensitive to the choice of parameters though, as may be seen in Table III.[18] All three

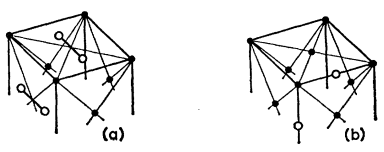


FIG. 9. Two equilibrium di-interstitial configurations. The (a) configuration may be stable, while (b) is a possible saddle-point configuration for migration.

[18] The numerical results in Table III are in slight disagreement with those in Table I. The parameter dependence runs were not

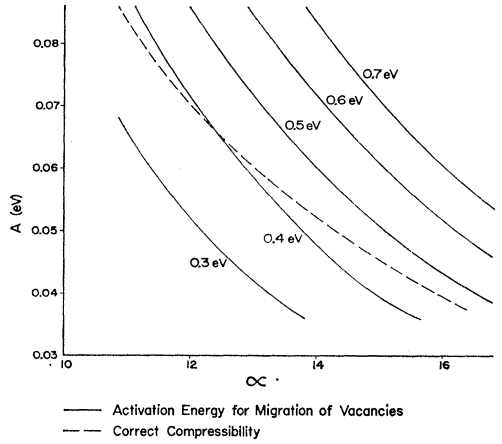


FIG. 10. Loci of values of A and α which give the same activation energy for migration of vacancies. The dashed line shows the values which give the correct compressibility.

sets of A and α in Table III give the correct compressibility.

The cutoff distance for the Born-Mayer potential does not seem to be of importance. This was found to be so in numerous cases when the energy contours were being investigated, but the best example is I_1, the body-centered interstitial. It is only necessary to allow the interstitial to interact with its six nearest neighbors, the face centers of an elementary cell. The cell corners move inward toward the body center just a little, and so that interaction distance is less than $\sqrt{3}a$. Including these eight interactions causes a negligible change in energy and configuration. More interactions than necessary were normally used throughout the calculations.

The body-centered interstitial was originally run with $\mathbf{u}_1$ and $\mathbf{u}_2$, as was done in Tewordt's work.[5] After convergence, C_2 was set equal to zero and the energy was recalculated. This gave a rise of only 0.006 eV, even though no further relaxation was allowed. A similar check with I_2, the 100 split (stable) interstitial, was made with corresponding results. It was also found that $\mathbf{u}_3$ and $\mathbf{u}_4$ were of negligible importance, i.e., there was very little tendency toward spheroidal deformation in this case, and what little was found was oblate rather than prolate. As is shown by Huntington and Johnson,[19]

TABLE III. Parameter dependence.

A (eV)	α	$E(V_1)$ (eV)	$C_1(V_1)$	$E(V_2)$ (eV)	$C_1(V_2)$
0.086	10.9	−1.21	−0.06	−0.83	−0.04
0.053	13.9	−0.74	−0.05	−0.30	−0.02
0.036	16.9	−0.50	−0.04	−0.03	−0.00

made with as full generality as the Table I runs, and their convergence was not as good. Thus, Table III should be used for parameter dependence only.

[19] H. B. Huntington and R. A. Johnson, Acta. Met. **10**, 15 (1962).

this deformation would be rather difficult to detect experimentally.

Calculations were made in which no elastic deformations were allowed, i.e. region I was relaxed as before, but the remainder of the crystal was frozen in its perfect lattice configuration. This was done for I_1, I_2, I_7, V_1, and V_2, and raised the energies by 0.114, 0.093, 0.091, 0.004, and 0.001 eV, respectively. It is seen that over-all energy changes are rather small, and the changes in the energy differences are very small. That such a major change in the elastic constraints gives rise to a relatively minor change in energies indicates that these calculations are rather insensitive to what manner of elastic constraints are used.

On the average, region I contained about 90 atoms, and region II contained about 150 atoms. To check the effect of the size of region I, a run was made in which the elastic constraints were taken off the region-II atoms and they were allowed to relax in the same manner as region-I atoms. This resulted in a decrease in energy of 0.009 eV, and a correspondingly minor change in the configuration.

A 100 split interstitial case was run in which 145 region-III atoms were added to the region-II atoms in the sum for finding $F(C_1)$ in Eq. (7). The resulting decrease in energy was less than one thousandth of an electron volt, and the change in C_1 was also negligible. This result does not necessarily justify the approximation in going from Eq. (6) to Eq. (7), but if the change was not negligible, then the approximation would not be good. This does indicate that the $1/r^2$ dependence of $\mathbf{u}_1$ is satisfactory.

As is seen from Eq. (8), the work term is normally obtained by an integration over the region-II, region-III boundary, i.e., normally the interaction energy is explicitly summed for about 240 atoms. To check if the energy calculation is sensitive to the radius at which the integration is carried out, a series of energies were computed at different radii and for different values of C_1. All atoms (except one at the origin) were displaced in accordance with a $\mathbf{u}_1$ elastic term. Then the energy was calculated for a number of different sizes of region I.

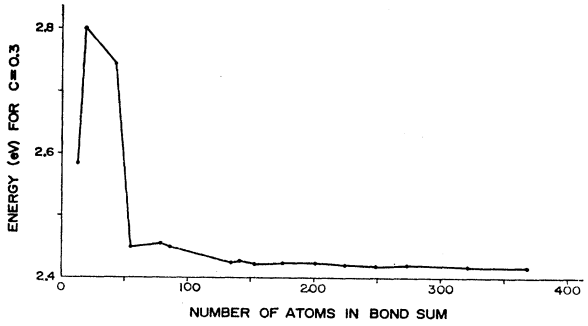


FIG. 11. Dependence of the calculated energy on the number of atoms explicitly included in the bond summation. For the case shown, the whole lattice was distorted by a $\mathbf{u}_1$ elastic term with $C_1=0.3$.

A plot of the energy as a function of number of atoms in the bond sum is given in Fig. 11 for the case of $C_1=0.3$. The amount of fluctuation with radius increases rapidly with increasing C_1, and C_1 has never been as large as 0.3 in an actual case. It can be seen that if less than about 50 atoms are in the bond sum, the energy calculation is not very accurate. From there on out it is quite good, and at 240 atoms it is fully satisfactory.

The energy calculation may be considered from a slightly different point of view. The energy is the sum of three terms: the bond energy within a given radius, the work done against the cohesive forces holding the perfect crystal together, and the energy stored in the elastic field outside the given radius. The second term is linear in C_1, and the third term is quadratic. The second term was calculated in two different ways; by a detailed computation of the coefficient required such that the change in energy with C_1 is zero when evaluated at the perfect lattice configuration, and by calculating the pressure from the change in bond energy density as the volume is changed, and taking the work as $P\Delta V'$ (the image force correction does not apply here). Both methods give the value of the linear coefficient as 9.25. The energy stored in the elastic field is calculated by standard elastic theory[20] and is found to give a small contribution of the order of 0.02 eV. The quadratic coefficient is 0.37. The bond energy here is computed differently from that of Eq. (8). In Eq. (8) the sum is over bonds lying completely within regions I and II. In this case one-half the energy in the bonds between regions II and III must also be added, as these bonds lie (on the average) half in region II and half in region III. When carried out on a test case, this method yielded results which differ by only 0.005 eV from those previously obtained.

COMPARISON WITH OTHER CALCULATIONS

A number of calculations have been made for some of the configurations considered in this paper.[2–11] The models used for each of these calculations differ in many respects, and it is not always possible to find the sources of any discrepancy. In several cases, however, the models are sufficiently similar so that comparisons can be made.

The model used in the present paper is essentially the one originally presented by Tewordt,[5] so that a direct comparison should be possible. The only essential difference is that Tewordt included a term to take into account the redistribution of electrons around the defect. Bennemann's calculation[11] is also based on the same model. The model of Gibson *et al.*[10] differs from ours only in that the elastic region is replaced by a boundary of compressed springs. Also included, for comparison purposes, is the work of Huntington[2] who used a small region **I**, and did not consider elastic contributions.

The comparison of results is given in Table IV. The differences between our results and those of Tewordt were traced to the fact that he did not include the term which is linear in C_1 (which accounts for the work done against the cohesive forces of the electrons). This apparently is an inconsistency in his treatment since this term is needed in order to make the energy calculation consistent with the force model he used. In particular, the absence of this term would imply that region I would bulge out even in the absence of a defect. The energy for this term may be estimated from the volume expansion reported by Tewordt, and if this is used to replace the electronic redistribution energy he used, the results are in substantial agreement with ours. Bennemann's energy calculation also does not include work done against cohesive forces, does not include an electronic term, but does include a surface term. He used different elastic terms than we did, and thus it is difficult to obtain a good approximation for the work done against cohesive forces from his volume expansion. Such a correction would raise his energy and would appear to bring it well above ours. Gibson *et al.* do consider work done against cohesive forces, and the spring constant they use at the surface of their crystallite is based on a $\mathbf{u}_1$-type expansion. Here we would expect good agreement with our results, but, as may be seen in Table IV, their energies are considerably lower than ours. The cause for this difference has not been found.

Note added in proof. An I_2 configuration was run using the Gibson *et al.* parameters in our program. This removed about 80% of the energy discrepancy, leaving 0.14 eV. As shown earlier, energy values, but not energy differences, are quite sensitive to the choice of parameters.

Gibson *et al.*, Bennemann, and the present report all give the energy difference between the 100 split and the body-centered interstitials as 0.1 eV, with the 100 split being lower. Gibson *et al.* first considered the I_7 configuration, and found its energy to be about 0.05 eV above the 100 split interstitial energy. Thus our energy differences agree well with theirs. Bennemann reports the 111 split interstitial as 0.550 eV above the 100 split,

TABLE IV. Comparison of results, in eV.

	Huntington[a]	Tewordt[b]	Tewordt[c]	Gibson *et al.*[d]	Bennemann[e]	Present
$E(I_2)$	4.43			3.39	3.584	4.139
$E(I_1)$	4.34	2.5	4.1	3.49		4.223
$E(I_3)$					4.098	4.613
$E(I_4)$		3.2	4.8			4.588

[a] See reference 2.
[b] See reference 5.
[c] Altered as discussed in the text.
[d] See reference 10.
[e] See reference 11.

[20] H. B. Huntington, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1958), Vol. 7.

whereas we find 0.474 eV for this. Also he finds the 111 split interstitial to be stable by 0.3 eV. Our calculations show no indication of such a situation. Meechan *et al.*[21] have postulated two types of interstitials with different activation energies to account for annealing data for irradiated copper. Thus, the question of whether there are metastable sites is of physical interest. For the configuration in question we find that the energy decreases rapidly as a 111 split is rotated towards a 100 split configuration, as is seen in Fig. 8. It is not likely that the discrepancy in the theoretical results can be attributed to differences in the models as they are much too similar.

DISCUSSION AND CONCLUSIONS

No attempt was made in this paper to treat the energy term arising from electronic redistribution around the defect. Although there have been calculations for this contribution based on simple models,[22] we prefer to regard this as an uncertainty in the calculation. It does not seem likely that this term will shift the configurations very drastically. This follows from the hardness of the Born-Mayer interaction. If this is the case, it may then be possible to take the configurations that have been obtained so far, and treat the electronic term merely as an energy correction. The magnitude of this correction will, in all likelihood, be dependent on the symmetry type of the defect, tending to raise the energy least for the most symmetrical defects. Thus it is possible that the body-centered interstitial may be shifted sufficiently to become the stable configuration. At present no very reliable theoretical estimate of this energy shift is available as all approximations are based on spherical symmetry.

In spite of the above uncertainty in the energies, some conclusions seem justified. For the case of vacancies, the electronic term will almost certainly raise the energy of the stable configuration less than that of the activated one. Thus, a proper theoretical value for the activation energy for vacancy motion will be larger than the present value of 0.43 eV. If the experimental value for this energy is taken as 0.88 eV,[23] we then have a rough calibration of the electronic redistribution term which may be used in clarifying the situation in regard to the interstitial. Certain general features of the single interstitial case are sufficiently pronounced that it seems doubtful that they will be altered by this correction. The energy of interstitials in the vicinity of the body center, including I_1, I_2, I_7, and I_8, is considerably lower that that for the remaining configurations. Within this region it is seen that it would not take a very great perturbation to rearrange the order of the configurations, perhaps even eliminating I_7 and/or I_8. Because of the steepness of the slope of the energy leading from other configurations to this region, it seems improbable that addition of the redistribution energy would cause the stable configuration or its activated configuration for motion to leave it. The possibility of a metastable configuration is not definitely ruled out, but the existence of another migration channel seems unlikely. Also, it seems doubtful that such changes could lead to the situation where the activation energy for motion of interstitials would be raised higher than that for motion of vacancies.

It was hoped that this method could be simply and quickly adapted to silver and gold, but unfortunately the Born-Mayer potential does not fit these metals at all well. A discussion of this point has been given by Neighbours and Alers.[24]

ACKNOWLEDGMENTS

We wish to thank Professor H. B. Huntington for many rewarding conversations and suggestions during the course of this work. We are also grateful to Dr. G. H. Vineyard for discussions during the project, and to Dr. J. W. Corbett for reading the manuscript and suggesting improvements. Thanks are due the Rensselaer Polytechnic Institute Computer Laboratory and the AEC Computing Center at New York University for their help and cooperation in performing the calculations.

[21] C. J. Meechan, A. Sosin, and J. A. Brinkman, Phys. Rev. **120**, 411 (1960).
[22] F. G. Fumi, Phil. Mag. **46**, 1007 (1955).
[23] R. O. Simmons and R. W. Balluffi, Bull. Am. Phys. Soc. **7**, 233 (1962). We thank the authors for sending us their results prior to publication.
[24] J. R. Neighbours and G. A. Alers, Phys. Rev. **111**, 707 (1958)