Distortion of the Lattice around an Interstitial, a Crowdion, and a Vacancy in Copper*

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A general method for calculating lattice distortions around point defects is proposed. Atoms in a sufficiently large region I around the defect and in a "boundary" region II around region I are treated as discrete particles. A set of proper elastic solutions is joined to the displacements of the atoms in region II. The equilibrium state of the lattice is determined by successive solution of sets of linear algebraic equations. Actual calculations have been done with the help of the Illiac digital computer for an interstitial, a crowdion, and a vacancy in copper. The changes in volume of the crystal arising from these defects are found to be 1.7, 1.1, −0.53 and 2.0, 1.3, −0.45 atomic volumes respectively for the two Born-Mayer repulsive potentials we have used. [See Eqs. (7).] In addition to the distortion of the lattice around an isolated defect, we treat the distortion around an interstitial-vacancy pair. The electronic contributions to the formation energies of the defects considered are estimated in a way similar to that used by Fumi in the case of a vacancy. However, the change in the effective charge of the defect with lattice dilatation is also taken into account. The formation energy of a crowdion is found to be about 0.6 ev higher than that of an interstitial. The calculated values of the change in volume are discussed in connection with recent experimental results on radiation damage in copper.

I. INTRODUCTION

THE nature of the lattice defects produced in noble metals during radiation-damage experiments at low temperatures is still an open question.[1] At least in the case of irradiation with electrons it is supposed that interstitial atoms and lattice vacancies are produced rather than larger defects such as supercooled displacement spikes. The following questions arise: Where are the interstitial atoms located in the lattice and how has the lattice relaxed? Is there a unique interstitial configuration with a formation energy markedly lower than other equilibrium configurations or are there several configurations (perhaps rather a continuum) with nearly the same energy of formation?

In this paper we treat particularly the distortion of the face-centered-cubic (f.c.c.) copper lattice and determine the change in volume of the crystal for two particular hypothetical models of an interstitial and for a vacant lattice site. The first interstitial model to be considered was introduced by Huntington and Seitz[2]; it is called "B" in their papers and simply "interstitial" here. In this configuration the interstitial atom lies at the center of an elementary cube of the f.c.c. lattice. The second model is the "crowdion" first proposed by Paneth,[3] where the interstitial atom lies in a closest packed row of the lattice.

Knowing the change in volume caused by one Frenkel pair (vacancy plus interstitial) when the interstitial is in one of the assumed configurations, one can determine the resistivity $\Delta\rho$ associated with one atomic percent of Frenkel pairs from the experimental values for the change in volume and increase in resistivity of an irradiated specimen. On the other hand, $\Delta\rho$ may be obtained by using the simple theory of displacement.[4] By comparing the two values thus obtained for $\Delta\rho$ with one another, it may be possible to decide whether one of the two proposed interstitial configurations actually occurs.

To the writer's knowledge the only calculations for crystal distortions due to defects which take into account the *atomic* structure of the crystal in the vicinity of the defect are those of Huntington,[5] Fues and Stumpf,[6] and Kanzaki.[7] Kanzaki's method is based *entirely* on the discrete nature of the lattice. His main point is the adoption of an expansion of the displacements, as in the dynamical theory, in normal coordinates. In the method developed by Fues and Stumpf the solution of the problem is reduced to the successive solution of systems of linear algebraic equations. The distortion of the lattice far from the defect is written as the superposition of displacement fields of point forces in the elastic continuum. These solutions are centered on several atoms near the defect. Huntington determines the distortion of the lattice around an interstitial atom in copper by treating atoms in the vicinity of the interstitial atom as discrete particles and by fitting proper elastic solutions to the atomic displacements.

The method proposed in this paper contains some features of the methods of Huntington and of Fues and Stumpf. The atoms in a sufficiently large region I around the defect and in a region II around region I are treated as discrete particles. A set of proper elastic solutions is joined to the displacements of the atoms in region II. The thickness of this "boundary" II between the nonelastically deformed region I and the elastically deformed continuum depends on the range of the atomic forces. The equilibrium state of the lattice is determined by successive solution of sets of linear algebraic equations. (The procedure for deriving these equations differs from that in reference 6.) At each step one calculates the displacements of the atoms from the

* Assisted by the Office of Naval Research.
[1] The present status of the entire topic is surveyed in an article by F. Seitz (to be published).
[2] H. B. Huntington and F. Seitz, Phys. Rev. **61**, 315 (1942).
[3] H. Paneth, Phys. Rev. **80**, 708 (1950).
[4] F. Seitz and J. S. Koehler, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press, Inc., New York, 1956), Vol. 2, p. 305.
[5] H. B. Huntington, Acta Meta. **2**, 554 (1954).
[6] E. Fues and H. Stumpf, Z. Naturforsch. **10a**, 136 (1955).
[7] H. Kanzaki, J. Phys. Chem. Solids **2**, 24 (1957).

"equilibrium positions" given in the previous step. In this way rapid convergence is attained. Application of the method to concrete problems is much less complicated and requires considerably less numerical effort than the methods of Kanzaki and of Fues and Stumpf.

In addition to the distortion of the lattice caused by an isolated interstitial, a crowdion, and a vacancy we treat the distortion around an interstitial-vacancy pair.

We also estimate the formation energies of the defects considered. The procedure is closely analogous to that used by Fumi[8] for the case of a vacancy. However, the effect of the lattice dilatation on the electron scattering is also taken into account.

II. GENERAL METHOD

Essentially this method for calculating lattice distortion around point defects involves a combination of the atomic with the continuum treatment of the crystal. Let the energy of the crystal disturbed by the defect be given by $U(\mathbf{v}_1, \mathbf{v}_2, \cdots)$, where the $\mathbf{v}_i$ are the displacements of the atoms from suitably chosen starting positions. The lattice relaxation is determined by minimizing U in a variational approach. The displacements from the original lattice positions of the atoms outside a sufficiently large region (called region I) around the defect are small and vary slowly from atom to atom. They correspond to an elastic solution $\mathbf{v}(\mathbf{r})$, where $\mathbf{v}$ is the displacement and $\mathbf{r}$ the position vector. By elastic solution we shall mean a solution of the elastic differential equations for the displacements. We expand $\mathbf{v}(\mathbf{r})$ in elastic solutions $\mathbf{u}_1(\mathbf{r}), \cdots, \mathbf{u}_n(\mathbf{r})$, which are members of a complete set, with coefficients $\gamma_1, \cdots, \gamma_n$:

$$\mathbf{v}(\mathbf{r})=\gamma_1\mathbf{u}_1(\mathbf{r})+\cdots+\gamma_n\mathbf{u}_n(\mathbf{r}). \quad (1)$$

Proper solutions $\mathbf{u}_\nu$ can be built, for example, from the derivatives of the fundamental integral of the elastic differential equations for the displacements. Then the $\mathbf{u}_\nu$ are displacement fields due to dipole, quadrupole, $\cdots$, forces centered on the point defect. Only solutions $\mathbf{u}_\nu$ which vary relatively slowly from atom to atom outside region I will be taken into account in the expansion (1). The number n of these solutions depends on the size chosen for region I and increases with increasing size of I.

Through relation (1) the crystal energy U becomes a function of the displacements $\mathbf{v}_1, \cdots, \mathbf{v}_j$ of the atoms $1, \cdots, j$ inside region I and of the coefficients $\gamma_1, \cdots, \gamma_n$ of the elastic solutions $\mathbf{u}_\nu$. Minimizing U with respect to these arguments leads to the conditions:

$$\frac{\partial U}{\partial \mathbf{v}_i}=0, \qquad (i=1, \cdots, j), \quad (2a)$$

$$\frac{\partial U}{\partial \gamma_m}=\frac{\partial U}{\partial \mathbf{v}_{j+1}}\cdot\mathbf{u}_m(\mathbf{r}_{j+1})+\frac{\partial U}{\partial \mathbf{v}_{j+2}}\cdot\mathbf{u}_m(\mathbf{r}_{j+2})+\cdots=0, \qquad (m=1, \cdots, n), \quad (2b)$$

[8] F. G. Fumi, Phil. Mag. 46, 1007 (1955).

where $j+1$, $j+2$, $\cdots$ denotes the atoms outside region I. In general the forces $-\partial U/\partial \mathbf{v}_\nu$ acting on the atoms depend on the positions of all the atoms in the crystal. In the case of a nonpolar crystal however it seems reasonable to assume that the effects of region I are negligibly small in a region sufficiently far from I. We denote this distant region by III and designate the boundary-region between I and III by II. With this assumption the atoms of region III are automatically in equilibrium for all elastic deformations of regions II and III, because all contributions to the forces acting upon atoms there arise from the elastically deformed regions. That is to say the forces $-\partial U/\partial \mathbf{v}_\nu$ in region III vanish. Therefore the infinite sum in Eq. (2b) reduces to a finite sum containing only terms associated with the atoms in region II.

Equations (2a), (2b) for the unknowns $\mathbf{v}_1, \cdots, \mathbf{v}_j$ and $\gamma_1, \cdots, \gamma_n$ can be reduced to a set of linear algebraic equations in these unknowns, if one approximates all forces $-\partial U/\partial \mathbf{v}_\nu$ by expressions containing only linear terms in the displacements. In the case of an interstitial atom in a noble metal the displacements of neighboring atoms from their original lattice positions are so large that an expansion of the corresponding exponential core repulsive forces in these displacements converges very slowly. This difficulty can be avoided by choosing starting positions, from which the displacements are calculated, different from the original lattice positions and which lie sufficiently near to the equilibrium positions. In an actual calculation proper starting positions can be obtained by trial.

The accuracy of the method is improved as the size of region I is increased. By successive solution of the systems of linear algebraic equations arising from Eqs. (2a), (2b), and (1) it is possible to determine the equilibrium positions of all atoms to any desired degree of accuracy, subject only to the limitations imposed by the size chosen for region I. At each stage the coefficients of the linear algebraic equations are calculated from the linear expansions of the forces $-\partial U/\partial \mathbf{v}_\nu$ in the displacements of the atoms from their "starting positions" obtained in the previous step as "equilibrium positions."

The main problem in determining lattice distortion is to find a sufficiently good approximation to the forces $-\partial U/\partial \mathbf{v}_\nu$ when expressed as functions of the lattice relaxation. Fortunately in the case of noble metals the overwhelming contributions to the forces

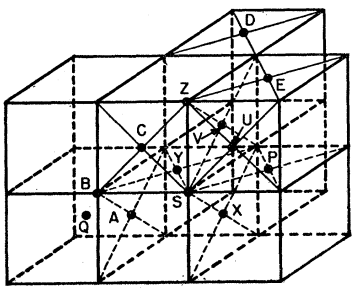

FIG. 1. Interstitial configuration in the face-centered-cubic lattice. Elementary cubes of the f.c.c. lattice are drawn. Q=interstitial atom. A, B, Y, S, X, V, C=atoms of region I. P, U, E, Z, D=atoms of region II.

probably arise from the repulsive interactions between adjacent closed-shell ions. In our actual calculations we take into account only these repulsive forces. Region II then contains only one layer of atoms. The stability of the lattice arises from the treatment of region III as an elastic continuum.

III. LATTICE DISTORTION DUE TO AN INTERSTITIAL AND A VACANCY

In Fig. 1 the f.c.c. lattice is shown with an interstitial atom Q in the "interstitial" configuration. The displacements of the lattice particles will have cubic symmetry with respect to the center Q and the axes parallel to the crystal axes. A number of typical atoms around the interstitial atom with nonequivalent displacements have been denoted by the letters A, B, Y, etc. (A, B, Y are first, second, third neighbors).

In the case of a noble metal the most important contributions to the forces arise from the repulsion between closed shells of adjacent ions. According to the Born-Mayer theory the repulsive potential between a pair of ions has the form,

$$V=V_0\exp[(r_0-r_{i\nu}')/\rho]. \tag{3}$$

V_0 and ρ are the constants of the potential, r_0 and $r_{i\nu}'$ are the distances between neighboring atoms i and ν in the undeformed and in the deformed crystal, respectively. As indicated in Sec. II we start from certain positions of the lattice particles, which are in general different from the original lattice positions. The radius vector from atom ν to atom i, both lying in their starting positions, is denoted by $\mathbf{r}_{i\nu}$. The displacements of the atoms are designated by $\mathbf{v}_i$ and $\mathbf{v}_\nu$ respectively. Therefore, $r_{i\nu}'$ in (3) is equal to

$$r_{i\nu}'=|\mathbf{r}_{i\nu}+\mathbf{v}_i-\mathbf{v}_\nu|=|\mathbf{r}_{i\nu}+\mathbf{v}_{i\nu}|, \tag{4}$$

with

$$\mathbf{v}_{i\nu}=\mathbf{v}_i-\mathbf{v}_\nu.$$

We expand the repulsive force $-\partial V/\partial\mathbf{r}_{i\nu}'$ upon atom i arising from atom ν in a Taylor series in $\mathbf{v}_{i\nu}$ and neglect terms involving quadratic or higher powers of $\mathbf{v}_{i\nu}$. Summing over all next-nearest neighbors ν of atom i, one obtains for the repulsive force $-\partial U_r/\partial\mathbf{v}_i$ acting upon atom i (U_r is the sum of the repulsive potentials),

$$-\frac{\partial U_r}{\partial\mathbf{v}_i}=\frac{V_0}{\rho}\sum_\nu\left\{\mathbf{e}_{i\nu}+[\mathbf{v}_{i\nu}'-\mathbf{e}_{i\nu}(\mathbf{e}_{i\nu}\cdot\mathbf{v}_{i\nu}')]-\mathbf{e}_{i\nu}(\mathbf{e}_{i\nu}\cdot\mathbf{v}_{i\nu}')\frac{r_{i\nu}}{\rho}\right\}\exp\left[\frac{1}{\rho}(r_0-r_{i\nu})\right], \tag{5}$$

with

$$\mathbf{e}_{i\nu}=\mathbf{r}_{i\nu}/r_{i\nu}\quad\text{and}\quad\mathbf{v}_{i\nu}'=\mathbf{v}_{i\nu}/r_{i\nu}.$$

For the potentials we use $r_{i\nu}$ is very much greater than ρ, so that we can neglect the second term in (5) in comparison with the third.

The elastic solutions are joined to the atoms P, U, E, Z, D, and the atoms equivalent to these. Equations (2a) need to be set up only for the nonequivalent atoms A, B, Y, X, S, V, and C of our region I, since consideration of other atoms yields no further independent equations. There are no repulsive forces from atoms of region I acting on the atoms outside P, $\cdots$, D in the elastic region. Therefore, by definition, they lie in region III, provided one neglects long-range effects arising from region I. Region II contains the atoms P, U, E, Z, D, and atoms equivalent to them. In setting up Eqs. (2b) with terms $(\partial U_r/\partial\mathbf{v}_\nu)\cdot\mathbf{u}_m(\mathbf{r}_\nu)$ one can make use of the fact that the scalar products are equal for equivalent atoms. There are 24 atoms of the type P, E, Z, D, and 48 of the type U.

Now we determine the elastic solutions $\mathbf{u}_\nu$ for our interstitial problem, assuming an isotropic elastic material. The general elastic solution can be represented as the sum of a gradient and a curl. Since we have full cubic symmetry the curl must vanish and the solution has the form gradψ, ψ having full cubic symmetry. In this case ψ must be a solution of Laplace's equation. Therefore ψ can be expanded in solutions with radial parts $r^{-(l+1)}$ and angular parts which are the Kubic Harmonics of type α and of order l given by Von der Lage and Bethe.[9] We use only the first two of these solutions. They are written in the form,

$$\begin{aligned}\mathbf{u}_1&=(a/2)^3\mathbf{r}/r^3,\\ \mathbf{u}_2&=(a/2)^7 10^2\,\mathrm{grad}\{(1/r)^5[(x^4+y^4+z^4)/r^4-\tfrac{3}{5}]\},\end{aligned} \tag{6}$$

where a is the lattice constant, and $\mathbf{r}$ is the radius vector from atom Q with length r and components x, y, z with respect to the cubic axes. By including solution $\mathbf{u}_2$ we can, for example, allow for the fact that atom E will be pushed outwards by a larger amount than atom P. With the factor 10^2 in $\mathbf{u}_2$, the displacements of atom P due to $\mathbf{u}_1$ and $\mathbf{u}_2$ have the same order of magnitude. The elastic solutions generated by the Kubic Harmonics of higher order cannot be used with our special choice of region I because they vary too rapidly from atom to atom outside region I.

We finally obtain from Eqs. (2a), (2b), together with Eqs. (1) and (5), a system of 13 linear algebraic equations with 13 unknowns, including the coefficients γ_1, γ_2 of the elastic solutions (6). The equilibrium state of the lattice is determined by iteration as described in Sec. II. The linear algebraic equations were solved on the Illiac. The results for copper shown in Table I refer to the two Born-Mayer potentials V_1 and V_2 [see formula (3)],

$$\begin{aligned}V_1&=0.053\exp[13.9(r_0-r_{i\nu}')/r_0]\text{ ev per ion pair},\\ V_2&=0.032\exp[17(r_0-r_{i\nu}')/r_0]\text{ ev per ion pair}.\end{aligned} \tag{7}$$

V_1 was proposed by Huntington[10] and V_2 by Huntington and Seitz.[2] (V_2 is given in the corrected form reported in reference 10.) The displacement vectors of the atoms A, B, Y, and V are designated by $(\alpha,0,0)$, $(b,-b,b)$,

[9] F. C. Von der Lage and H. A. Bethe, Phys. Rev. **71**, 612 (1947).

[10] H. B. Huntington, Phys. Rev. **91**, 1092 (1953).

TABLE I. Lattice distortion, volume change of the crystal, and formation energy for an interstitial, a vacancy, and a crowdion in copper. Results are given for Born-Mayer potentials V_1 and V_2 [Eqs. (7)]. In the first column are shown the results obtained by Huntington.[a] (Displacements of the atoms in units of $a/2$, where a is the lattice constant. Volume changes in units of $\Omega=a^3/4$=one atomic volume. All energies are in ev.)

		Interstitial				Vacancy			Crowdion	
		V_1	V_1	V_2		V_1	V_2		V_1	V_2
Components of displacements	α	0.210	0.246	0.257	λ	−0.023	−0.019	α'	0.599	0.605
	b		−0.013	−0.008	δ	−0.002	−0.002	y'	0.395	0.413
	y_1	0.052	0.048	0.053				x'	0.218	0.237
	y_3	0.052	0.052	0.057				c_1'	0.043	0.049
	v_1		0.017	0.020				c_3'	0.031	0.039
	v_3		0.016	0.018				z'	−0.041	−0.048
Coefficients of elastic solutions	γ_1	0.320	0.177	0.213	γ_1	−0.054	−0.046	γ_1'	0.354	0.416
	γ_2		0.072	0.105				γ_2'	0.046	0.047
								γ_3'	0.124	0.130
Total volume change Δv		3.01	1.67	2.01		−0.53	−0.45		1.10	1.25
Volume change $\Delta v'$		2.01	1.11	1.34		−0.35	−0.30		0.73	0.83
Closed-shell repulsive energy ΔU_r			2.3	2.1					3.6	3.4
Electron energy ΔE_{el}			0.2	0.5		0.9	1.0		−0.4	−0.2
Formation energy E_f			2.5	2.6		0.9	1.0		3.2	3.2

[a] See reference 5.

$(y_1,0,y_3)$, and $(v_1,0,v_3)$, with components referring to the cubic axes. The displacements of atoms X, S, C are not included in Table I; they are found to be quite different in direction and magnitude from displacements proportional to $\mathbf{u}_1$. For purposes of comparison the table contains the results obtained by Huntington[5] using repulsive potential V_1. Huntington's calculation differs from ours not only in the general procedure employed, but also in the following respects: He joins $\mathbf{u}_1$ to atoms X, S, V, C; higher order solutions than $\mathbf{u}_1$ are not considered; displacements of atoms B are neglected and the displacements of atoms Y are restricted to the directions given by the radii vectors from atoms A to Y.

Table I also contains the values of the change in volume of the crystal caused by an interstitial. These values are calculated from the coefficients γ_1 of the elastic solution $\mathbf{u}_1$ by using a formula due to Eshelby[11] which takes into account the effect of the image displacement field produced by the surface tractions,

$$\Delta v=2\pi\gamma_1\Omega[3(1-\nu)/(1+\nu)], \tag{8}$$

where ν is Poisson's ratio, $\Omega=a^3/4$ is one atomic volume in the f.c.c. lattice, and ν in copper is taken to be $\frac{1}{3}$. In addition to the total change in volume Δv the table contains the volume $\Delta v'=2\pi\gamma_1\Omega$ which is displaced through any closed surface, containing the defect, in an *infinite* matrix.

The change ΔU_r of the closed-shell repulsive energy given in Table I is measured relative to the repulsive energy of the regular lattice plus the "interstitial" atom lying at the surface. Only repulsive "bonds" of the atoms of region I were considered in calculating ΔU_r. The change in energy of the exterior of region I is determined by calculating the elastic energy from the elastic solutions. This contribution is found to be always smaller than 2.5% of ΔU_r.

The procedure for calculating the crystal distortion due to a lattice vacancy in copper is in close analogy to that used in the case of an interstitial. Region I is defined to include the first and second nearest neighbors of the vacant lattice site. The elastic solution $\mathbf{u}_1$ is joined to the next-nearest atoms to region I. The results are shown in Table I. The displacement vectors of a first and a second nearest neighbor lying in the positions $(1,1,0)a/2$ and $(2,0,0)a/2$ are represented by $(\lambda,\lambda,0)$ and $(\delta,0,0)$ respectively.

IV. LATTICE DISTORTION AROUND A CROWDION

We consider a crowdion lying in a closest packed (110)-row of the f.c.c. lattice. In Fig. 2 the atoms G', X', Y', A', A, Y, X, G lie along the axis of the crowdion, atom A', for example, being the extra atom. Atoms at the corners of rectangles centered on the

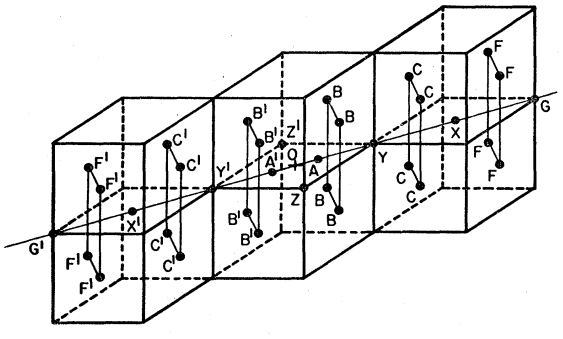

FIG. 2. Crowdion configuration in the face-centered-cubic lattice. Elementary cubes of the f.c.c. lattice are drawn. The axis through G' and G is the crowdion axis. 0=center of inversion. A, B, Y, X, C, Z and A', $\cdots$, Z'=atoms of region I. F, G, F', G', $\cdots$=atoms of region II.

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

crowdion axis and lying in (110)-planes are labeled F', C', B', B, C, F. The point O that was occupied by atom A before the interstitial atom A' was introduced, is a center of inversion in the deformed lattice. The lattice would also be in equilibrium if one put the extra atom A' at a point where the crowdion axis is cut by one of the rectangles drawn in Fig. 2. In this case the extra atom itself is a center of inversion. In general these two configurations will have different formation energies, one being the stable and the other the saddle-point configuration.

We have treated only the configuration shown in Fig. 2. The deformed lattice is invariant with respect to reflections in (110), ($\bar{1}10$), and (001)-planes passing through the point O. In our calculation region I was defined to include the atoms A, Y, X, B, C, Z, and atoms equivalent to them. Of the three elastic solutions which are joined to the next-nearest atoms to region I, two correspond to two "double forces without moment"[12] acting at the point O along the ($\bar{1}10$) and (001)-axes, respectively. (In a "double force" the distance between the points at which the two forces of opposite direction are applied is infinitely small.) The other elastic solution corresponds to two point forces in the directions (110) and ($\bar{1}10$) acting at the original lattice positions of atoms X and X', respectively. This solution is more appropriate than that corresponding to a *double force* at O in the (110)-direction, because the crowdion is much extended along its axis. Higher order elastic solutions corresponding to quadrupole, $\cdots$, forces are neglected. The elastic solutions for the two double forces in an isotropic elastic material,[12] designated by $\mathbf{u}_2'$ and $\mathbf{u}_3'$, are written in the form,

$$\mathbf{u}_\lambda'(\mathbf{r})=(a/2)^3(1/r)^2[2(1-2\nu)\cos\theta\mathbf{e}_\lambda + (3\cos^2\theta-1)\mathbf{r}/r]. \quad (9)$$

Here $\lambda=2, 3$. The quantities $\mathbf{e}_\lambda$ are the unit vectors in the directions ($\bar{1}10$) and (001), respectively. The quantity $\mathbf{r}$ is the radius vector from 0, θ is the angle between $\mathbf{r}$ and $\mathbf{e}_\lambda$, and ν is Poisson's ratio. The other elastic solution denoted by $\mathbf{u}_1'$ is the superposition of the solutions $\mathbf{u}(\mathbf{r})$ for the two point forces,[12] with

$$\mathbf{u}(\mathbf{r})=(a/2w)(a/2)^2(1/r)[(3-4\nu)\mathbf{e}+\cos\theta\mathbf{r}/r], \quad (10)$$

where $\mathbf{e}$ is the unit vector in the direction (110) and ($\bar{1}10$), respectively, and $\mathbf{r}$ is the radius vector from the original lattice position of atom X and X', respectively. The quantity θ is the angle between $\mathbf{r}$ and $\mathbf{e}$, and w is the distance between the original lattice positions of the atoms X and X'.

The lattice relaxation was again calculated in the way described in Sec. II. The number of linear algebraic equations is 13, the unknowns being the components of the displacements of the atoms A, Y, X, B, C, Z and the coefficients γ_1', γ_2', and γ_3' of the elastic solutions $\mathbf{u}_1'$, $\mathbf{u}_2'$, $\mathbf{u}_3'$. Results for potentials V_1 and V_2 obtained with the help of the ILLIAC are included in Table I. Only components of the displacements of atom A with respect to O and of atoms Y, X, C, and Z' with respect to their original lattice positions are shown. The displacement vectors are represented by (α',0,0), (y',0,0), (x',0,0), (c_1',c_2',c_3'), and (0,z',0), with components referring to axes in the (110), ($\bar{1}10$) and (001)-directions. At large distances from O the elastic solution $\mathbf{u}_1'$ corresponds to that of a double force at O in the direction (110). The factor $(a/2w)$ is introduced in Eq. (10) so that the coefficient γ_1' of $\mathbf{u}_1'$ can be compared directly with the coefficients γ_2' and γ_3' of the solutions $\mathbf{u}_2'$ and $\mathbf{u}_3'$ for double forces.

The change in volume of the crystal due to a crowdion depends both on the shape of the crystal and on the position of the crowdion in the crystal. The values for Δv and $\Delta v'$ shown in Table I refer to a crowdion lying at the center of a sphere whose surface is free or lying inside an infinite matrix. The relation $\Delta v=\Delta v'3(1-\nu)/(1+\nu)$ originally derived by Eshelby for the case of the elastic solution $\mathbf{u}_1$ and surface of an arbitrary shape still holds in this particular case.

It should be pointed out that in calculating the change ΔU_r in the repulsive energy only repulsive "bonds" of the atoms of region I were considered.

V. FORMATION ENERGY

The procedure for calculating the change in the electron energy when an interstitial or a vacancy is created in a monovalent metal is closely analogous to that used by Fumi[8] in the case of a vacancy. However, the effect of the change in volume $\Delta v'$ of the metal arising from the strain field around the defect is also taken into account. The metal is represented as a large spherical box in which the positive charge of the ions is distributed uniformly and the electrons are free. In order to create a vacancy an ion is removed from the center of the sphere and spread over its surface, whereas in the case of the creation of an interstitial a charge equal to one ion is removed from the surface and brought into the center. Then a change $\Delta v'$ in the volume of the sphere is produced by applying the elastic solution $\Delta v'\mathbf{r}/4\pi r^3$. The change in the energy of the conduction electrons is calculated in two steps. In the first step the electrons are distributed uniformly over the contracted or expanded metal containing the vacancy or the interstitial, respectively. Upon comparing the total kinetic energy of the electrons with the total kinetic energy in the normal metal, it turns out that the energy of the electrons has altered by

$$\Delta E_{\rm el}'=\frac{2}{5}E_F\left(Z-\frac{\Delta v'}{\Omega}\right). \quad (11)$$

Here $Z=-1$ for a vacancy and $Z=+1$ for an interstitial, Ω is one atomic volume, and E_F is the Fermi energy. In the second step the change in energy $\Delta E_{\rm el}''$

[12] See, for example, A. E. H. Love, *Mathematical Theory of Elasticity* (Cambridge University Press, New York, 1952).

caused by the redistribution of the electrons is determined. In the case of a spherically symmetric self-consistent potential $V(r)$ around the defect, $\Delta E_{el}''$ is given by

$$\Delta E_{el}''=-\frac{\hbar^2}{m^*}\int_0^{k_F} kZ(k)dk, \tag{12}$$

with

$$Z(k)=\frac{2}{\pi}\sum_l (2l+1)\eta_l(k). \tag{13}$$

In these equations k_F is the momentum of the electrons at the Fermi level, and $\eta_l(k)$ is the phase shift of the radial l waves for a free electron having energy $\hbar^2k^2/2m^*$. Fumi has shown that the potential $V(r)$ can be eliminated with the help of the Friedel sum rule if one uses the Born approximation to calculate the phase shifts. The Friedel sum rule[13] states that

$$Z(k_F)=Z', \tag{14}$$

where $-eZ'$ is the "displaced charge" around the defect, Z' being the number of electrons locally attracted or repelled from the defect to give complete screening of the Coulomb potential (e is the positive elementary charge). Fumi's result for $\Delta E_{el}''$ in the Born approximation, which was originally applied to a vacancy, can be generalized easily to the case of a defect with a displaced charge $-Z'e$. The result is

$$\Delta E_{el}''=-\tfrac{2}{3}E_FZ'. \tag{15}$$

It would be wrong to set Z' equal to $+1$ or -1 in the case of an interstitial or a vacancy, for the change in volume $\Delta v'$ of the metal alters the displaced charge in the defect region. If $-Ze$ is the displaced charge when there is no volume change $\Delta v'$,

$$Z'=Z-(\Delta v'/\Omega). \tag{16}$$

This can be seen in the following way. The displaced charge is equal to the negative of the net excess charge which remains in the defect region when the electrons are distributed uniformly over the metal. Around the defect draw a sphere of a radius sufficiently large that the elastic solution $\Delta v'\mathbf{r}/4\pi r^3$ is valid outside it. It is clear that if the net excess charge inside this sphere is Ze before volume change, the net excess charge inside the expanded (or in the case of a vacancy, contracted) sphere is $Z'e$, since the amount of positive charge inside the expanded sphere is unchanged whereas the charge of the uniformly distributed electrons inside this expanded sphere has altered by $-\Delta v'e/\Omega$.

Combining Eqs. (15) and (16), we have,

$$\Delta E_{el}''=-\frac{2}{3}E_F\left(Z-\frac{\Delta v'}{\Omega}\right). \tag{17}$$

From Eqs. (11) and (17) one obtains for the total change in energy ΔE_{el} of the electron gas,

$$\Delta E_{el}=-\frac{4}{15}E_F\left(Z-\frac{\Delta v'}{\Omega}\right). \tag{18}$$

Fumi found that if he approximated $V(r)$ for a vacancy by a square-well potential with a radius equal to r_S, the radius of the Wigner-Seitz sphere, a more exact calculation gave $\Delta E_{el}''=0.57E_F$ instead of $2E_F/3$ as it is obtained from Eq. (17) for $\Delta v'=0$. However, a self-consistent calculation by Huntington[14] has shown that the displaced charge around a vacancy extends over distances much larger than r_S. We repeated Fumi's calculation, taking the radius of the square-well potential equal to $2r_S$ and values of Z' in the Friedel sum rule (14) given by Eq. (16), and found the values of $\Delta E_{el}''$ to be nearly the same as those given by Eq. (17).

The values of ΔE_{el} calculated from Eq. (18) are displayed in Table I. The Fermi energy in copper was taken to be $E_F=5.1$ ev. This value is derived using an effective mass of $m^*=1.38$ which was deduced from measurements of the heat capacity of copper reported by Rayne.[15]

VI. LATTICE DISTORTION AROUND AN INTERSTITIAL-VACANCY PAIR

Blewitt *et al.*[16] found that the ratio of the energy released and the decrease in resistivity during the annealing of copper bombarded with neutrons near 10°K appears to be much smaller than might be expected on the assumption that interstitials and vacancies annihilate one another. A possible explanation of this "energy paradox"[1] might be that interstitials and vacancies come so close together, without actually recombining, that the resistance due to the associated pairs is much less than that due to the dissociated pairs. To check this proposal one must first find the stable pair configuration with the smallest distance between the interstitial atom and the vacancy.

We have treated in detail the configuration in which the vacancy lies at the position Y relative to the interstitial atom Q (see Fig. 1). The calculation of the lattice distortion follows the general procedure described in Sec. II. As starting positions in the first step we choose the equilibrium positions of the atoms around an isolated interstitial atom at Q. Atom Q and most of the atoms equivalent to atoms A, B, Y are allowed to relax (atom Y itself is absent), whereas the atoms farther away from Q are considered as fixed. Consideration of these more distant atoms would give only small corrections. We obtain sets of 15 linear algebraic equations which have been solved on the ILLIAC. The result is that there exists no equilibrium state of the lattice for

[13] J. Friedel, Phil. Mag. **43**, 153 (1952); J. Friedel, in *Advances in Physics*, edited by N. F. Mott (Taylor and Francis, Ltd., London, 1954), Vol. 3, p. 446.

[14] H. B. Huntington, Phys. Rev. **61**, 325 (1942).

[15] J. A. Rayne, Australian J. Phys. **9**, 189 (1956).

[16] Blewitt, Coltman, Noggle, and Holmes, Bull. Am. Phys. Soc. Ser. II, **1**, 130 (1956).

the pair configuration considered: the atom A moves into the vacant lattice site at Y.

The interference effects in the electron scattering arising from possibly stable interstitial-vacancy pairs with a distance between the defects larger than that between atoms Q and Y are estimated in the Born approximation. The scattering potentials are approximated by square-well potentials. By using Friedel's sum rule the strengths of the potentials can be expressed in terms of the effective charges of the defects. It turns out that if one uses reasonable values of the well-radii and takes the distance between interstitial atom and vacancy to be at least as large as the distance between atom Q and atoms X and C respectively, the decrease in resistance is always less than about 10% of the resistance of the dissociated pair.

It should be pointed out that the configuration with the vacancy at B and the interstitial atom at Q may be stable. However, in order to reach this configuration during annealing, the system must pass through an unstable configuration which leads to recombination.

VII. DISCUSSION

The values of the change in volume of the crystal due to an interstitial, a vacancy, and a crowdion in copper, shown in Table I, have been determined by taking into account only the repulsion of closed shells of the ions. With our present knowledge it does not seem possible to decide which of the two proposed Born-Mayer repulsive potentials V_1 and V_2 [see Eqs. (7)] is the better one.

A further uncertainty arises from the neglect of other types of forces. The error introduced may not be negligibly small, as can be seen from the following. The volume change arising from an interstitial has been calculated by taking into account the dependence of the electron energy ΔE_{el} upon this volume change. [See Eq. (18).] By minimizing the *sum* of the closed-shell repulsive energy ΔU_r and the electron energy ΔE_{el} with respect to the lattice relaxation we obtain approximate volume changes of 1.5 and 1.8Ω for the two Born-Mayer potentials instead of about 1.7 and 2.0Ω as derived by minimizing ΔU_r alone. (Ω=one atomic volume.) In addition to this effect there may be others because, even if it is correct to assume that contributions to the formation energy other than ΔE_{el} and ΔU_r are small compared with these two, it is possible that the derivatives of small contributions with respect to the lattice relaxation are comparable in magnitude with the derivative of ΔE_{el}.

A third possible source of error is the use of elastic solutions for an *isotropic* continuum. In the case of copper one should consider the elastic anisotropy. Elastic solutions $\mathbf{u}_\nu$ can be constructed, for example, from the approximation to the fundamental integral of the anisotropic elastic differential equations given by Kröner.[17]

[17] E. Kröner, Z. Physik **136**, 402 (1953).

It is reasonable to suppose that the deviation of the actual lattice distortion from that derived from the closed-shell repulsion alone will be relatively small in the case of an interstitial or a crowdion, because the exponential repulsive forces are large and vary much more rapidly with interionic separation than other possible forces. In the case of a vacancy, where the distances between adjacent ions are nearly the same as in the normal lattice, the error may be large. In fact, Huntington[14] and Seeger and Bross[18] conclude that there is no lattice relaxation around a vacancy. Huntington finds that the electrostatic forces between the shielded vacancy and its first neighbors are repulsive and balance the Born-Mayer forces. However, one should also take into account the effect of the electron energy ΔE_{el} [Eq. (18)] upon the lattice relaxation. It turns out that the corresponding forces on the first neighbors, which are directed towards the vacant lattice site, are large enough to outweigh the electrostatic repulsive forces determined by Huntington. Now Seeger and Bross consider only the effect of $\Delta E_{\text{el}}'$ [Eq. (11)] upon the lattice relaxation; according to their calculations this acts to prevent a contraction of the lattice. We have seen in Sec. V, however, that the derivative of the contribution $\Delta E_{\text{el}}''$ to ΔE_{el} with respect to the volume change is of opposite sign and larger in magnitude than that of $\Delta E_{\text{el}}'$. From this it appears probable that there is a contraction of the lattice around a vacancy.

In the following, the calculated values of volume change are used in connection with experimental results on radiation damage. Simmons[19] has measured the lattice expansion of copper held near 10°K during bombardment with deuterons. He derives a ratio of resistivity change to relative volume expansion that is equal to 2.3×10^{-4} ohm-cm. We shall assume that the deuteron damage consists of Frenkel pairs with interstitials in an "interstitial" configuration. Resistivities arising from one atomic percent of interstitials, vacancies and pairs are designated by $\Delta\rho_i$, $\Delta\rho_v$, and $\Delta\rho$, respectively. Taking 1.5Ω as a lower limit and 1.67Ω as an upper limit for the volume change due to an interstitial, -0.53Ω for the volume change arising from a vacancy, one obtains from the experimental result a pair resistivity $\Delta\rho$ in the following range,

$$2.2\leq\Delta\rho\leq2.6\ \mu\text{ohm-cm}.$$

From the results of the quenching experiments of Bauerle and Koehler[20] on gold, one derives

$$\Delta\rho_v=1.4\ \mu\text{ohm-cm},$$

if one assumes that the volume change due to a vacancy in gold is the same as that determined for copper. On theoretical grounds, $\Delta\rho_v$ for copper and gold would be expected to be closely similar for similar lattice

[18] A. Seeger and H. Bross, Z. Physik **145**, 161 (1956).

[19] R. O. Simmons, thesis, University of Illinois, 1957 (unpublished).

[20] J. E. Bauerle and J. S. Koehler, Phys. Rev. **107**, 1493 (1957).

strains. From these values of $\Delta\rho$ and $\Delta\rho_v$, one deduces that $\Delta\rho_i$ lies in the range

$$0.8 \leq \Delta\rho_i \leq 1.2 \ \mu\text{ohm-cm}.$$

Using the volume changes calculated in the case of repulsive potential V_2, one obtains resistivities larger than those determined above for potential V_1, namely $3.1 \leq \Delta\rho \leq 3.6$, $\Delta\rho_v = 1.7$, and $1.4 \leq \Delta\rho_i \leq 1.9$ μohm-cm.

Recently Harrison[21] calculated values for the resistivities of interstitials and vacancies of $\Delta\rho_i = 0.15$ and $\Delta\rho_v = 0.6$ μohm-cm. His values are derived by assuming strains around the defects which differ from those obtained here. Nevertheless the order of magnitude of the resistivities would probably be the same when calculated from Harrison's theory using the strains found by us. Comparison of these low values of the resistivities obtained by Harrison with the values found above might be interpreted as indicating that the deuteron damage in copper does not consist of interstitial-vacancy pairs. There are, however, other theoretical values of $\Delta\rho_i$ and $\Delta\rho_v$ which lie inside the ranges obtained above from the deuteron irradiation experiments.[22] The electron irradiation experiments reported by Corbett *et al.*[23] provide further evidence for these higher resistivities. If the results of these experiments are interpreted by the simple theory of displacement[4] under conditions in which the latter is reliable, it appears probable that $\Delta\rho \geq 1.88$ μohm-cm.[1]

Crowdions have been proposed by several authors for a variety of reasons. (See, for example, Lomer and Cottrell,[24] and Blewitt *et al.*[25]) Using the values of the volume change obtained for the crowdion configuration treated in Sec. IV (see Table I) instead of those due to an interstitial in the above considerations of deuteron damage, one obtains resistivities for one atomic percent of crowdions of nearly zero and 0.2 μohm-cm, respectively, for the two repulsive potentials.

The formation energies calculated for a vacancy in copper (see Table I) are somewhat lower than the experimental value, which lies near 1.1 ev. The reason for the discrepancy might be that the volume contraction around a vacancy is somewhat smaller than that determined from the closed-shell repulsion alone. The electron energies ΔE_{el} for crowdions shown in Table I are calculated from Eq. (18) which is derived for a spherically symmetric defect. Upon using these values of ΔE_{el}, the formation energy of a crowdion is found to be about 0.6 ev higher than that derived for an interstitial for both repulsive potentials. It should be emphasized that all values for the formation energy are very rough estimates. It appears that it would be very difficult to decide definitely from more detailed calculations whether the interstitial or the crowdion configuration is preferred energetically.

We see from the above considerations that it is not yet possible to decide from the calculated volume changes, in combination with the experimental and theoretical results considered here, whether interstitials or crowdions are actually produced by charged-particle irradiation. This is due mainly to the uncertainty in the theoretical values of the resistivities of the defects considered and of the volume change arising from a vacancy.

We should point out a further consequence of the calculations. It has been suggested that the sharp drop of about 40% in the radiation-induced resistivity near 35°K during the annealing of copper which had been irradiated with deuterons at about 12°K[26] is due to the trapping of interstitials in vacancies. (Compare the discussion in Sec. VI of the stored energy measurements made by Blewitt *et al.*[15] in the case of neutron damage.) However, in Sec. VI we estimated that the decrease in resistivity due to the association of interstitials and vacancies, without their actually recombining, is always less than about 10%. It therefore appears probable that this explanation is not correct.

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[21] W. A. Harrison (to be published).

[22] The entire topic is surveyed by F. J. Blatt, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press, Inc., New York, 1957), Vol. 4, p. 321. See also L. M. Roth, thesis, Radcliffe College, 1956 (unpublished).

[23] Corbett, Denney, Fiske, and Walker, Phys. Rev. **104**, 851 (1956).

[24] W. M. Lomer and A. H. Cottrell, Phil. Mag. **46**, 711 (1955).

[25] Blewitt, Coltman, Klabunde, and Noggle, J. Appl. Phys. **28**, 639 (1957).

[26] Cooper, Koehler, and Marx, Phys. Rev. **97**, 599 (1955).