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Mobility of Interstitial Atoms in a Face-Centered Metal

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Calculation of the energies of interstitial atoms in copper have been carried through in some detail using a free-electron model and approximating the repulsion of closed shells with a Born-Mayer potential. Alternate choices of constants in this potential have been employed to explore the extent of the associated uncertainty. Results show that interstitials require an activation energy of about $\frac{1}{4}$ ev or less for motion. Applications to various current experiments are pointed out.

CURRENT interest in radiation damage in metals has indicated the importance of the behavior of interstitial atoms. Earlier theoretical study[1] had tended to discount the role of interstitials as a mechanism for diffusion because of the large amount of energy needed in their creation but had indicated that if formed their mobility might be high. Under radiation by energetic massive particles large numbers[2] of lattice displacements consisting of vacancies and displaced interstitial atoms result. There is evidence from the low-temperature annealing of this damage[3] that there exists a mechanism (perhaps several) for atom motion with low activation energy.

Accordingly this paper is an attempt to study the interstitial atom in a metal such as copper in more detail and with particular emphasis on the relative energy difference between the two equilibrium configurations for the interstitial atom since this difference is the activation energy for interstitial motion. The general procedure follows that of I. The copper metal is represented by a lattice of positive point ions immersed in a uniform, compensating distribution of electrons. Each ion repels its neighbors according to an exponential potential, involving two semi-empirical constants, which represents the repulsion of closed shells after the Born-Mayer treatment. This treatment is, however, more detailed and differs from I at three points. In the first place, the form of the exponential repulsion of the closed shells of copper has been revised to fit with more recent findings. Secondly, the electrostatic potential of the interstitial position has been evaluated, whereas formerly it was assumed to be zero. Lastly, the method has been altered to consider the relaxation of neighbors *before* the redistribution of electron charge. The effect of the latter, always difficult to estimate, is greatly reduced and the reliability of the method is thereby improved. It should be emphasized that such a technique is not limited to the treatment of individual interstitials but should prove useful for treating more complex lattice defects such as may be generated in metals by radiation damage or cold work.

A. THE EXPONENTIAL CLOSED-SHELL REPULSION

1. Constructing the Potential

Besides I, other papers[4,5] have employed exponential repulsive potentials for copper. The common features have been to use the elastic moduli to determine the constants in the formula. The variation of compressibility with pressure and behavior of the Hartree wave functions for the copper atom have also been invoked to substantiate the final result. Since different authors have come up with somewhat different expressions, it appears worth while to investigate critically the causes for these divergences.

Let the interaction energy of two adjacent ions be written $U(r)=Ae^{(r-r_0)/\rho}$, where r_0 is the equilibrium separation, A gives the interaction energy at this distance, and r_0/ρ is a dimensionless number whose magnitude is a measure of the rigidity of the repulsion. Contributions to the elastic constants for the face-centered lattice from the close range forces may be computed[6] from the equations

$$(c_{11}'+2c_{12}')/3=(6/9)N[r^2U'']_{r_0}, \tag{1}$$

$$c_{44}'=\tfrac{1}{2}N[r^2U''+3rU']_{r_0}, \tag{2}$$

$$c_{11}'-c_{12}'=\tfrac{1}{2}N[r^2U''+7rU']_{r_0}, \tag{3}$$

where N is number of ions per unit volume. Primed elastic constants are corrected for the effects of long-range forces. The nature of these corrections will be discussed below.

The bulk modulus of copper is 13.9×10^{11} dynes/cm². Values for the shear moduli given by Goens and Weerts[7] and by Lazarus[8] are in close agreement for $c_{11}-c_{12}=4.7\times10^{11}$ dynes/cm² and $c_{44}=7.5\times10^{11}$ dynes/cm². With the model that is used here to represent the metal, namely, nearly free electrons and a lattice of singly charged ions, the long-range forces are the elec-

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[1] H. B. Huntington and F. Seitz, Phys. Rev. **61**, 315 (1942); hereafter called I.

[2] F. Seitz, Discussions Faraday Soc. No. 5, 271 (1949).

[3] C. J. Dienes in *Annual Review of Nuclear Science* (Annual Reviews, Inc., Stanford, 1953), Vol. II; Marx, Cooper and Henderson, Phys. Rev. **88**, 106 (1952); A. W. Overhauser, Phys. Rev. **90**, 393 (1953); R. R. Eggleston, Bull. Am. Phys. Soc. **27**, No. 6, 9 (1952).

[4] C. Zener, Acta Cryst. **3**, 346 (1950).

[5] G. J. Diennes, Phys. Rev. **86**, 228 (1952).

[6] K. Fuchs, Proc. Roy. Soc. (London) **A153**, 622 (1936).

[7] E. Goens and J. Weerts, Physik. Z. **37**, 321 (1936).

[8] D. Lazarus, Phys. Rev. **76**, 545 (1949).

trostatic interactions and the pressure of the electron gas. The latter will contribute to the bulk modulus, while the former will affect the shear moduli.

The actual bulk modulus will be

$$(c_{11}+2c_{12})/3=N(\hbar k_m)^2/5m^*+(c_{11}'+2c_{12}')/3, \quad (4)$$

where the first term on the right is the bulk modulus of the electron gas. The value for m^*, the effective electron mass, was taken to be $1.47m$ in accord with low-temperature measurements of specific heat.[9] In establishing the values used for A and ρ in his work, Zener[4] omitted Eq. (1) because of uncertainty of the correction term in Eq. (4). Besides the lack of supporting theoretical evidence for the value of m^*, this model of the free-electron metal as used by Fuchs[6] was relatively unsuccessful in explaining the cohesion of copper. Nevertheless, it turns out that the contribution to the bulk modulus from the compression of a gas of free electrons is only about 20 percent of the experimental bulk modulus so that the remaining contribution to the bulk modulus from the short-range forces is fairly well known.

In his work on copper,[6] Fuchs calculated the electrostatic contributions to the shear constants arising from distorting a lattice of positive point charges in a uniform negative charge distribution. They[10] are $(c_{11}-c_{12})_{\text{elec}}=0.57$ and $(c_{44})_{\text{elec}}=2.57$ in units of 10^{11} dynes/cm^2. Though these terms are relatively small, they affect c_{44} much more than $c_{11}-c_{12}$ and so alter the anisotropy ratio $2c_{44}/(c_{11}-c_{12})$. As Zener has remarked, the r_0/ρ is quite sensitive to this ratio. Since the electron density does not stay uniform with elastic shear distortion but changes to neutralize in part the electrostatic stored energy in the distorted point lattice, the terms calculated by Fuchs represent an upper limit for this effect. Zener,[4] in his consideration of this point, concluded that electron compensation made the electrostatic contributions negligible, but he made no direct calculation on this point.

In Appendix A, a variational calculation has been carried out on an approximate model to determine what fraction of the electrostatic terms is really operative. A shear distortion of the angle between two cubic axes in a face-centered cubic lattice has the effect of decreasing the distances between atoms in the (110) direction and increasing the distances in the (1-10) direction, so an effective charge deformation is generated in a criss-cross pattern with a period of $d/\sqrt{2}$, where d is the lattice constant. The variational calculation using a very simple form of modulation shows a reduction of 25 percent in the electrostatic energy of deformation. Since more elaborate methods should give greater reduction, it seems reasonable to put these contributions to the elastic constants at one-half their value for the uniform electron distribution.

TABLE I. Data for determining A and ρ. All values are given in units of 10^{11} dynes/cm^2.

	$\frac{1}{3}(c_{11}+2c_{12})$	$c_{11}-c_{12}$	c_{44}
Experimental elastic constants	13.9	4.7	7.5
Contributions from long-range forces	2.6	0.28	1.28
Primed quantities	11.3	4.42	6.22

All these considerations are summarized in Table I and can now be applied to determining A and (r_0/ρ).

With values of the primed shear constants as obtained in Appendix A together with the correction to the primed bulk modulus given in Eq. (4), Eqs. (1)–(3) can be solved by the least-squares method to give $(r_0/\rho)=14.9$ and $A=0.056$ ev, with a relative deviation less than 6 percent in every case.

In the corresponding expression developed by Zener,[4] the value of r_0/ρ was some 10 percent lower. In addition to using the ratio of the shear constants, Zener also adduced supporting evidence from two other sources, one arising from the exponential behavior of the d electrons for the Cu$^+$ ion in the Hartree-Foch solution[11] at a radial distance corresponding to mid-point between ions in the metal and the second from the change of compressibility of copper with pressure as determined by Bridgman[12] and Lazarus.[13] The treatment of the pressure data was reviewed by the author taking into account the effect of the electron gas on the compressibility and variation of compressibility with pressure and using the condition of equilibrium in a somewhat different manner. We obtained essentially the same result as Zener. A formula for $U(r)$ closely resembling his was adopted for subsequent work:

$$U_a(r)=0.053\exp[13.9(r_0-r)/r_0]\text{ev per ion pair.} \quad (5a)$$

Since the treatment of the elastic data given above called for a somewhat larger value of r_0/ρ, it was decided to bracket this value by carrying out alternate calculations with a function[14] of considerably larger r_0/ρ,

$$U_b(r)=0.038\exp[17.2(r_0-r)/r_0]\text{ ev per ion pair.} \quad (5b)$$

2. Repulsive Energies for Interstitial Configurations

Interstitial atoms in face-centered lattices have two equilibrium configurations as depicted in Fig. 1. Con-

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[9] See F. Seitz, *Modern Theory of Solids* (McGraw-Hill Book Company, Inc., New York, 1940); Estermann, Friedberg, and Goldman, Phys. Rev. **87**, 582 (1952).

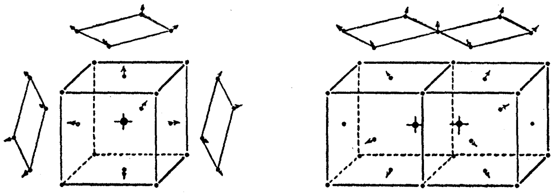
[10] See N. F. Mott and H. Jones, *The Theory and Properties of Metals and Alloys* (Oxford University Press, London, 1936), pp. 147–150.

[11] D. R. Hartree and W. Hartree, Proc. Roy. Soc. (London) **A157**, 490 (1936).

[12] P. W. Bridgman, Proc. Am. Acad. Arts Sci. **77**, 198 (1949).

[13] See reference 8.

[14] This potential is quite close to the one used by Huntington and Seitz in I and displayed as curve (2) in Fig. 1 of that paper. The values quoted in connection with this curve on p. 317 of I are in error. Corrected, they should read: $\rho=0.284$ in Bohr units (not angstroms), and $A=5.64\times10^4$ ry per ion pair (where the factor 10^4 was inadvertently omitted). A curve based on these values was used in the actual calculations. However, this curve was obtained using rather different shear constants and incorporating the full value of the electrostatic terms.



Configuration B Configuration C

FIG. 1. B and C configurations for an interstitialcy.

figuration B (following notation of I, Fig. 2) represents the interstitial atom at the cube center and the associated disturbance has spherical symmetry. In configuration C two atoms appear on opposite sides of a vacant lattice site and the accompanying disturbance has only cylindrical symmetry. The procedure is to consider the relaxation of nearest neighbors, 6 for B and 8 for C, and in addition the relaxation of each quartet of ions most directly opposing the motion of each of the nearest neighbors. This brings the number of neighbors considered up to 30 for B and 36 for C. The relaxation of outermost ions which were not considered in I lowers the energy in each case by amounts of at least $\frac{1}{2}$ ev.

For configuration B, the origin of coordinates is put at the interstitial ion. The outward displacements of the nearest neighbors is given by a vector of the type $\frac{1}{2}\epsilon d$, 0, 0, where d is the lattice constant. The displacements of the ions at the positions of type $(d, \frac{1}{2}d, 0)$ is taken to be outward from the next neighbors and to be represented by vectors $\delta d/\sqrt{2}$, $\delta d/\sqrt{2}$, 0. The first part of the calculation consists in treating each nearest neighbor and the four ions against which it is pushed as forming a complex whose energy is minimized with respect to δ for each value of ϵ. The interaction of these complexes with the interstitial ion is then minimized with respect to ϵ.

For configuration C, the origin of coordinates is put at the empty site and the two ions flanking this position have coordinates $\pm(1-\lambda)d/2$, 0, 0. The eight next neighbors at $(\pm d/2, \pm d/2, 0)$ and $(\pm d/2, 0, \pm d/2)$ are given outward displacements of the type $\lambda\nu d/2$, $\nu d/2$, 0. The displacements of the more remote ions at positions $(d, d, 0)$, $(d/2, d, d/2)$, and $(0, d, 0)$ are all assumed to point outward from the next neighbors and are given magnitudes $\eta_1 d/\sqrt{2}$, $\eta_2 d/\sqrt{2}$, and $\eta_3 d/\sqrt{2}$, respectively. The procedure here is to assume an approximate value for $\lambda (\lambda=0.4)$ and for different values of ν to find the minimum values for the η's, taking into account only interaction with the 28 remote neighbors. The interaction of the interstitials with the complexes formed around the eight next neighbors is next minimized with respect to ν. The final step is to vary λ and to compute the energy of the configuration at the minimum values for all parameters, taking care to count all interactions only once.

TABLE II. Summary of closed-shell repulsive terms.

Configuration B	$U_a(r)$	$U_b(r)$
Minimizing value for ϵ	0.21	0.23
Minimizing value for δ	0.03_2	0.04_0
Energy minimum	4.34	4.85
Configuration C		
Minimizing value for λ	0.42	0.39
Minimizing value for ν	0.15	0.17
Minimizing value for η_1, η_2, η_3	$(0.03_6, 0.023, 0.008)$	(0.045, 0.028, 0.014)
Energy minimum	4.43 ev	4.74 ev

In each case, the energy is calculated from the normal lattice plus isolated "interstitial" ion as zero potential. It is to be noted that the ions whose relaxation was most important were not always those nearest the defect. For the B configuration, ions at the $(d/2, d/2, d/2)$ positions were passed over because the effect of ion repulsion was less important for them than for $(d, d/2, 0)$ neighbors. In configuration C, a similar remark holds for neighbors at the $(d/2, d/2, 0)$ positions. The final results of these calculations are given in Table II for configurations B and C.

From Table II one can judge how critical the choice of repulsive potential turns out to be for these configurations. With U_b, the "harder" potential, the level of both B and C configurations is raised by about $\frac{1}{2}$ ev. For U_b also, the B configuration lies higher by about 0.10 ev; whereas for U_a the difference is reversed. In both cases this difference is too small to imply much physical significance.

B. ELECTROSTATIC TERMS

The interstitial configurations at this stage where the electrons are uniformly distributed may be considered as consisting of point ions introduced into the lattice (one positive ion for Configuration B and two positive and one negative for Configuration C), a number of large dipoles which arise from the displacements of the nearest neighbors and a larger number of smaller dipoles because of the displacements of the more distant ions. The electrostatic energies associated with these configurations are subdivided into the following terms: (1) the lattice potential at the points where the ions are introduced, (2) the Coulombic interaction of these ions (for C configuration only), (3) ion-large dipole interactions (must treat dipoles as finite), (4) large dipole-dipole interactions, (5) large dipole-lattice interactions, (6) ion-small dipole interactions, (7) large-small dipole interactions, (8) small-small dipole interactions, (9) small dipole-lattice interactions. These quantities are evaluated by assuming that the ions are situated at the equilibrium positions determined in Sec. A. Since the closed shell repulsive forces treated there vary much more rapidly with distance than the electrostatic forces, this seems to be a reasonable approximation. Moreover, in a metal the electrons will tend to shield the ions to an extent that is difficult to determine, and so the electrostatic forces are less effec-

TABLE III. Electrostatic terms (all energy values in e^2/d).

Term	Configuration B Formula	With U_a	With U_b	Configuration C Formula	With U_a	With U_b
(1) Lattice potential	$V_e(d/2, 0, 0)$	-0.303	-0.303	$2V_e\{d(1-\lambda)/2, 0, 0\}-V_e(0)$	4.390	4.218
(2) Ion-ion				$-3/(1-\lambda)$	-5.175	-4.918
(3) Ion-large dipole	$+12[(1+\epsilon)^{-1}-1]$	-2.088	-2.244		-1.440	-1.640
(4) Large-large dipole	$10.5\epsilon^2$	0.464	0.556	$12.58\nu^2$	0.283	0.363
(5) Large dipole-lattice	$12.6\epsilon^2$	0.555	0.660	$19.5\nu^2$	0.439	0.565
(6) Ion-small dipoles	18.2δ	-0.582	-0.728		-0.266	-0.33
(7) Large-small dipoles	$-11.2\epsilon\delta$	-0.075	-0.103		-0.046	-0.07
(8) Small-small dipoles	$216\delta^2$	0.222	0.346		0.062	0.10
(9) Small dipole-lattice	$203\delta^2$	0.208	0.325		0.113	0.18
Total		-1.599	-1.491		-1.640	-1.53

tive in determining the equilibrium positions of the ions than might appear on the basis of uniform electron distribution. In Table III below are given the values for the various electrostatic terms.

For the calculation of the lattice potential the Ewald[15] method is used,

$$V_e(x)=e[\pi/4d+(\pi\Omega)^{-1}\textstyle\sum_l{}' h_l^{-2}\exp-(\pi h_l/s)^2 + \sum_n |r-R_n|^{-1}\{1-\phi(s|r-R_n|)\}-\pi/s^2\Omega], \quad (6)$$

where the R_n are the translation vectors of the lattice, the h_l are the translation vectors of the reciprocal lattice, and s is an arbitrary parameter whose choice is governed by the need to have both series converge sufficiently rapidly. (In this work $s=\pi/d$ was chosen.) The symbol $\phi(x)$ stands for the error function. The first term inside the square bracket, namely $\pi/4d$, is introduced to take into account the dipole layer at the surface of a large spherical lattice. The derivation of this term, which does not appear to have been developed elsewhere, is given in Appendix B. The $V_e(0)$ is the potential at a lattice site when the ion at that position is missing. It is $-3.80_0 e/d$, and is obtained by omitting from Eq. (6) the term for which $R_n=r$ in the second summation and adding a term $2s/\pi^{\frac{1}{2}}$.

In many cases of dipole-dipole interactions, the formula for infinitessimal dipoles proved to be sufficiently accurate, namely,

$$V_{d-d}=\tfrac{1}{2}\textstyle\sum_{ij}[(\mathbf{D}_i\cdot\mathbf{D}_j)/r^3-3(\mathbf{D}_i\cdot\mathbf{r}_{ij})(\mathbf{D}_j\cdot\mathbf{r}_{ij})/r_{ij}^5], \quad (7)$$

where the $\mathbf{D}_i$ are the dipole moments and r_{ij} their mutual separations. Since the displacements are somewhat different according to whether U_a or U_b is used, results are given separately for both.

The dipole lattice term is the increase in electrostatic energy when an ion is displaced from its equilibrium position. It can be adequately approximated for our use by $ex^2/2r_s^3=8.4(e/d)(x/d)^2$, where x is the displacement from equilibrium.

In Table III formulas have been given, where possible, for the various electrostatic terms as functions of the displacement parameters. Such formulas were more difficult to use in configuration C because of its greater complexity and lower symmetry. For the terms involving the smaller dipoles, the multiple values of η made formulas impractical. In general, no accuracy is claimed for the last figure of the numbers in this table.

From Table III it can be observed that the reduction in energy throughout was greater with the U_b than with U_a, because in general U_b forced the greater displacements, hence the greater effective polarization. Because the electrostatic disturbance associated with the interstitial alone is less concentrated for configuration C, the lowering of the electrostatic energy is here considerably greater. When the effective polarizations of first the large and then the small dipoles are successively introduced, the $B-C$ difference is continually reduced to a value of about 0.04 e^2/d in the final total. Somewhat fortuitously perhaps the final values for the $B-C$ difference appear to be independent of the force law used to within the accuracy of the calculation.

The calculations so far are referred for zero potential to the isolated ion and the regular lattice. The energy to form an isolated ion is the sum of the cohesive energy plus the ionization of the atom minus the work function of the metal which is regained as the freed electron is returned to the lattice. For copper these quantities total about 7.2 ev. Also, for copper, the e^2/d unit is 4.0 ev. The summary of the results obtained so far, under the assumption of uniform electron distribution, is given in Table IV, where the results of Tables II and III are combined with the 7.2 ev for forming the isolated ion.

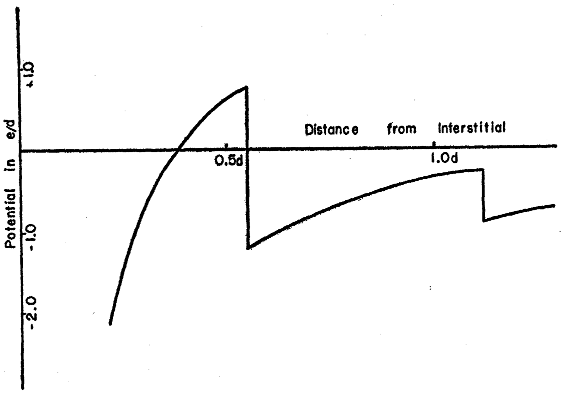


FIG. 2. Electrostatic potential for B configuration.

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[15] P. P. Ewald, Ann. physik 49, 1, 117 (1916); 64, 253 (1921): Z. Kryst. 56, 129 (1921).

TABLE IV. Summary of results. All energies are in ev.

Configuration	*B*		*C*	
Closed-shell force law	(a)	(b)	(a)	(b)
Closed-shell repulsion (Table II)	4.34	4.85	4.43	4.74
Electrostatic terms (Table III)	−6.40	−5.96	−6.56	−6.12
Formation of isolated ion	7.2	7.2	7.2	7.2
Energy on basis of uniform distribution	5.14	6.09	5.07	5.82

Table IV shows the calculated values for the interstitial configurations to be about 0.9 ev higher on the basis of U_b as compared with U_a, but the value for the $B-C$ difference is considerably less, 0.07 ev for U_a and 0.24 ev for U_b. On the basis of either force law, the configuration of lower symmetry C is favored as the equilibrium state.

C. VARIATION OF THE ELECTRON DISTRIBUTION

The study of the effect of the redistribution of electron density injects some calculational difficulties into what has been up to now a straightforward attack based on an easily applied model. We shall proceed by a simple variational approach and choose trial functions,

$$\psi_k(x) = V^{-\frac{1}{2}} e^{i\mathbf{k}\cdot\mathbf{r}} F(r), \qquad (8)$$

where all the wave functions[16] are modulated by the same function F which depends only upon distance from the interstitial ion. The value of $F(r)$ is more than one near the interstitial ion and infinitesimally less than one elsewhere, so that the total number of electrons is conserved. V stands for the volume of the metal. The theory of a very similar case has been worked in I, and the analysis there shows that three terms enter into the variational calculation:

(1) The interaction of the change in charge distribution with the potential field of the defect. This field includes the contribution from the displacement dipoles as well as that from the interstitial ion.

(2) An increase in the kinetic energy arising from the modulation, which can be reduced to

$$-(\hbar^2/2m^*)\int F(r)\nabla^2 F(r) d\tau.$$

(3) The self-energy of the change in charge distribution.

The considerations governing the choice of the function $F(r)$ rested not so much on physical grounds as on mathematical convenience since the evaluation of three terms above in convenient closed forms was most desirable. The function chosen for configuration B was

$$F(r) = (1 + B\cos 2br)^{\frac{1}{2}} \quad \text{for} \quad r < \pi/4b, \qquad (9)$$

where the quantity B is determined to be 0.340 $(bd)^3$ by the condition that the interstitial defect appears electrically neutral at large distances in the metal. Beyond $r=\pi/4b$, $F(r)-1$ is of the order of $1/N$, where N is total number of atoms.

(1) For calculating (1), the interstitial potential is approximately $-e/r$ and the displacement dipoles are replaced by dipole spherical shells of equal total strength, so that one has a potential as shown in Fig. 2 of a Coulomb attraction with steps at the position of the dipole layers. For the choice $\epsilon=0.20$ and $\delta=0.032$, these potential steps turn out to be $V_1=1.98e/d$ for $r_1=0.55d$ and $V_2=0.61e/d$ at $r_2=1.12d$. Qualitatively their effect is to repel the neutralizing electronic charge so that it is spread over a greater volume than would be the case if the dipoles were not there. The expression for this interaction using trial function (9) is

$$[-2.43bd + 4.21G(\xi_1) + 1.30G(\xi_2)]e^2/d, \qquad (10)$$

where $\xi_1 = 2br_1$, $\xi_2 = 2br_2$ and $G(\xi) = (\xi^2-2)\sin\xi + 2\xi\cos\xi$.

(2) For the change in kinetic energy one can integrate by parts to get

$$-\frac{\hbar^2}{2m^*}\frac{4}{\Omega_0}\int_0^{b\pi/4} F(r)(\nabla^2 F(r)) r^2 dr$$

$$= \frac{2\pi\hbar^2}{m^*\Omega_0}\left[\left(\frac{\pi}{4b}\right)^2 Bb + \frac{(Bb)^2}{(2b)^3}\int_0^{\pi/2}\frac{\sin^2 x x^2 dx}{1+B\cos x}\right]. \qquad (11)$$

Because of the widely spread charge, B turns out to be small[17] and can be dropped from the denominator of the integral. This can be evaluated and itself shown to be negligible compared with the first term.

(3) The potential of the change in electron charge distribution ϕ_e can be found from Poisson's equation,

$$\nabla^2\phi_e(r) = (4eB/\Omega_0)\cos 2lr,$$

to be

$$\phi_e(r) = \phi_e(\pi/4b) + 4.26eb[4/\pi + \cos\xi_1 - 2\sin\xi_1/\xi_1]. \qquad (12)$$

The value for the self-potential term is

$$(e/2\Omega_0)\int \phi_e(r) B\cos(2br) d\tau = 0.91be^2. \qquad (13)$$

In Table V is given the results of minimizing the sum of Eqs. (10), (11), and (13) with respect to b. The table shows that the variation of the electron distribution in the above manner lowers the energy by $0.223e^2/d$ or 0.89 ev. This number serves to give the order of magnitude of the energy gain but may be too small for many reasons. As in any variational calculation, the arbitrarily chosen trial function can usually be improved. A radial function which decreases less rapidly at larger distances than the cosine might effectively shield out the farther dipoles. Further gains could be introduced by departure from spherical symmetry; i.e., let

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[16] The validity of the subsequent results may be challenged because the trial functions are not orthogonal. There is indication, however, that this is not a serious shortcoming.

[17] The fractional error introduced by neglecting the nonothogonality of the trial functions is proportional to B, which is of the order of 0.01.

$F=F(r,\theta,\phi)$. Aside from these considerations associated with the variational procedure, there are still the electron correlation effects which would tend to reduce the self-potential term [see Eq. (13), which amounts to about +1.2 ev in the above reckoning]. From these considerations one estimates roughly that the energy gain from variation for configuration B will lie between 1.0 ev to 2.0 ev, which, when combined with the results of the preceding sections, yields an activation energy for interstitial diffusion bracketed between 3.8 ev to 5.1 ev. This seems to be well outside the range of experimental values for copper.

The application of a variational attack on configuration C does not appear warranted in view of the necessary complication. One expects that the energy lowering in such a process would be about the same as for configuration B, though perhaps somewhat smaller. There are two reasons why electron redistribution might be expected to be less effective for C. First, the departure from spherical symmetry might be expected to increase the change in the kinetic energy of the electron wave functions that is caused by the modulation. A second and more important reason is that the C configuration is slightly more spread out than the B, for example, 8 near neighbors and 28 next nearest as compared with 6 near neighbors and 24 next-nearest neighbors. It has already been pointed out that largely as a result of this spreading, the C configuration has a considerably lower electrostatic energy than B. The relaxations of the first and second neighbors reduces this difference markedly. Likewise, the modulation of the electron distribution might be expected to decrease the difference somewhat further and to favor B over C—perhaps by about 10 percent of the total energy lowering.

D. CONCLUSIONS

The results of this calculation indicate that once an interstitial atom is formed, it is relatively mobile because of the small activation energy required for it to jump from one equilibrium position to another. The calculation indicates an average value for this energy of about $\frac{1}{4}$ ev, with the less symmetrical configuration C as the more probable equilibrium position, though the reverse possibility that C is a saddle point cannot be definitely ruled out. Wherever a large nonequilibrium number of interstitials exists in the lattice, motion of interstitials will be important. On the other hand, the calculation shows that interstitial diffusion in copper is ordinarily unimportant because the energy to form an interstitial, while less than originally estimated (see I), is still greater by a considerable amount than the activation energy experimentally observed.

The possibility of mobile interstitials has bearing on the results of some current experiments. Recently the measurement[18] of changes in resistance found in the annealing of cold-worked wires of gold, silver, and copper at fixed temperatures for fixed periods of time has been reported, indicating clearly that at least two distinct atomic mechanisms are operative in the anneal. For one the activation energy is about $\frac{1}{4}$ ev or less, for the other the energy values fall around $\frac{3}{4}$ ev, for these metals. Manintveld has proposed that the second mechanism corresponds to the motion of single vacancies. We should like to suggest that the first effect can be attributed to the annealing out of interstitials formed by the cold work.

TABLE V. Variation of electron distribution. (Energies in units of e^2/d.)

$-1.52\ bd$	-0.517	$(bd)_{\min}=0.34$
$4.21\ G(\xi_1)$	0.076	$B=0.013$
$1.30\ G(\xi_2)$	0.160	
ΔKE Eq. (11)	0.058	
Total energy gain	-0.223	

Recent work[19] at the University of Illinois has shown similar results from the study of resistance changes in radiation-damaged wires of copper, silver, gold, nickel, and tantalum. The investigators found at low temperatures activation energies for anneal in the range of 0.2 to 0.3 ev for all of these metals. More recent measurements reported on copper[20] from widely different sources agree on another activation energy for anneal of 0.68 ev but indicated that the situation is complex at lower energies. One explanation for this complexity may be that multiple vacancies formed along the track of the fast particle may require about the same energy for motion as the interstitials. (At still lower energy, the direct recombination of nearby vacancies and interstitials might be expected.) Experiments[21] with very rapid quenching of pure gold wires from high temperatures reveal an activation energy of 0.4 ev. Since the presence of interstitials after quench is unlikely, it would seem that this effect might arise from coupled vacancies[22] which result from a large density of vacancies frozen in from high temperature.

By way of interpretation, it is tempting to assign the 0.68 ev energy in copper to the motion for single vacancies. On the other hand, it is difficult to decide from theory or experiments performed so far, whether the interstitial or the coupled vacancy has the lower energy for motion or which plays the more important role in the radiation-induced changes in resistance.

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APPENDIX A

The amount by which the electrostatic energy of the elastic deformation in shear of a point lattice is reduced by the motion

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[18] J. A. Manintveld, Nature 169, 623 (1952).

[19] Marx, Cooper, and Henderson, Phys. Rev. 88, 106 (1952).

[20] A. W. Overhauser, Bull. Am. Phys. Soc. 27, No. 6, 8 (1952); R. R. Eggleston, Bull. Am. Phys. Soc. 27, No. 6, 9 (1952).

[21] J. W. Kauffman and J. S. Koehler, Phys. Rev. 88, 149 (1952).

[22] Calculations by J. H. Bartlett and G. J. Dienes, Phys. Rev. 89, 848 (1953), show that the energy for motion of paired vacancies should always be less than the energy for motion of a single vacancy.

of the electrons can be estimated for a particular model by a variational procedure. By an extension along the (110) direction and a compression along the (1–10) direction, a shear without dilation may be produced. If the electron distribution is maintained uniform, the potential in regions lying between ions along the (110) direction will be decreased. Between ions along the (1–10) direction, the potential will be increased. We shall approximate this potential distribution by two mutually perpendicular standing waves,

$$V(x,y)=V_0[\cos(lx)-\cos(ly)], \tag{A1}$$

where x is measured in the (110) direction and y is measured in the (1–10) direction, and $l=2\sqrt{2}\pi/d$ (d is the lattice constant). For our purpose it will be sufficient to consider only one of the terms in Eq. (A1). If one chooses $V_0=4\pi ea/l^2\Omega$, where Ω is the volume per ion, then one can consider that V is the result of a varying charge distribution caused by superimposing standing waves of the form

$$\rho(x)=(e/\Omega)a\cos(lx), \tag{A2}$$

where a is seen to be the fractional variation of charge density. The stored energy per unit volume for such a charge distribution is given by

$$\tfrac{1}{2}\int_\Omega \rho(x)V(x,0)d\tau=\frac{\pi}{\Omega}\left(\frac{ae}{l}\right)^2. \tag{A3}$$

This stored energy may be decreased by modulating the uniform electron distribution. One takes for the wave functions of the electrons in the electrostatic field

$$\psi_k'=\psi_k[1+b\cos(lx)], \tag{A4}$$

where the ψ_k are the orthogonal, normalized electron wave functions corresponding to the original uniform distribution. Though the new wave functions are not strictly orthogonal nor normalized these defects are not serious since terms in b^2 will be neglected ($b\sim a\ll 1$). The electron charge density is now altered by

$$\Delta\rho(x)=-(e/\Omega)2b\cos(lx). \tag{A5}$$

Correspondingly, a change in potential occurs,

$$\Delta V(x)=-(8\pi be/l^2\Omega)\cos(lx). \tag{A6}$$

The quantity b is determined by minimizing the sum of three terms: (1) a kinetic energy term $\hbar^2l^2b^2/4m^*$ per electron (where m^* is the effective mass of the conduction electrons), (2) a potential term

$$\int_\Omega V(x)\rho(x)d\tau,$$

and (3) a self-potential term

$$\tfrac{1}{2}\int_\Omega \Delta V(x)\rho(x)d\tau.$$

Accordingly this sum can be written

$$E=[(\hbar l)^2/4m^*+4\pi e^2/l^2\Omega]b^2-4\pi abe^2/l^2\Omega, \tag{A7}$$

with

$$b_{\min}=\frac{a}{2}\left[1+\frac{(\hbar l)^2}{4m^*}\frac{l^2\Omega}{4\pi e^2}\right]^{-1}\simeq 0.123a, \tag{A8}$$

where m^*/m is taken equal to 1.47. It follows that

$$\frac{E_{\min}}{4\pi e^2/l^2\Omega}=-\left(\frac{a}{2}\right)^2\left[1+\frac{(\hbar l)^2}{4m^*}\frac{l^2\Omega}{4\pi e^2}\right]^{-1}\simeq -0.062a^2. \tag{A9}$$

On comparing this result with the total stored energy, Eq. (A3), which is $\pi(ae)^2/\Omega l^2$, one finds that this very simple trial wave function lowers the electrostatic energy to 75 percent of its original value. Presumably more detailed variations could lower this value substantially. In addition, the effect of electron-electron correlations of any sort will tend to decrease the self-potential term and subsequently $E_{\min}$ still further. For these reasons, we have subtracted off from the experimental values of the shear moduli only $\frac{1}{2}$ the electrostatic contributions as computed by Fuchs for the uniform electron distribution,

$$\begin{aligned} c'_{11}-c'_{12}&=4.7-\tfrac{1}{2}(0.57)=4.42\times 10^{11}\ \text{dynes/cm}^2,\\ c'_{44}&=7.5-\tfrac{1}{2}(2.57)=6.22\times 10^{11}\ \text{dynes/cm}^2. \end{aligned} \tag{A10}$$

APPENDIX B

The calculation of the electrostatic energy associated with taking an ion from infinity and putting it at an interstitial position cannot be found directly from an application of the usual Ewald method since this procedure is based on the assumption of an infinite lattice filling all space. From a physical standpoint, the difficulty arises from the unspecified dipole surface layer which raises or lowers the potential of the whole lattice by an arbitrary constant. In the text the actual dipole layer of the metal is used in incorporating the work function value into the 7.19 ev, the energy for compressing the electron gas. The actual dipole layer gives the lattice a positive bias of a few tenths ev[23] as compared to a surface situation made up of s spheres, or atomic polyhedra, where the electron distribution goes sharply from average value to zero at the polyhedra surfaces. There are two problems here: (1) to determine what surface conditions would give the reference potential of the usual Ewald function (without the $\pi e/4d$ term) and (2) to calculate the potential change in going from this surface condition to that of the atomic polyhedra.

The first question can be answered by realizing that the space summation in the Ewald calculation, which can be made to predominate by the choice of a small value for s, is equivalent to the Coulomb potential of a collection of point charges, whose magnitudes depend only on distance, immersed in a compensating uniform charge distribution of opposite sign. Such radial symmetry implies a fundamental condition, where the compensating charge stops at the surface of a sphere just large enough to enclose the exact amount of uniformly distributed charge needed to compensate the enclosed point charges.

We have not been able to demonstrate in a formal manner that the potential difference from the surface condition of the large sphere to that of the close-packed duodecahedra of the face-centered lattice is $e\pi/4d$, but a process of induction makes it seem likely. First we calculated the potentials associated with the dipole layers which arise when the polyhedron surface is cut in turn by planes (100), (110), and (111) at the proper positions to ensure electrical neutrality. These potentials turned out to be respectively 1/12, 1/6, and 1/36 in units of $\pi e/d$. Single directions, however, intercept infinitesimal area on the large sphere. To average over solid angle, one must include deviations from the exact Miller indices. As a result, the tangent plane to the sphere makes in these cases small angles s/L with the crystal planes, where s is the distance between atom planes and L the interval of periodicity along the tangent plane. The potential of the resulting dipole layer is found from Poisson's equation,

$$\nabla^2 V_s=4\pi(4e/d^3)\tfrac{1}{2}(1-2x/s). \tag{B1}$$

The second factor on the right is the uniform charge density in the interior. The factor $\frac{1}{2}$ enters because regions of charge overlap and charge deficit are spread equally over the tangent plane. These regions are wedge-shaped, and the final factor takes into account their linear decreases in cross section with distance from the surface as measured by the variable x. The dipole layer potential is then obtained from Eq. (B1) integrated twice with respect to x from $-s/2$ to $s/2$, namely,

$$V_s=(2\pi e/3d)(s/d)^2.$$

When one adds this quantity to the results already found for the surface potential in the exact direction of the Miller indices, one obtains in each case ($e\pi/4d$).

A similar procedure has been applied to calculating the surface potential in a simple cubic lattice in (100), (110), and (111) directions. In each case the results were ($e\pi/6d$). For the b.c.c. lattice, different results were obtained in different directions. Possibly the situation is more complex here because the atomic polyhydra have two different kinds of faces.

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[23] See work function calculations on sodium by J. Bardeen, Phys. Rev. 49, 653 (1936).