

Mechanism for Self-Diffusion in Metallic Copper

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The problem of the mechanism of diffusion in metallic copper is discussed from the standpoint of the modern theory of metals. Three competing processes are considered in detail, namely the mechanism of direct interchange of atoms, the mechanism of interstitial diffusion, and the mechanism of vacancy diffusion. The energies of the equilibrium and saddle-point configurations for the processes are determined first in an approximation in which the electronic charge distribution is assumed to be uniform throughout the lattice, and second in a further approximation in which polarization is taken into account by a simple variational method based on the one-electron scheme. The results indicate that the vacancy mechanism is strongly preferred and yield a value of the activation energy for diffusion in reasonable agreement with the observed one. The vacancy process is considered in greater accuracy in a paper by Huntington following this.

I. INTRODUCTION

THERE are three reasonable mechanisms of atomic diffusion in the interior of solids, namely diffusion by direct interchange of neighboring atoms in a perfect lattice, diffusion by means of interstitial atoms, and diffusion by means of vacancies. The likelihood of each of these processes has been examined¹ most completely for ionic crystals since the computational techniques for this type of solid are most widely known and easiest to apply. As a result of this work, it seems to be generally agreed that diffusion by means of holes is the most probable in all ionic crystals in which the ions have rare gas configurations and the coordination number is high. This includes, for example, the alkali halides possessing sodium chloride and cesium chloride structures and such divalent salts as magnesium oxide. On the other hand, it seems likely that interstitial atoms play an important role both in crystals of low coordination number, such as oxides and sulfides having zinblende and wurtzite lattices, and in highly coordinated crystals, such as the silver halides, in which the metal ion contains a newly closed *d* shell. A large amount of supporting evidence concerning the crystals of low coordination number has been

obtained by Wagner² and his associates on experimental grounds, whereas the evidence for salts such as the silver halides is still mainly theoretical.

The purpose of this paper is to examine the diffusion mechanism in metals more closely than has been done hitherto. Naturally, it would be most convenient from the purely theoretical side to carry out computations for the alkali metals, since their cohesive properties are most fully understood. Unfortunately there is not available at the present time experimental information on diffusion in these metals and it seems unlikely that such information will become available in the immediate future. For this reason, we have decided as a compromise to work with copper, in which self-diffusion has been measured by radioactive tracer methods.³ The theory of copper has been investigated extensively by Fuchs⁴ and the results of his work, which will now be described briefly, are summarized in

TABLE I. Copper data.

	Fuchs	Observed
Cube edge distance	4.2A	3.609A
Sphere radius r_s		2.64a
Atomic ionization energy		7.7 ev
Cohesive energy	33 kg cal./mole	81 kg cal./mole
Compressibility	0.69×10^{-6} cm ² /kg	0.70×10^{-6} cm ² /kg
$c_{11} - c_{12}$	5.10×10^{11} dy/cm ²	5.1×10^{11} dy/cm ²
c_{44}	8.9×10^{11} dy/cm ²	8.2×10^{11} dy/cm ²

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¹ W. Jost and C. Nehlep, *Zeits. f. physik. Chemie* **B32**, 1 (1936). See also the book by W. Jost, *Diffusion und Chemische Reaktionen in festen Stoffen* (J. Steinkopf, 1937).
N. F. Mott and M. J. Littleton, *Trans. Faraday Soc.* **34**, 485 (1938).

² C. Wagner, *Zeits. f. physik. Chemie* **B22**, 181 ff. (1933).

³ J. Steigman, W. Shockley, and F. Nix, *Phys. Rev.* **56**, 13 (1939); B. D. Rollin, *Phys. Rev.* **55**, 231 (1939).

⁴ K. Fuchs, *Proc. Roy. Soc.* **151**, 585 (1935); **153**, 622 (1936); **157**, 444 (1936).

Table I. It should be mentioned at this point that the inherent accuracy of Fuchs' computations for copper is considerably less than that for lithium and sodium. It seemed worthwhile to proceed with copper in spite of this fact, for, as will be shown, the results in which we are particularly interested turn out to be relatively insensitive to the weaker points of Fuchs' work.

Fuchs determined approximate wave functions for copper by the cellular method and con-

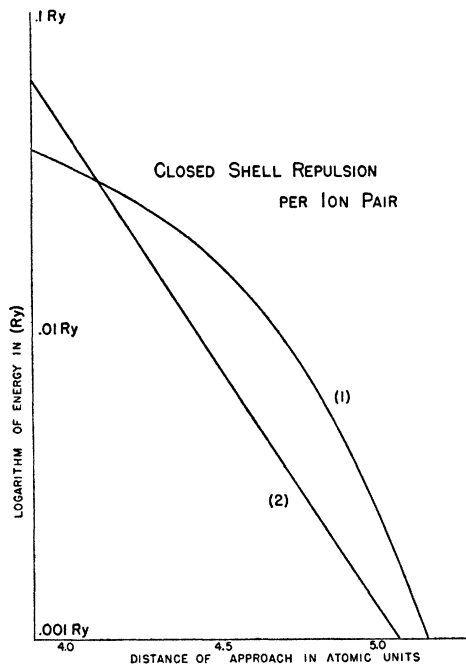


FIG. 1. Comparison of the two alternative curves for the closed-shell repulsive force, (1) the displaced Fuchs model and (2) the exponential force law. The equilibrium distance of nearest neighbors is $4.77 a_0$.

cluded that the electrons are very nearly free, as in sodium. We shall accept this approximate result as a basic assumption in deriving the Fermi energy, exchange energy and correlation energy for the metal. In this approximation, the electronic energy of the valence electrons in the metal is⁵

$$E = N \left(\epsilon_0 + \frac{\hbar^2}{2m} \frac{2.21}{r_s^2} + \frac{e^2}{2N} \int \rho(\mathbf{r}_1) \int \frac{\rho(\mathbf{r}_2)}{r_{12}} dV_1 dV_2 \right. \\ \left. + \sum_{\alpha} \int_c \rho(\mathbf{r}_1) \frac{e^2}{r_{1\alpha}} dV - \frac{0.458e^2}{r_s} - \frac{0.288e^2}{r + 5.1a_0} \right), \quad (1)$$

⁵ See for example, *The Modern Theory of Solids*, Chapter X (McGraw-Hill Book Company, 1940).

in which N is the number of unit cells in the lattice, r_s is the radius of the sphere whose volume is equal to that of the unit cell, ϵ_0 is the energy of the lowest electron in the field of the nearest ion core, and $\rho(\mathbf{r})$ is the valence electron charge distribution function. The terms in the right-hand side of Eq. (1) have the following interpretation. The first is the combined potential and kinetic energy of the lowest energy electron, exclusive of its potential energy of interaction with other valence electrons and with ions other than that in the unit cell in which it is temporarily located. These two energy terms are given, respectively, by the third and fourth terms in (1), the integration in the fourth being over a single cell and the sum extending over all ions in the lattice except that in the given cell. The integration in the third term extends over the entire crystal. The second term in (1) is the mean kinetic energy of all electrons relative to the kinetic energy of the lowest, and is the same as the expression for the mean kinetic energy of a set of perfectly free electrons in a Fermi distribution. If the effective electron mass were not unity, as Fuchs' work indicates to be nearly the case, the m in the denominator would be replaced by the effective electron mass m^* . The fifth term in the expression is the mean exchange energy of one of the valence electrons and the last is the correlation energy.

Fuchs computed the ion-ion repulsive interaction with the aid of an interaction potential derived by a modified Fermi-Thomas method. We shall call this interaction the "Fuchs potential" in the following discussion. Now the ion-ion interaction is of fundamental importance for determining the elastic constants in a metal of the type of copper, so that the merits of a particular interaction can be evaluated by examining the elastic constants computed with it. Fuchs found that his interaction gave excellent results for the theoretical equilibrium spacing of the lattice, which, unfortunately, is about 17 percent larger than the actual spacing (Table I). We may conclude from this that his potential is too large at the actual spacing.

As a result of this difficulty it was decided to use two alternative ion-ion interaction functions. One of these was a curve derived from Fuchs' by displacing his to shorter distances by 17

percent, and the other was a two-parameter exponential function of the type used by Born and Mayer⁶ in their treatment of ionic crystals, where the parameters were chosen to yield the best least square determination of the three elastic constants. If the Born-Mayer function is taken in the form $Ae^{-(r/\rho)}$, the best values of A and ρ are $A=5.64$ Rydberg units per ion pair and $\rho=0.284\text{\AA}$. As may be seen from Fig. 1, the two types of curve differ appreciably. It was hoped that by considering both a good idea could be obtained of the importance of the ion-ion interaction in two rather extreme cases. Actually we have every reason to expect that the Born-Mayer type of curve is the more accurate of the two for, not only does it yield reasonable results in the case of ionic crystals, but in addition, it would lead to a compressibility that would steadily decrease as the crystal is compressed, whereas the displaced Fuchs curve would lead to a compressibility nearly independent of the volume in the neighborhood of the equilibrium spacing, in contradiction with experiment.

In addition to the exchange repulsion energy between ions, we are interested in the van der Waals attraction between ions. This has been discussed by Mayer and Levy⁷ in connection with computations of the stability of the copper halides. They employed a function of the form

$$4.1 \times 10^{-60}/r^6 \text{ erg}$$

for the van der Waals energy of two copper ions, r being the distance of separation in cm. The contributions arising from this term are practically negligible compared with other quantities for the values of r with which we shall be concerned.

We shall now proceed with the computation of the activation energy for the three diffusion processes described above. In each of the cases this activation energy may be divided into two parts, namely, (1) the energy required to form the lattice defect in an equilibrium state, and (2) the additional activation energy required

to pass from one equilibrium position to another. The first of these is of course zero for the mechanism of direct atomic interchange. As we shall see, the two energies may be evaluated individually in two successive stages of approximation, namely, a first approximation in which the electronic charge distribution is regarded as uniform throughout the crystal, and a later approximation in which the redistribution of charge in the immediate neighborhood of the diffusing atom is taken into account. Steigman, Shockley, and Nix give 2.6 ev as the experimental value for the activation energy for self-diffusion in copper.

II. ACTIVATION ENERGIES IN APPROXIMATION IN WHICH ELECTRONIC REDISTRIBUTION ABOUT DIFFUSING ATOMS IS NEGLECTED

The equilibrium and saddle-point configurations for the three types of diffusion to be con-

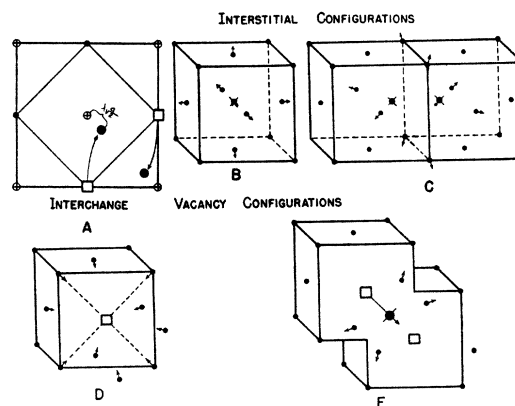


FIG. 2. Configurations involved in the various mechanisms for diffusion. ● denotes an atom at an ordinary lattice site. * denotes an interstitial atom. □ denotes a vacancy. Small arrows indicate displacements under the influence of the closed-shell repulsive force. Configuration A shows the plane of interchange (100). Atoms in planes directly above and below are indicated by ⊕.

sidered are shown in Fig. 2. In the case of direct interchange, the equilibrium configuration is, of course, that for the perfect lattice, whereas the saddle-point configuration is shown in Fig. 2A. In this arrangement two nearest neighbors, namely those indicated by squares at the face-center positions, have rotated through 90° about a (100) axis bisecting perpendicularly their line of centers. The spacing of these neigh-

⁶ M. Born and J. E. Mayer, *Zeits. f. Physik* **75**, 1 (1932) *et seq.*

⁷ J. E. Mayer and R. B. Levy, *J. Chem. Phys.* **1**, 647 (1933).

bors will of course change in general during the process. Figure 2B shows the probable equilibrium position for the interstitial atom at the center of the unit cube, whereas Fig. 2C shows the saddle-point configuration in which the interstitial atom and one of its six nearest neighbors have become symmetrically disposed relative to one of the cube faces. The neighboring atoms are shifted from normal sites in both of these cases in the manner suggested by the arrows. It evidently is not clear at this stage of our reasoning which of the two configurations has the lower energy, but subsequent work will show that the assignment probably is as given. Figure 2D shows the equilibrium vacancy configuration whereas E shows the transition configuration during diffusion.

1. Direct Interchange

For investigation of the saddle-point for direct interchange, consider the two diffusing ions to be taken from their equilibrium positions and placed near adjoining "interstitial sites," i.e., body centers and edge centers. If we designate their distance from the respective neighboring interstitial sites by $\sqrt{2}\lambda a/2$, where λ is a parameter and a is half the cube-edge distance, their mutual distance of separation is $(1-2\lambda)\sqrt{2}a$. Similarly, we shall designate the distance by which the nearest neighbors in the plane of motion move in the (100)-type directions by $\mu a/2$, and shall designate the displacement vectors of neighbors to the interstitial sites lying in other planes by $(\nu a/2, 0, 0)$, etc. The total change in repulsive energy is then given by

$$\begin{aligned} \Delta E(\lambda, \mu, \nu) = & \left[R \left\{ \frac{\sqrt{2}a}{2}(1-2\lambda) \right\} + 4R \left\{ \frac{a}{2}((1+\nu)^2 + 2\lambda^2)^{\frac{1}{2}} \right\} + 4R \left\{ \frac{a}{2}((1+\lambda+\mu)^2 + \lambda^2)^{\frac{1}{2}} \right\} \right. \\ & - 23R \left\{ \frac{\sqrt{2}a}{2} \right\} + 16R \left\{ \frac{a}{2}((1-\nu)^2 + 1)^{\frac{1}{2}} \right\} + 16R \left\{ \frac{a}{2}((1-\mu)^2 + 1)^{\frac{1}{2}} \right\} \\ & \left. + 8R \left\{ \frac{a}{2}((1+\mu)^2 + (1+\nu)^2)^{\frac{1}{2}} \right\} - 40R \left\{ \frac{\sqrt{2}a}{2} \right\} \right], \quad (2) \end{aligned}$$

where $R(x)$ is the energy of repulsion per ion pair at an interatomic distance x . When the two diffusing atoms are taken from their equilibrium positions, 23 repulsive contacts are broken since these atoms had one contact in common. The first three terms in Eq. (2) represent the new contacts established in this configuration. Each of the four atoms in the plane in which the interchanging atoms move, which are displaced by an amount determined by the μ parameter, alters its contacts with other atoms behind it. These changes account for the coefficient 16 in the sixth term. The situation for the atoms whose displacements are determined by the ν parameter is similar. By evaluating this expression numerically for suitable ranges of the parameters the minimum value was determined. Since the interesting ranges of the parameters turn out to be small, it was found permissible to disregard all but the linear terms in the expansion of the arguments of the functions.

With the use of the exponential repulsive curve, it was found that the energy minimum occurred at about 6.2 ev for $\lambda=0.11$, $\mu=0.2$, and $\nu=0.08$. The displaced-Fuchs type of repulsive function, on the other hand, leads to meaningless results in the present case because of the fact that it varies comparatively slowly with interionic distance, as we remarked in the previous section.

In addition to the energy arising from ion-ion repulsion, it is also necessary to take into account the change in electrostatic energy resulting from the motion of the ions through the electron cloud. Assuming that the electronic cloud remains uniform, we found that the electrostatic energy increased by more than 11 ev in going from the normal to the saddle-point configuration. This gain would be diminished somewhat by including the effect of polarization of the valence electron distribution, perhaps to a third or half of its original value.

2. Interstitial Configurations

In order to find the energy required to form an interstitial atom under the assumption that the electron distribution remains neutral, it is necessary to consider the situation in which an ion is taken from the surface and placed in an interstitial site and the electronic charge which previously surrounded the ion is distributed in a thin, uniform layer throughout the crystal. Consider the change in kinetic and electrostatic energy of the system. If we regard the lattice from the standpoint of the "s sphere approximation,"⁵ we see that the interstitial ion is very near to the peripheries of the s spheres of the surrounding atoms, so that its *net* electrostatic interaction with the electrons and remaining ions lattice is small. Thus the increase in electrostatic energy may be obtained in first approximation by considering the remaining system alone. Each of the electrons is still in the electrostatic field of an ion, so that there is no change in ϵ_0 [see Eq. (1)]. On the other hand, the electron gas is compressed, so that the other terms are altered. The changes in Fermi, exchange, and correlation energies may easily be derived by noting that the effective sphere radius is changed from r_s to $r_s(1-1/3N)$. Similarly, the change in the electrostatic self-energy of the electrons may be derived by noting that the new electron density is $(1+1/N)$ and that it extends over $N-1$ cells instead of N . Hence the total change in electrostatic energy is

$$\begin{aligned} & \frac{2}{3} \times \frac{2.21}{r_s^2} \frac{\hbar^2}{2m} - \frac{1}{3} \times \frac{0.458e^2}{r_s} - \frac{0.288r_s e^2}{3(r_s+5.1)^2} \\ & + \frac{e^2}{2} \int \rho(\mathbf{r}_1) \int \frac{\rho(\mathbf{r}_2)}{r_{12}} dV_2 dV_1. \quad (3) \end{aligned}$$

For the uniform electron distribution, the self-energy of the electrons in a cell is $0.6e^2/r_s$. Taking r_s equal to $2.64 a_0$ for copper, we obtain 7.34 ev for (3).

A value of this energy could also be obtained from experiment by considering a process in which an atom is evaporated from the surface, ionized, and the electron is replaced in the metal at the top of the Fermi band. If the dipole layer at the surface of the metal is small, the net

energy required should be nearly equal to (3), since the isolated ion at infinity, like the interstitial ion in the present approximation, would not interact electrostatically with the rest of the metal. A computation of this energy, based on the measured quantities leads to a value of 7.19 ev, in remarkably close agreement with the foregoing value. Since it is reasonable to suppose that the surface dipole moment of pure copper is not larger than 1 ev, this agreement suggests that the free electron approximation is reliable.

The nearest neighbors of the interstitial ion will retreat from it under the influence of the short-range repulsive forces discussed in Section 1. This motion will, of course, influence the electrostatic energy of the interstitial ion, but it seems unwise to compute this effect at present since it should be considered along with the energy resulting from polarization of the electron cloud by the ion. The change in the short-range energy may be evaluated approximately as follows. In taking an ion from the surface and placing it at an interstitial site, six surface repulsive bonds at the ordinary interatomic distance ($\sqrt{2}a/2$) are broken and six new repulsive bonds are formed at a distance $(1+\lambda)a/2$. If the six neighbors remained at their normal sites, the parameter λ evidently would vanish. If we neglect the displacements of next nearest neighbors, the change in repulsive energy can then be written

$$\begin{aligned} \Delta E_{\text{rep}} = & 6 \left[R \left\{ \frac{a}{2}(1+\lambda) \right\} + 2R \left\{ \frac{\sqrt{2}a}{2}(1+\lambda) \right\} \right. \\ & \left. + 4R \left\{ \frac{a}{2}((1-\lambda)^2+1)^{\frac{1}{2}} \right\} - 7R \left\{ \frac{\sqrt{2}a}{2} \right\} \right] \quad (4) \end{aligned}$$

in analogy with (2). This has a minimum of 5.5 ev at $\lambda=0.2$ for the exponential repulsive function and a minimum of 3.85 ev at $\lambda=0.1$ for the displaced Fuchs repulsion. Addition of the 7.34-ev term derived from Eq. (3) leads, respectively, to values of 12.84 ev and 11.19 ev for the energy of configuration *B* (Fig. 2) in the present approximation.

Using the repulsive force, we have estimated that the additional repulsive energy required to go from the *B* configuration to the *C* configuration is about 0.5 ev.

TABLE II. Ion-core contributions for "E" configuration.

	Exponential	Displaced Fuchs
Broken repulsive contacts	-0.69 ev	-1.65 ev
Energy of mutual neighbors	0.51 ev	1.59 ev
Energy of 14 other neighbors	-0.19 ev	-0.40 ev
Value for λ -parameter	-0.37 ev 0.125	-0.46 ev 0

3. Vacancy Configuration

In the vacancy case, those terms which appeared in Section 2 as a result of compressing the electron gas now appear with reversed sign since the electron gas expands by an amount equal to the volume of a single cell when an ion is taken from an interior site and placed on the surface. However, this gain of 7.34 ev [see Eq. (3)] is counterbalanced by the fact that in the present approximation the vacancy is occupied uniformly by an electronic cloud uncompensated by a positive charge. Thus in the sphere approximation this electron distribution has an energy equal to $-\epsilon_0$, the energy of the lowest electron in the filled band. One may estimate $-\epsilon_0$ from the sum of the ionization energy, the heat of sublimation, and the mean Fermi energy to be about 15.5 ev. As a result, the increase of electron energy needed to form a hole can be taken as 8.2 ev for a basis of comparison at this stage.

The change in repulsive energy may be computed next following the same general procedure.

$$\Delta E_{\text{rep}} = 4 \left[R \left\{ \frac{6^{\frac{1}{2}}a}{4} (1+\lambda) \right\} + R \left\{ \frac{10^{\frac{1}{2}}a}{4} \right\} + 3R \left\{ \frac{a}{2} (2-\lambda)^{\frac{1}{2}} \right\} + \frac{1}{2}R \left\{ \frac{a}{2} (2+2\lambda)^{\frac{1}{2}} \right\} \right. \\ \left. + 2R \left\{ \frac{a}{2} (2-3\lambda)^{\frac{1}{2}} \right\} + 2R \left\{ \frac{a}{2} (2+\lambda)^{\frac{1}{2}} \right\} - 7^{\frac{1}{2}}R \left\{ \frac{\sqrt{2}a}{2} \right\} \right], \quad (6)$$

in which terms in λ^2 have been omitted in the expansion of the arguments. Using the exponential repulsion function we obtained a net energy increase of 0.51 ev relative to the normal lattice for $\lambda=0.125$, whereas the increase was 1.59 ev for $\lambda \approx 0$ when the displaced Fuchs function was used. Now each of the two "half vacancies" in the *E* configuration have seven neighbors whose environment is indirectly affected as a

For the simple vacancy distribution *D*, the number of ordinary repulsions will be decreased by 6 in taking the ion to the surface, but a further decrease results from the motion of the atoms neighboring the vacancy toward it. This change is

$$\Delta E_{\text{rep}} = 12R \left\{ \frac{\sqrt{2}a}{2} (1+\lambda) \right\} + 48R \left\{ \frac{\sqrt{2}a}{2} (1+\lambda+\lambda^2)^{\frac{1}{2}} \right\} \\ + 24R \left\{ \frac{\sqrt{2}a}{2} (1-\lambda) \right\} - 90R \left\{ \frac{\sqrt{2}a}{2} \right\}, \quad (5)$$

in which the displacement of nearest neighbors is given by $\lambda\sqrt{2}a/2$. The decrease is about 0.4 ev for the exponential repulsion with $\lambda=0.025$ and about 1.0 ev for the displaced Fuchs function with $\lambda=0.038$.

The configuration *E* of Fig. 2 is the saddle-point arrangement for the process since its energy is higher than that of the configuration just discussed. In the new arrangement, two ions are taken from adjacent positions in the interior and one is placed at the surface with a net decrease of 17 repulsions (12+11-6). Next, the other ion is placed at the center of the rectangle formed by the four ions that are mutually adjacent to both vacancies. These ions retreat, as a result, and the displacement vectors may be represented in the form $(\lambda a/2, \lambda a/4, \lambda a/4)$. The part of the change in repulsive energy arising from the variation in λ is

result of the presence of the vacancies. For an order of magnitude estimate, their change in energy was taken to be the same as the decrease found in the case of Fig. 2D for the neighbors of the simple vacancy. Adding together the three results (see Table II), we obtain as the repulsive energy for the *E* configuration -0.37 ev when the exponential curve is used and -0.48 ev when the displaced Fuchs curve is employed.

III. COMPUTATION OF THE ELECTRONIC REDISTRIBUTION BY A VARIATIONAL SCHEME

An easy method for estimating the lowering of the energy which results from electronic redistribution is a variational procedure based on the use of one-electron functions of the form

$$\psi_k(1+f(r)). \quad (7)$$

The ψ_k are the normalized, free-electron functions $V^{-1/2} \exp [2\pi i \mathbf{k} \cdot \mathbf{r}]$, for the case in which the charge is uniformly distributed, and $f(r)$ is a function equal practically to zero everywhere except in the immediate vicinity of the interstitial atom or vacancy, where its value is to be determined by variation. We shall assume that it is radially symmetric about the lattice defect. The functions (7) may be readily normalized by the use of the condition

$$\int (1+f(r))^2 dV = V, \quad (8)$$

in which the integration extends over the entire lattice and V is the volume of the lattice. The function f is not exactly zero at large distances, because the redistribution affects the density of electronic charge infinitesimally throughout the

crystal. It is convenient to introduce at this point for later use a function, $g(r)$, which is exactly zero except in the neighborhood of the lattice defect and is defined by setting $(N/V)[1+g(r)]$ equal to the electronic density in the lattice. The density can also be expressed in terms of $f(r)$, as

$$\frac{N \pm 1}{V} [1+f(r)]^2. \quad (9)$$

The plus or minus sign applies according to whether we are dealing with an interstitial or vacancy defect respectively. It follows that

$$g(r) = [2f(r) + f^2(r)] \pm 1/N. \quad (10)$$

The functions (7) are not, however, mutually orthogonal and therein lies the chief weakness of the present method. It is simple only if the functions are treated as though they were orthogonal. Fortunately the results obtained here by assuming orthogonality are in reasonable agreement with those obtained by a more exact procedure employed in the following paper. This indicates that the lack of orthogonality does not prevent the method from giving sensible answers to problems concerning energy.

The total energy of the system is then⁸

$$E_T = \sum_k \epsilon'_k - \frac{e^2}{2} \sum_k \sum_{k'} \iint \frac{|\psi_k(r_1)(1+f(r_1))|^2 |\psi_{k'}(r_2)(1+f(r_2))|^2}{|\mathbf{r}_1 - \mathbf{r}_2|} dV_1 dV_2 + \frac{1}{2} \sum'_{\alpha, \beta} \frac{e^2}{r_{\alpha\beta}} - \sum_{\alpha} V_d(r_{\alpha}) + E_e + E_c + E_r, \quad (11)$$

in which E_e and E_c are the total exchange and correlation energies for the electrons and E_r is the ion-ion repulsive energy. The third term is the mutual electrostatic interaction of the ions of the lattice, and the fourth term gives their interaction with the lattice defect. The energy parameter ϵ'_k is the mean value of the Hamiltonian for the k th electron wave function,

$$\epsilon'_k = \int \psi_k(1+f) H \psi_k(1+f) dV. \quad (12)$$

For this problem the Hartree Hamiltonian operator for the system of wave functions (7) becomes

$$H = -\frac{\hbar^2}{2m} \Delta + V_i(r) + V_d(r) + e^2 \sum_k \left\{ \int \frac{|\psi_k(r_1)(1+f(r_1))|^2}{|\mathbf{r} - \mathbf{r}_1|} dV_1 - \int \frac{|\psi_k(r_1)|^2}{|\mathbf{r} - \mathbf{r}_1|} dV_1 \right\}, \quad (13)$$

⁸ See, for example, reference 5, Chapter VI.

in which $V_l(r)$ is the potential of the lattice for a uniform charge distribution, $V_d(r)$ is the radial symmetric potential of the lattice defect, either interstitial atom or vacancy, and finally the term in braces is the difference in potential resulting from redistribution.

Now we can write

$$\begin{aligned} \sum_k \epsilon'_k = & \sum_k \int \psi_k^*(1+f) \left(-\frac{\hbar^2}{2m} \Delta + V_l + V_d \right) \psi_k(1+f) dV \\ & + \sum_{k, k'} e^2 \int |\psi_k(r_1)(1+f(r_1))|^2 \left[\int \frac{|\psi_{k'}(r_2)|^2 (2f(r_2) + f^2(r_2))}{|\mathbf{r}_1 - \mathbf{r}_2|} dV_2 \right] dV_1. \end{aligned} \quad (14)$$

The summand in the first term of this expression can be transformed to

$$\begin{aligned} \int \psi_k^*(1+f)^2 \left(-\frac{\hbar^2}{2m} \Delta + V_l \right) \psi_k dV - \int |\psi_k|^2 (1+f) \left(-\frac{\hbar^2 \Delta}{2m} + V_d \right) (1+f) dV \\ - \frac{\hbar^2}{m} \int \psi_k^*(1+f) \text{grad } \psi_k \cdot \text{grad } f dV. \end{aligned} \quad (15)$$

The first term in (15) is evidently equal to ϵ_k , the energy parameter for the uniform distribution, whereas the third term is

$$-\frac{1}{V} \frac{\hbar^2}{m} \int 2\pi i \mathbf{k} \cdot \text{grad } f (1+f) dV,$$

which vanishes when summed over the range of k values occurring in a uniformly filled band. Hence the sum of terms arising from (15) becomes as a result of the plane-wave character of the ψ_k ,

$$\sum_k \epsilon_k - \frac{\hbar^2}{2m} \frac{N}{V} \int (1+f) \Delta (1+f) dV + \frac{N}{V} \int (1+f)^2 V_d dV. \quad (16)$$

The second term in (14) may be expanded to give

$$\frac{N^2}{V^2} e^2 \iint \frac{2f(r_2) + f^2(r_2)}{r_{12}} dV_1 dV_2 + \frac{N^2 e^2}{V^2} \int 2f(r_1) + f^2(r_1) dV_1 \int \frac{2f(r_2) + f^2(r_2)}{r_{12}} dV_2. \quad (17)$$

If the second term in (11) is expanded in a similar way and added to (17), we obtain

$$-\frac{N^2}{V^2} \frac{e^2}{2} \iint \frac{1}{r_{12}} dV_1 dV_2 + \frac{N^2}{V^2} \frac{e^2}{2} \int g(r_1) dV_1 \int \frac{g(r_2)}{r_{12}} dV_2. \quad (18)$$

The quantities involving $1/N$ which appeared in the last term can be easily shown to be negligible.

Combining all these results, we find

$$\begin{aligned} E_T = & \left\{ \sum_k \epsilon_k - \frac{N^2}{V^2} \frac{e^2}{2} \iint \frac{1}{r_{12}} dV_1 dV_2 + \frac{1}{2} \sum_{\alpha, \beta} \frac{e^2}{r_{\alpha\beta}} + E_e + E_c + E_r \right\} - \sum_{\alpha} V_d(r_{\alpha}) \\ & + \frac{N}{V} \int (1+f)^2 V_d dV - \frac{N}{V} \frac{\hbar^2}{2m} \int (1+f) \Delta (1+f) dV + \frac{N^2}{V^2} \frac{e^2}{2} \int g(r_1) dV_1 \int \frac{g(r_2)}{r_{12}} dV_2. \end{aligned} \quad (19)$$

If we assume that E_e and E_c are changed by relatively small amounts during the redistribution of charge, the expression in brackets gives the energy of the lattice before redistribution, except for terms involving the potential of the lattice defect.

1. The Interstitial Case

From the terms in (19) not in the bracket one can set aside

$$-\sum_{\alpha} V_d(r_{\alpha}) + \frac{N}{V} \int V_d dV. \quad (20)$$

They represent the interaction of the interstitial atom with the lattice in the state of uniform electronic distribution. We have previously shown by the s sphere argument that this quantity is small. The remaining terms in (19) give then the lowering of the energy with the polarization of the electronic charge.

By an application of Green's theorem,

$$\int (1+f)\Delta(1+f)dV = \int (1+f)\Delta f dV = \int (2+f)\Delta f dV, \quad (21)$$

we can express this polarization energy in the form

$$\frac{N}{V} \int (2+f) \left(-\frac{\hbar^2}{2m} \Delta + V_d \right) f dV + \frac{N^2}{V^2} e^2 \int g(r_1) dV_1 \int \frac{g(r_2)}{r_{12}} dV_2. \quad (22)$$

Though the integration indicated in the first term is over the whole lattice, it can be shown that the only non-negligible contribution arises from the region in the vicinity of the interstitial atom. A convenient estimate of the size of this term can be made by taking $f(r)$ to be the eigenfunction of the valence electron in a free copper atom, and, with this choice, the energy becomes

$$\epsilon_{Cu} \frac{N}{V} \int (2f+f^2) dv + \frac{N^2 e^2}{V^2} \int g(r_1) \int \frac{g(r_2)}{r_{12}} dV_1 dV_2, \quad (23)$$

in which $-\epsilon_{Cu}$ is the ionization energy of copper, namely 7.7 ev. For the limited region of integration, indicated by dv , $(2f+f^2)$ is equivalent to g . It is obviously necessary to assume that the interstitial ion polarizes the electronic charge distribution by one electronic unit since this is just sufficient to neutralize its charge at large distances. This means that $(N/V) \int g(r) dv = 1$. If the second integral of (22) is evaluated for the copper functions with the use of the same normalization for $g(r)$, it is found to have the value 5.0 ev. Thus the polarization energy is found to be about 2.5 ev in the present approximation. This indicates that the polarization energy is not sufficient to reduce the 13 ev of activation energy computed in the previous section for the unpolarized system to a value comparable with the observed value of 2.6 ev. As a result we may conclude that the interstitial mechanism is highly improbable in copper.

2. The Vacancy Case

We can make use of Eq. (19) also in computing the energy needed to form a vacancy. That part of the energy of the lattice before redistribution, which is represented by the expression in the brackets, excluding E_r , has already been discussed at length and shown to lie 7.34 ev below E_n , the energy of a normal lattice containing the same number of copper ions.

TABLE III. Summary of results.

	Direct Interchange A	Interstitial B C	Vacancy D E			Direct Interchange A	Interstitial B C	Vacancy D E	
Electronic energy in uniform distribution	11 ev	7.34 ev	8.2 ev		Total energy (Fuchs)		~8 ev	.4 ev	
After polarization		~4 ev	1.4 ev		Repulsive energy (exponential)	6.6 ev	5.5 ev	6 ev	-.4 ev
Repulsive energy (Fuchs)		3.85 ev	-1.0 ev		Total energy (exponential)	over 8 ev	~9.5 ev	1.0 ev	
				-.46 ev					

The first term which follows the bracket in (19) gives the electrostatic, ion-ion interactions which must be subtracted when a vacancy is formed. According to the sphere approximation this is equivalent to

$$-\frac{N}{V} \int (1+g_s) V_d dV, \quad (24)$$

in which g_s is a "step function" which is zero everywhere but in the vacant cell where it has the value minus one, and V_d is no longer the potential field of a copper ion, as it was in the case of the interstitial defect, but this field with a reversed sign, since the defect is now a vacancy. In the next term one may replace $(2f+f^2)$ by g . The combination of these two terms gives then

$$\frac{N}{V} \int (g-g_s) V_d dV. \quad (25)$$

The total energy can now be expressed,

$$E_T = E_n - 7.34 \text{ ev} + \Delta E_r + \frac{N}{V} \int (g-g_s) V_d(r) dV + \frac{N^2 e^2}{V^2} \frac{1}{2} \int g(r_1) \int \frac{g(r_2)}{r_{12}} dV_1 dV_2 + \frac{\hbar^2}{2m} \frac{N}{V} \int |\text{grad } f|^2 dV. \quad (26)$$

We evaluated the last three terms with the use of the function

$$f(r) = \begin{cases} \alpha r - 1 & r < 1/\alpha \\ 0 & r > 1/\alpha, \end{cases} \quad (27)$$

in which $\alpha^3 = 2/5r_s^3$, and obtained the result

$$\frac{0.12e^2}{r_s} + \frac{\hbar^2}{2m} \left(\frac{5}{2}\right)^{\frac{1}{3}} \frac{1}{r_s^2} + \frac{0.53e^2}{r_s}. \quad (28)$$

The first term was evaluated by determining the potential arising from the distribution $(N/V)e^2(g-g_s)$ and assuming that the ionic charge is localized within the region near the origin where this potential is nearly constant. Numerical evaluation of (28) gives $E_t - E_n = 1.9 \text{ ev} + \Delta E_r$. This result is not very sensitive to the analytic form chosen for (27). A function which avoids the discontinuity in derivative is a Gauss error function,

$$f(r) = -e^{-(r/d)^2}, \quad (29)$$

in which normalization determines d to be $0.775 r_s$. The corresponding energy needed to form a vacancy turns out to be 1.4 ev.

These results, like those found in the interstitial case, do not include the change in exchange and correlation energies that occurs in polarizing the distribution, nor does it include the change in ion

repulsion. The former will be discussed in detail in the paper by Huntington, whereas the latter was found in the preceding section to be -0.4 ev when the exponential-type function was used for the equilibrium configuration. The variational procedure then indicates about 1.0 ev as the complete energy needed to form a vacancy. For the saddle-point configuration, the change in the repulsive energy, when the exponential function is used, is found nearly the same, -0.37 ev, but the polarization of the electronic distribution is far less effective in lowering the energy for this configuration because of the more complicated density modulation that is involved.

IV. CONCLUSION

The results of these computations are summarized in Table III, and seem to show beyond a reasonable doubt that the vacancy mechanism of diffusion is greatly preferred over the other two types considered here for copper. A more careful treatment of the vacancy case, presented in the paper by Huntington, supports this conclusion further.

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Self-Consistent Treatment of the Vacancy Mechanism for Metallic Diffusion*

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Previous calculations have indicated the predominance of the vacancy mechanism in metallic self-diffusion. Here a more detailed calculation of the energy needed to form a vacancy has been carried out. A self-consistent solution to the Hartree-Fock equation was used with a free-electron model corresponding to the copper lattice. The result agreed essentially with the value predicted by Huntington and Seitz. In addition a rough upper limit was established for the energy required to move a vacancy. This value compares satisfactorily with the observed energy of activation for copper self-diffusion. The anisotropy recently observed in zinc self-diffusion can also be qualitatively explained to some extent on the basis of a vacancy process. In the case of the alkali metals present considerations are insufficient to decide between the interstitial and vacancy mechanisms.

INTRODUCTION

LATTICE vacancies are physically important in metallic diffusion. In the preceding paper¹ by Huntington and Seitz we investigated three possible mechanisms which might be responsible for diffusion in a typical metal, copper. Energetic considerations indicated definitely that vacancy diffusion plays the dominant role, as against interstitial diffusion and diffusion by direct interchange. The calculation for the energy needed to form a vacancy had, however, two short-

comings. In the first place, the wave functions used in the variational procedure were not a mutually orthogonal set, though the simplified treatment there employed necessarily used them as though they were. Secondly, no account was taken of the change in the exchange potential which must accompany any modulation of the electron distribution. Therefore it was decided to undertake a self-consistent solution of the problem in the Hartree-Fock approximation.

I. SELF-CONSISTENT SOLUTION FOR THE VACANCY PROBLEM

1. Potential Field near the Vacancy

To handle the problem at all it was necessary to use throughout the free-electron model with

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¹ Frederick Seitz and H. B. Huntington, *Phys. Rev.* **61**, 315 (1942); preceding paper. Equations, figures, and tables of this paper will be designated by primed references.