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 paper[1] 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 shortcomings. 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.

TABLE I. Wave function formulae.

		For r large	For r small	Density at small r
Uniform distribution	S	$\frac{\sin(kr)}{kr}$	$1-\frac{(kr)^2}{6}$	$\frac{k_m{}^3}{3}-\frac{k_m{}^5r^2}{15}$
	P	$\frac{\sin(kr)-kr\cos(kr)}{(kr)^2}$	$\frac{kr}{3}\left[1-\frac{(kr)^2}{10}\right]$	$\frac{k_m{}^5r^2}{45}$
Barrier distribution	S	$\frac{\sin(kr-\alpha_S)}{kr}$	$\frac{\sin(kR-\alpha_S)\sinh(Kr)}{\sinh(KR)kr}$	$\int_0^{k_m}\left[\frac{K\sin(kR-\alpha_S)}{\sinh(KR)}\right]^2dk$
	P	$\frac{d}{dr}\frac{\sin(kr-\alpha_P)}{k^2r}$	$\frac{\sin(kR-\alpha_P)}{\sinh(KR)}\times\frac{Kr\cosh(Kr)-\sinh(Kr)}{(Kr)^2}$	$\int_0^{k_m}\left[\frac{Kkr\sin(kR-\alpha_P)}{3\sinh(KR)}\right]^2dk$

uniform distribution to represent the original state of the copper lattice. Any lattice defect, such as a vacancy at a lattice site, would bring about a disturbance in the electron distribution, which would nearly possess spherical symmetry. The solution to the problem is then most simply expressed in a series of spherical harmonics which reduce at large distances to the well-known expansion of plane waves. Since the vacancy cell is a region of high potential, the electronic density is there necessarily reduced. The situation is closely analogous to a scattering problem in which electrons of various energies impinge from every direction upon a spherical barrier.

The form of this potential barrier is, to some extent, dependent upon the assumption made in setting up the problem. Since one wishes the solutions to reduce to plane waves at large distances, it is not practical to use the actual lattice potential, but rather to replace it everywhere by a constant value. The withdrawal of an ion to form a vacancy involves the introduction of a potential peak $-V(r)$, where $V(r)$ is the potential field of the ion, upon the uniform potential plane. As a consequence our potential field near the vacancy goes infinite as $r\rightarrow 0$, in contradiction to what one knows must be the case. This error is unimportant, however, because the region concerned is small and because it is the very region in which the uniform-distribution model breaks down. Since this potential infinity had no physical meaning, it was a great help in the work of numerical solution to consider the potential as being flat from $r=0.8a_0$ into $r=0$.

Besides the potential $-V(r)$ of the missing, or pseudo-"negative," ion at the vacancy site, there is also an electrostatic contribution from the electronic charge displaced from this region. This displaced charge is assumed equivalent to one electron, so that the vacancy region may be neutral at large distances.

2. Exchange Potential

In addition to these electrostatic forces some account was taken of the change in the "exchange potential" in the neighborhood of the vacancy as a result of the decrease in the electronic distribution. In general such an "exchange potential," $A_k(x)$, is written

$$A_k(x)=\frac{e}{2\chi_k(x)}\int\frac{\chi_k(x_1)\sum^{k'}\chi_{k'}(x_1)\chi_{k'}(x)}{|r-r_1|}dV_1 \quad (1)$$

and so varies with k. The χ_k are the wave functions of the metal. The summation over k' includes all the electrons of both spins. The use of such a set of A_k in solving for the self-consistent χ_k would lead to non-orthogonal functions. To avoid this it was decided to replace the $A_k(x)$ by a suitable average over k, $A(x)$. The procedure for averaging is determined only to the extent that $A(x)$ must reduce to $0.916e/r_s$ for plane wave functions, the eigenvalue for the exchange operator in that representation. Therefore in the interest of simplicity the following average was chosen,

$$A(x)\cdot\rho(x,x)=\frac{e}{2}\int\frac{\rho(x,x_1)^2}{|r-r_1|}dV_1, \quad (2)$$

where

$$\rho(x_1,x_2)=\sum^{k}\chi^*{}_k(x_1)\chi_k(x_2).$$

The problem of finding the exchange potential in the neighborhood of the vacancy is, to some extent, the radial analogue of the one-dimensional problem of the metal surface, which Bardeen[2] investigated when studying the influence of the double layer on the work function. (Bardeen used the $A_k(x)$ as he was concerned with the electronic densities rather than energies.) Since the problem involves spherical symmetry, it was convenient to expand the plane waves into spherical harmonics:

$$e^{ik\cdot r}=\sum^{n}(2n+1)i^n j_n(kr)P_n(\cos\theta). \qquad (3)$$

Here the $j_n(x)$ are the spherical Bessel functions[3] and the P_n are the Legendre polynomials. It soon became evident that only the S, P, and D parts of the wave (i.e., $n=0$, 1, 2) would be appreciably affected by the disturbing potential at the vacancy.

It is to be emphasized that the exchange contributions to this disturbing potential are the differences between the exchange potentials for the vacancy wave functions and those for the free electrons. Moreover, the exchange contribution is different for each harmonic. To see this one expands the vacancy wave functions also into spherical harmonics:

$$\begin{aligned}&S(kr)+3iP(kr)P_1(\cos\theta)\\&\qquad -5D(kr)P_2(\cos\theta)+\text{etc.}\end{aligned} \qquad (4)$$

Then A_S and A_P, the respective exchange potentials for the S and P parts, are evaluated from the expressions:

$$\begin{aligned}&\int|S(kr)|^2dV_k\cdot A_S\\&\qquad=\frac{e}{2}\int\int\frac{S^*(kr)S(kr_1)\rho(x,\,x_1)}{|r-r_1|}dV_kdV_1,\\&\int|P(kr)|^2dV_k\cdot A_P\\&\qquad=\frac{e}{2}\int\int\frac{P^*(kr)P(kr_1)\rho(x,\,x_1)}{|r-r_1|}dV_kdV_1,\end{aligned} \qquad (5)$$

where the summation over k states has been replaced by integration, not only as shown explicitly but also implicitly in the expression for $\rho(x,\,x_1)$. The k-volume element is $(2\pi)^{-3}2k^2dkd\omega_k$, where k is integrated from 0 to $k_m=1.92r_s$, and $d\omega_k$ is the solid angle in k-space. (The factor 2 is supplied by summation over spins.) This choice insures the normalization of electron density to unity over the unit cell.

Because of the complications involved, a general evaluation of the A's is very difficult. Instead one can expand about the center of the vacancy in powers of r (henceforth called ϵ) and investigate the size and curvature of A_S and the size of A_P, at this point. Since this point will give the largest values of the differences between vacancy and free-electron exchange potentials, a reasonable estimate can be deduced for the behavior throughout of this contribution to the disturbing potential. The factor $|\epsilon-r_1|^{-1}$ can be replaced by its expansion in harmonics:

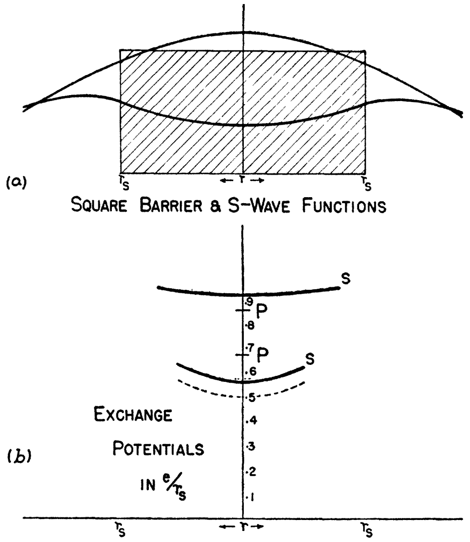

FIG. 1. (a) Comparison of $S(kr)$ for a square barrier with corresponding plane wave, $j_0(kr)$, for the free electron. The square-cut barrier is superimposed. (b) The exchange potentials for the harmonics in the neighborhood of the vacancy center. The upper full lines are for the free-electron functions, the lower full lines for the solutions of the square barrier, and the dotted lines for the self-consistent solutions.

$$\begin{aligned}&1/|\epsilon-r_1|\\&\qquad=\begin{cases}(1/r_1)\sum^{n}(\epsilon/r_1)^nP_n(\cos\theta) & \text{for } \epsilon<r_1,\\ 1/\epsilon & \text{for } \epsilon>r_1.\end{cases}\end{aligned} \qquad (6)$$

All three of the integrations over solid angle can

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[2] J. Bardeen, Phys. Rev. **49**, 653 (1936).

[3] See P. Morse's *Vibration and Sound*, pp. 246, 335.

now be carried out, with the help of the relation,

$$\int P_n(\cos\theta)P_n(\cos\theta')d\omega = 4\pi(2n+1)P(\cos\theta''), \quad (7)$$

where θ and θ' are referred to poles which make an angle of θ'' with each other. By considering no terms of higher order than ϵ^2, i.e. no D terms, one obtains the following expressions for the A's:

$$\begin{aligned} S(\epsilon,\epsilon)\cdot A_S(\epsilon) &= \frac{2e}{\pi}\left\{\int_0^\infty\left[\frac{|S(\epsilon,r)|^2}{r} + \frac{\epsilon}{r^2}S(\epsilon,r)P(\epsilon,r)+\cdots\right]r^2dr \right. \\ &\quad \left. -|S(\epsilon,\epsilon)|^2\int_0^\epsilon\left(\frac{1}{r}-\frac{1}{\epsilon}\right)r^2dr\right\} \quad (8) \\ P(\epsilon,\epsilon)\cdot A_P(\epsilon) &= \frac{2e}{\pi}\int_0^\infty\left[\frac{|P(\epsilon,r)|^2}{r} + \frac{\epsilon}{3r^2}S(\epsilon,r)P(\epsilon,r)+\cdots\right]r^2dr. \end{aligned}$$

Here $S(x,y)$ is an abbreviation for $\int_0^{k_m}S(kx)\times S(ky)k^2dk$ and similarly for $P(x,y)$.

If we consider first the A's for the free-electron distribution, then $S(kr)=j_0(kr)=(\sin kr)/kr$ and $P(kr)=j_1(kr)=(\sin kr - kr\cos kr)/(kr)^2$. All integrations over k and r can be performed exactly and give:

$$\begin{aligned} &\int_0^\infty |S(\epsilon,r)|^2 rdr = \frac{k_m^4}{4}-\frac{5k_m^6\epsilon^2}{36}, \\ &\int_0^\infty |P(\epsilon,r)|^2 rdr = \frac{k_m^6\epsilon^2}{108}, \quad (9) \\ &\int_0^\infty S(\epsilon,r)P(\epsilon,r)dr = k_m^6\epsilon/54. \end{aligned}$$

Solving for the $A_S(\epsilon)$ and the $A_P(\epsilon)$ we obtain [see Fig. 1b]

$$\begin{aligned} A_S(\epsilon) &= \frac{3ek_m}{2\pi}\left[1+\frac{2(k_m\epsilon)^2}{135}\right], \\ A_P(\epsilon) &= \frac{3ek_m}{2\pi}\,\frac{25}{27}. \end{aligned} \quad (10)$$

The constant free-electron exchange, $0.916e/r_s$, is given by $3ek_m/2\pi$. Moreover, if we take the weighted sum $S(\epsilon,\epsilon)A_S+3P(\epsilon,\epsilon)A_P$, the terms quadratic in ϵ drop out, as one would expect, since A is a constant for free electrons.

To obtain values for the exchange potential with vacancy distribution, one must make some choice of starting functions from which to work towards self-consistency. It was decided to represent the potential in the neighborhood of the vacancy by a square-wall barrier in the first approximation with height H for $r<R$ and zero elsewhere. For this case the wave solutions can be found immediately by fitting at the barrier wall. In Table I are compiled the analytic expressions for the S and P functions of both uniform and square-barrier distributions inside and outside the barrier. The respective contribution of each function to the density at the origin is also given. The α_S and the α_P are the phase shifts which appear in the vacancy wave functions as a result of the repulsive potential. For the S waves the α_S are given exactly as a function of k by

$$\cot(kr-\alpha_S)=(K/k)\coth KR, \quad (11)$$

where $\frac{1}{2}(K^2+k^2)$ in atomic units is equal to H. Expressions for α_P and α_D proved to be more complex, but could be closely approximated by

$$\tan\alpha_P=(2/45)kR^3H\sin^2 kR,$$

and

$$\tan\alpha_D=(2/1575)k^3R^5H\sin^2 kR. \quad (12)$$

The greater sensitiveness of the higher harmonics to the extent of the potential barrier is shown by the presence of the R^{2n+1} factor. On the other hand the height of the barrier appears only to the first power in each expression for the wave shifts. An actual barrier was next chosen with R equal to r_s and H equal to $\frac{1}{4}k_m^2$, since this seemed about the size needed to displace one electron from the region of the vacancy. A comparison between a square-barrier function $S(kr)$ and the corresponding $j_0(kr)$ of the uniform distribution is shown by way of illustration in Fig. 1(a). The square-barrier potential has been schematically superimposed.

The integrations over k, indicated in the expressions for $S(x,y)$ and $P(x,y)$, were next approximated by summing appropriately over five evenly spaced values of k. Then the inte-

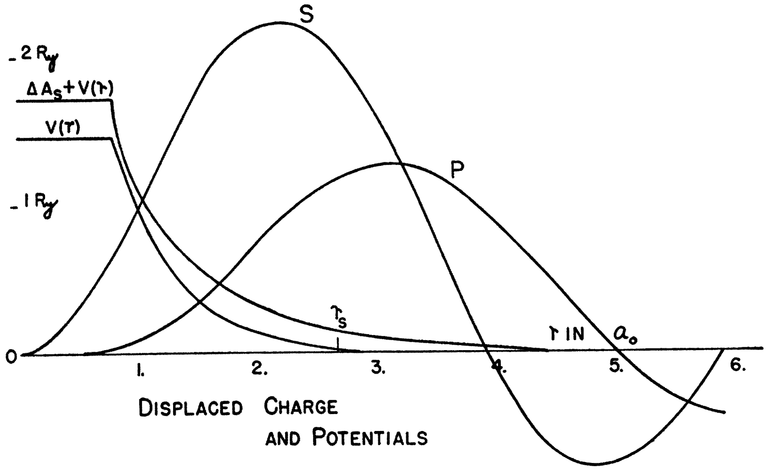

FIG. 2. The electrostatic potential for the first integration is shown here; also the potential used for the S functions formed by adding ΔA_S. The distribution of the displaced charge for the S and P functions are superimposed for comparison.

grations over r were carried out numerically with the following results:

$$\begin{aligned} S(\epsilon,\epsilon)&=(0.357-0.044\epsilon^2)r_s^{-3},\\ P(\epsilon,\epsilon)&=0.155\epsilon^2 r_s^{-3},\\ \int_0^\infty |S(\epsilon,r)|^2 r dr&=(0.164+0.081\epsilon^2)r_s^{-4},\\ \int_0^\infty |P(\epsilon,r)|^2 r dr&=(0.061\epsilon^2)r_s^{-4},\\ \int_0^\infty S(\epsilon,r)P(\epsilon,r)dr&=0.072\epsilon^2 r_s^{-5}. \end{aligned} \tag{13}$$

Here ϵ is measured in units of r_s. Substituting these values in Eq. (8), one obtains

$$A_S(\epsilon)=(0.56-0.26\epsilon^2)e/r_s$$

and

$$A_P(\epsilon)=0.67e/r_s. \tag{14}$$

In Fig. 1(b) these data for the square-barrier exchange potentials are shown in full lines. The corresponding quantities for the uniform distribution, also in full lines, lie above them. By subtracting one set from the other, one obtains

$$\Delta A_S(\epsilon)=(0.35-0.20\epsilon^2)e/r_s$$

and

$$\Delta A_P(\epsilon)=0.18e/r_s. \tag{15}$$

These differences describe the contributions of the exchange terms to the disturbing potential of the vacancy in the region of its center. Moreover these contributions must become negligible at about that distance where the distribution regains its normal density, or near $1.8r_s$. This information was sufficient to determine A_S with accuracy sufficient for our purpose, since the exchange terms did not play the dominant role in displacing the electrons. The shape of ΔA_P was taken similar to ΔA_S.

3. Integration of the Self-Consistent Solution

The contributions of the exchange potentials were next added to the potential of the "negative ion" and of the initial distribution of the displaced charge, which has been previously discussed. The initial distribution, which determines the shape of the "hole" formed in the electronic fluid about the vacancy site, was composed of about 60 percent of an S electron, 30 percent of a P electron, and 10 percent of a D electron. In their respective potential fields S and P functions were next integrated numerically for five evenly spaced values of k. If one writes $N_0R_{0,k}(r)$ for $krS(kr)$ and $N_1R_{1,k}(r)$ for $krP(kr)$, etc., the wave equation becomes

$$d^2R_{n,k}(r)/dr^2 - \left[2V_n(r)-k^2+\frac{n(n+1)}{r^2}\right]R_{n,k}(r)=0, \tag{16}$$

for the radial part of the nth harmonic, where

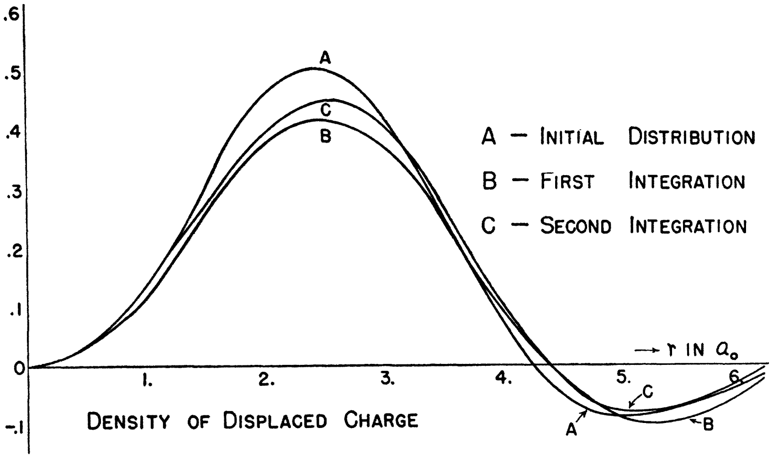

FIG. 3. Comparison of densities of displaced charge in units of ea_0^{-1} for the various distributions of each step in the self-consistent process.

atomic units have been used throughout. In the region from $r=0$ to $0.8a_0$ the V_n (the potentials appropriate to the harmonics in question) were taken to be constants, for reasons which have been previously discussed. Thus the starting conditions for the R_n were determined at $0.8a_0$ to fit with hyperbolic functions of the type used for the square barrier. Beyond the value $5a_0$, the $V_n(r)$ become nearly zero and one could identify N_0R_0 with $\sin(kr-\alpha_S)$ and N_1R_1 with $(1/kr)[\sin(kr-\alpha_P)-kr\cos(kr-\alpha_P)]$. The phase shifts α_n, could then be determined together with the normalizing constants, N_n.

After these functions were obtained, the next steps were to normalize them with multiplication by N_n, to square them, to average over k, and finally to subtract these densities from the corresponding quantities computed from the free-electron harmonics to get the distribution of displaced charge. In Fig. 2 the S and P contributions to this distribution are shown for this stage of the solution. What is plotted is the density of charge in a spherical shell of radius r as a function of r. The electrostatic potential and $V_{n=0}$ used in the integration are superimposed on the same graph. The results from this step give 0.49_0S electron and 0.35_8P electron. Little could be said about the D function with certainty, since the exchange potential was not known. Investigations of this potential in the region around $r=0$ would be necessarily laborious and give little information about this term at distances where the D function would be most sensitively affected. Certainly the effect of the exchange potential will decrease with increasing order of the harmonic. For the D function it may well be negligible. One integration was carried out by using the electrostatic potential alone. Comparing the phase shift so obtained with that of the corresponding square-barrier function, one could estimate, on the basis of an approximate treatment applied to the latter, that less than 3 percent of a D electron was displaced. In all this gives a total of nearly 88 percent electron displaced at this stage.

In the next step a new electrostatic potential was devised, essentially by treating the 88 percent electron as a whole. (It seemed reasonable to assume that the vacancy cell will be neutral at large distances.) New integrations gave 47 percent S electron and 44 percent P electron, whereas about four or five percent D electron was estimated. With the second step in the self-consistent process about 96 percent of an electron had been displaced. A new potential calculated from this distribution would differ but slightly from the previous one—it would show in fact a small increase. Adequate self-consistency, under the condition that one electron be displaced, seems assured to the accuracy with which it is feasible to determine the displaced D. The behavior of the initial distribution and of those from the two successive integrations is illustrated in Fig. 3.

With the final wave functions the exchange calculations were repeated, both to check the previous work and to determine the sensitiveness of the A_n to the distribution used. The results gave:

$$\Delta A_S = (0.42_4 - 0.27_8 \epsilon^2) e/r_s$$

and

$$\Delta A_P = 0.27_5 e/r_s. \tag{17}$$

The potentials from which these values are obtained are represented by dotted lines in Fig. 1, where they may be compared with the other exchange potentials.

4. Energy of the Vacancy

The procedure for setting up the expression for the energy of the vacancy is somewhat involved. Fortunately it resembles that followed in the preceding paper by Huntington and Seitz where the vacancy was treated by a variational method. Except for two important changes, the development is the same. In the first place the self-consistent wave functions are actually eigenfunctions of the vacancy problem in the expanded lattice. The mean value of the Hamiltonian for the kth electron, which was formerly written[4]

$$\begin{aligned}\int \psi_k(1+f) H \psi_k(1+f) dV &= \epsilon_k - \frac{\hbar^2}{2mV}\int (1+f)\Delta(1+f) dV \\ &+ \frac{1}{V}\int [1+f(r_1)]^2 \\ &\times \left[V(r_1) + \frac{e^2}{V}\int \frac{2f(r_2)+f(r_2)^2}{|r_1-r_2|} dV_2 \right] dV, \end{aligned} \tag{18}$$

now nearly corresponds with the energy parameter, ϵ'_k, of our self-consistent solution. The correspondence is not exact because in this paper we have been dealing with the Hartree-Fock equation, whereas in the other no attempt was made to take into account any change in the exchange energy. This marks the second important difference between the two procedures.

Let us investigate the ϵ'_k of the self-consistent solution. They differ from $(\hbar k)^2/2m$ of the free electrons because of the wave shifts introduced by the vacancy barrier. The new wave functions must satisfy the same boundary conditions as the eigenfunctions of the expanded lattice. At large distances the principal difference between the two sets of functions arises from the wave shifts, $\alpha(n, k)$. If we consider our copper specimen to be a sphere of radius R, then the wave number k' of the self-consistent solutions must be related to the k of the expanded lattice by the equation,

$$(k'R - \alpha) = kR, \quad \text{or} \quad k' = k + (\alpha/R). \tag{19}$$

There is then a small change in k, inversely proportional to the linear dimensions of the copper crystal. The change in energy parameter of a given electron wave is given by $2k\alpha/R$ in Ry. The number of wave functions belonging to the same harmonic but to different values of k is given by $N = k_m R/\pi$. For a given harmonic it follows that the increase in the energy parameters is given by

$$\Delta E_n = \frac{2(2n+1)}{\pi} \sum_0^{km} k\alpha(n, k) \text{ in Ry.} \tag{20}$$

The value of the summation was approximated by taking k_m times the evenly weighted average of the five values for $k\alpha$ obtained from the five integrations for S and P harmonics. Results gave $\Delta E_0 = 0.103$ Ry for S and $\Delta E_1 = 0.048$ Ry for P.

In the final expression for the energy in the variational scheme, Eq. (19′), the term involving the Laplacian of f appears. It measures the difference in the kinetic energies of the modified wave functions and the free-electron waves of the "expanded lattice." Since the left-hand side of Eq. (18) can be evaluated as the sum of the ϵ'_k of the self-consistent solution, one can solve this equation for the kinetic term and obtain the expression

$$\Delta E_0 + \Delta E_1 - \int \rho_s(r_1) \times \left[V(r_1) + e^2 \int \frac{\rho_s(r_2) - \rho_u(r_2)}{|r_1 - r_2|} dV_2 \right] dV_1. \tag{21}$$

Here the subscripts u and s on the density functions refer to the uniform and self-consistent functions, respectively.

There is still to be treated the second point of difference between the two procedures. When the

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[4] Compare with Eq. (12′) and (13′).

variational attack was used, no attempt was made to take into account any change in the exchange potential. Now that the recent method has incorporated into it a term of this nature in the potential field used in solution, one must finally subtract away one-half of the average exchange potential, in accordance with the standard procedure for obtaining the total energy in the Hartree-Fock approximation. The quantity to be included can be written as follows:

$$-\tfrac{1}{2}\int (A_s\rho_s - A_u\rho_u)dV =$$

$$-\tfrac{1}{2}\int (A_s - A_u)\rho_s dV + \tfrac{1}{2}\int A_u(\rho_u - \rho_s)dV. \quad (22)$$

The exchange operator for plane waves, A_u, is a constant, and consequently the second term on the right vanishes. The first term can be treated by breaking it up into S and P parts.

A compilation of the terms which enter into the energy of the formation of a vacancy follows here. It contains the energy of the "extended lattice" and the potential terms analogous to those appearing in the earlier treatment, the kinetic energy expressed in its new form, and finally the exchange terms just discussed above.

TABLE II. Energy contributions from neighbors for "D" configuration.

	Exponential	Displaced Fuchs
Lattice potential term	0.00 ev	0.02 ev
Dipole interactions	0.00 ev	0.03 ev
Shielded vacancy ion potential	0.84 ev	0.90 ev
Ion-core repulsions	−0.24 ev	−0.68 ev
	0.60 ev	0.27 ev
Value for λ-parameter	0.00	0.01

Energy of the "extended lattice"	−0.544 Ry
Self-energy of the displaced charge	0.393
$\int\left[\rho_u - \rho_s - \frac{N}{V}g_s\right]V(r)$ (see Eq. (31′))	0.168
Change in the energy parameters for the S functions	0.103
Change in the energy parameters of the P functions	0.048
$-\int \rho_s(r_1)\left[V(r_1) + e^2\int\frac{\rho_s(r_2)-\rho_u(r_2)}{\lvert r_1-r_2\rvert}dV_2\right]dV_1$	−0.017
Exchange term for the S function	−0.051
Exchange term for the P function	−0.009
	1.23 ev = 0.091 Ry

This result is surprisingly close to the 1.4 ev found by the variational method with the use of a function of the Gauss error type in the neighborhood of the vacancy. Evidently the decrease in energy, which one would expect in a numerical solution, has been compensated in part by the inclusion of the change in the exchange potential.

The radial distributions plotted in Fig. 3 show that the density is *greater* than its normal value at distances of $5a_0$ and $6a_0$. Apparently the electrostatic potential of the vacancy is actually positive at a radius equal to the interatomic distance. Some electrostatic considerations can now be used in conjunction with the results already obtained for the repulsions of closed shells to redetermine the positions of next neighbors. There are first the potentials of the vacancy and of the lattice,

$$12\left[E\left(\frac{\lambda a}{2}, \frac{\lambda a}{2}, 0\right) - E(0) + \left\{-V(r_1) - e^2\int\frac{\rho_s(r_2)-\rho_u(r_2)}{\lvert r_1-r_2\rvert}dV_2\right\}_{r_1=a\sqrt{2}(1-\lambda)/2}\right]. \quad (23)$$

The potential of the lattice for an ion in its own cell, $E(x)$, can be accurately calculated by some method such as Ewald's, but for these purposes it will be adequately represented by the quadratic term of central symmetry, r^2/r_s^3 Ry. The displacement of nearest neighbors toward the vacancy is given by $\lambda\sqrt{2}a/2$. There are, in addition to (23), the interactions of the displacements of the various neighbors, which may be calculated by the standard formula for dipole-dipole energy. The results after including these quantities are shown in Table II. The exponential repulsion gives the energy of neighbors as 0.6 ev, the Fuchs repulsion as 0.3 ev with λ equal to 0.01. In each case the positive contribution from the electrostatic interactions has overbalanced the decrease in the repulsive energy. Final values for the energy needed to form a vacancy are 1.8 ev and 1.5 ev, according to the exponential and Fuchs repulsion, respectively.

The large increase in the electrostatic energy just considered is to some extent a spurious effect, which arises because the spherical modulation of the wave function alone is inadequate at large distances from the vacancy center. This situation with the next neighbors contributes the largest uncertainty in the value for the energy of vacancy formation. The next largest causes for error arise from the use of the free-electron model and from the limited degree of accuracy to which the self-consistent solution has been carried.

II. UPPER LIMIT TO THE ENERGY OF THE SADDLE-POINT

Unfortunately the saddle-point for vacancy diffusion, configuration E,[5] cannot be treated as rigorously as the situation in the preceding section. Here the problem is more complicated because only symmetry about the direction of diffusion remains. A direct attack by the variational method would give a reasonably good answer, since the variational and Hartree-Fock methods have shown substantial agreement in the preceding case. Unfortunately the integrations involved in the self-potential and kinetic terms would be extremely awkward. I have chosen instead a rather makeshift approach, which nevertheless can give considerable information. There follows a discussion of the model employed and the assumptions which are necessarily made in treating it.

1. Description of the Assumed Electronic Distribution

As before, we start from a uniform distribution in the "expanded" lattice with its energy of -7.34 ev. Next in the region of diffusion two vacancy cells are placed at adjoining sites, and a diffusing ion is put halfway between them. Suppose this ion brings with it its atomic cell and that this cell is deformed to include the region about the diffusing ion which is not part of the polyhedron cells of its four nearest neighbors.[5] Then the deformed atomic cell will fill up one-half of each of the vacancy cells on either side. The rest of these vacancy cells will be henceforth referred to as the "regions outside atomic cells," and they may be taken to be hemispherical in shape, as shown by the cross-hatched areas in Fig. 4(a). These regions have a high potential energy as compared with the rest of the lattice. In line with previous treatment one must introduce some modification of the electronic distribution to decrease the density of charge at these places. The only kind of distribution which can be dealt with simply, i.e., without introducing extremely complicated spatial integrations for the kinetic and potential terms, must possess spherical symmetry. Accordingly a model was chosen in which there were removed two spherical distributions, each of charge $\frac{1}{2}e$, one from each hemisphere. The center of each distribution was placed at the centroid of the respective hemisphere, and its radial behavior was taken to be the same as that of the self-consistent solution in Part I for the single vacancy, except that the radial scale was reduced by the factor $1/\sqrt[3]{2}$ (see Fig. 4(b)).

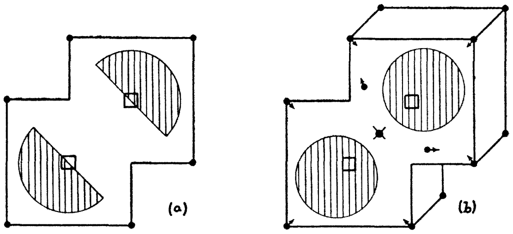

FIG. 4. (a) A model for the two-vacancy configuration, where the "regions outside atomic cells" are shown as two hemispheres separated by the cell of the diffusing atom. (b) Here the spherical holes of charge $\frac{1}{2}e$ have been made in the electronic distributions, as represented by the cross-hatched, circular areas. The centers of these charge holes coincide with the centroids of the hemispheres shown in (a).

There are several apparent defects in this model and it is well to examine them critically before proceeding. In the first place no account has been taken of the change in form of the self-consistent solution when applied to the smaller "region outside atomic cells." Such a charge hole will be relatively more shallow, as a rigorous solution would show. To obtain an upper limit for the energies involved, however, the present procedure will suffice. A far more serious shortcoming, I believe, is the fact that the charge taken from the hemispherical "regions outside atomic cells" has been assumed to have a spherical arrangement. This is very different from what is actually the case, but one must remember that, even for the exact solution of the problem of the hemispherical potential barrier, the surfaces of equal electronic density will have a more nearly spherical form than the equipotentials of the barrier itself. This reduces modulation of the

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[5] See Fig. 2 in preceding paper.

wave functions and resulting kinetic energy. At a later point an estimate of the involved error will be made by calculating the increase in kinetic energy which would accompany the deformation of our charge holes from spherical form into oblate spheroids of the same volume. Finally the assumed electronic distribution of the two charge holes leaves the density of charge about the diffusing ion at its uniform value, whereas we know that this cell is at a higher potential than the rest of the crystal and consequently collects some extra charge within it. This latter is, however, a minor defect and probably causes only a small error in the final energy value for this model.

2. The Ion-Ion Electrostatic Interaction

Before proceeding with the charge holes, one considers the increase in the ion-ion electrostatic interaction which comes about when the diffusing atom moves to the saddle-point position. If one starts with a vacancy and the uniform distribution of the "extended" lattice, then the increase in energy of the lattice as a whole, when one of the neighboring ions moves halfway in to fill up the vacancy, is given by

$$E(\tfrac{1}{4}a,\, \tfrac{1}{4}a,\, 0)-E(0)-\sqrt{2}e^2/a. \tag{24}$$

The last term comes from the change in the Coulomb interaction of the diffusing ion with the "vacancy ion" (negative). Actually the expression (24) gives a negative result. The reason for this is that, while the diffusing cell moves to a higher potential, the self-potential energy of the charge outside atomic cells has decreased from that of a uniformly charged sphere to that of two uniformly charged hemispheres at a distance L apart, where L, the distance between the centroids of the two hemispheres, is $\frac{1}{2}\sqrt{2}a+\frac{3}{4}r_s$. The classical problem of the self-potential of a uniformly charged hemisphere cannot be solved in closed form but estimates (as obtained in Appendix I) place the size of this energy at approximately nine-tenths of that for a sphere of the same charge density and total charge. For a uniformly charged sphere the self-potential is $0.6C^2/R$, where C is the total charge and R is the radius. Then the change in the energy of the charge outside atomic cells is given by

$$0.6\left[\frac{e^2}{r_s}-2(0.9)\left(\frac{e}{2}\right)^2\frac{\sqrt[3]{2}}{r_s}\right]-\frac{e^2}{4L} \tag{25}$$

and this term must be added to (24) to give the increase in the electrostatic ion-ion interaction for the diffusing ion.

3. Consideration of the Charge Holes

At this point one introduces "vacancy ions" of charge $-\frac{1}{2}e$, placed at the centroids of the hemispheres. The uniform distribution is replaced by the modulated distribution containing the two charge holes, as has already been postulated. The terms which occur in the expression for the energy for the one-vacancy "D" configuration can now be taken over into this calculation, after they have been multiplied by the appropriate factor, as determined by dimensional analysis. For the "D" configuration the kinetic energy in Eq. (21) was obtained from the difference between the change in the energy parameters of the electron waves and the integral of the final distribution in the final vacancy field. Within vacancy cells, whose linear dimensions are reduced by the factor $2^{-\frac{1}{3}}$, this term is accordingly multiplied by $2^{\frac{2}{3}}$. In considering the potential terms the relatively less important exchange potentials were combined with the corresponding electrostatic terms. The self-energy quantities were multiplied by $2^{-\frac{2}{3}}$, as obtained from reasoning exactly analogous to that applied above to the uniformly charged spheres. In addition the interaction of the two charge holes gives $e^2/4L$, which cancels a similar term of the opposite sign in Eq. (25) of the preceding paragraph. A factor $2^{-\frac{2}{3}}$ multiplies also the quantity

$$\int\left[\rho_u-\rho_s-\frac{N}{V}g_s\right]V(r)dV. \tag{26}$$

These considerations do not give the complete energy for the formation of the two charge holes, since there has been omitted any account of the error introduced by replacing the high potential hemispheres with "vacancy ions" of charge $-\frac{1}{2}e$. There seems, however, no convenient way to compute simply and directly this effect.

4. Behavior of Nearest Neighbors

Some revision of those quantities, as given in Table II , which relate to atoms adjacent to the site of the diffusion jump, can now be made by including electrostatic forces with the ion-ion repulsions. In our procedure we have added to the regular lattice potential, two negative "vacancy ions," one positive diffusing ion, and two holes in the negative electron charge. For the four nearest neighbors of the diffusing ion, the following electrostatic terms are to be considered in addition to the previously calculated ion-core repulsions:

(a) The potential of the lattice for the ion in its cell, which can be conveniently approximated as before by r^2/r_s^3 Ry.

(b) The energy gained by allowing each ion to retreat from the diffusing ion a fraction, λ, of its equilibrium distance, which is given per ion by

$$\frac{2\sqrt{2}e^2}{\sqrt{3}a}\left[\frac{1}{1+\lambda}-1\right].$$

(c) Finally, the Coulombic interactions with the "negative ions" and the charge holes. Here the λ displacement can be treated as a dipole of moment $-\frac{1}{4}6^{\frac{1}{2}}\lambda ae$. The distance between the diffusing ion and a charge hole is nearly $\frac{1}{2}a$. The distances from the displaced neighbor to the negative ions and to the charge holes are, respectively, $\frac{1}{2}\sqrt{2}a$ and $\frac{1}{4}10^{\frac{1}{2}}a$. Accordingly these terms give

$$-\frac{6^{\frac{1}{2}}}{4}\lambda ae\left[-2e\cdot\frac{\sqrt{3}}{2}\cdot\frac{2}{a^2}+e\cdot\left(\frac{3}{5}\right)^{\frac{1}{2}}\cdot\frac{8}{5a^2}\right]. \quad (27)$$

TABLE III. Energy contributions from neighbors to "E" configuration.

	Exponential	Displaced Fuchs
17 broken repulsive contacts	−0.69 ev	−1.65 ev
Energy of 14 "D"-type neighbors	0.98 ev	0.99 ev
Energy of 4 neighbors of diffusing ion	0.89 ev	1.56 ev
	1.18 ev	0.90 ev
Value of λ-parameter for 4 neighbors	0.08	0.025

The combination of these three contributions with the curves for ion-core repulsion has a minimum of about 0.89 ev with λ equal to 0.08—exponential repulsion, and a minimum of 1.56 ev with λ equal to 0.025—Fuchs repulsion.

As before the fourteen neighbors, which adjoin only one or the other of the two vacancies, can be treated as though they were simply neighbors of a "D"-type vacancy. This is not strictly true, but a detailed consideration would hardly be consistent with the other approximations involved. The energy of such a neighbor of a "D"-type vacancy has already been treated in the preceding section. All the terms for the saddle-point, which depend upon neighboring ions, are compiled in Table III. The energy for exponential repulsion is given as 1.18; for the Fuchs repulsion, 0.90 ev.

5. Compilation of Terms

From the terms so far considered some idea can be gained of the energy for the E configuration as follows:

$E(\frac{1}{4}a, \frac{1}{4}a, 0)-E(0)$	$1.177\ e^2/a$	
$-\sqrt{2}e^2/a$	$-1.414\ e^2/a$	
$0.6\ e^2/r_s[1-(2)^{-\frac{2}{3}}(0.9)]$	$0.663\ e^2/a$	
Ion-ion electrostatic energy	$0.426\ e^2/a=$	1.698 ev
Kinetic energy term		2.94 ev
Self-energy of charge in electronic distribution		2.84 ev
$\int[\rho_u-\rho_s-(N/V)g_s]V(r)dV$		1.43 ev
Expanded lattice term		−7.34 ev
		1.55 ev

	Exponential		Displaced Fuchs
With the inclusion of neighbor terms	2.73 ev	or	2.45 ev

6. Estimate of an Upper Limit

Because an important potential term has been omitted in obtaining these values for the energy with the two spherical charge holes, the results cannot be considered to represent an upper limit to the activation energy for diffusion. It is possible to estimate the error by the following argument.

The potential term which has been neglected in the preceding treatment would have been unimportant if the shape of the charge distribution had been chosen to minimize its interaction with the hemispheres of high potential. A nonspherical distribution would have also a lower self-energy but its kinetic energy would be increased. One can estimate the increase by this device: Suppose $F(r)$ is a spherically symmetric wave function for which the associated kinetic energy is known. By a volume-conserving transformation of coordinates one obtains a new wave function $F\{[(x^2/\lambda^2)+\lambda y^2+\lambda z^2]^{\frac{1}{2}}\}$. It can be shown (see Appendix II) that the kinetic energy resulting from the Laplacian of the new function is $\frac{1}{3}(\lambda^{-2}+2\lambda)$ times that of the old. Let the x axis coincide with the direction of the diffusion and set λ equal to the ratio of the radius of the hemisphere to the diameter of the equivalent sphere, namely 0.628. Consequently the kinetic energy associated with the new wave function is higher by 27 percent than that of the spherically symmetric one. This increase, or 0.79 ev for our case, is a measure of the inaccuracy of the two-vacancy procedure. If it is added to the other results, it gives for *upper limits* to the energy of the saddle-point, 3.52 ev on the exponential basis, and 3.24 ev with the displaced Fuchs curve.

The experimental value for the energy of activation for copper is 2.6 ev, as given by Steigman, Shockley, and Nix.[6] This lies in the region where the present results indicate that the energy for configuration E is also located. The approximations throughout have the effect of putting the energy values too high with a probable error of roughly 35 percent. Within such limits the agreement is satisfactory. On the other hand Fuchs made use of a modified free-electron model in his work on copper. His result for the binding energy is less than half the experimental value, as can be seen from Table I′ in the preceding paper. That such a discrepancy has not been encountered here in calculating the activation energy for diffusion indicates that the computed energies for vacancy configurations are not greatly sensitive to the inadequacies of the models assumed for the normal state of the metal.

The ion-core repulsion term is relatively unimportant for the vacancy configurations. It is fortunate that the uncertainty of its behavior did not prevent the determination of the favored mechanism for diffusion. In this regard it may be emphasized that these results definitely complete the case for vacancy diffusion from the theoretical standpoint. It has been shown that the energy of the saddle-point for this process lies below those required in either interstitial or direct-interchange diffusions.

III. EXTENSION TO OTHER METALS

It is natural to inquire to what extent these results for copper may be applied to other metals. It should be pointed out that it is the ion-core repulsion which plays the dominant role in eliminating from consideration the interstitial and direct interchange processes. There is reason to believe that the same forces would be important for metals near copper in the periodic table.

The self-diffusion of zinc, both in single crystals and in polycrystalline specimens, has been studied by Banks and Miller.[7] Their results indicate that diffusion in this substance is strongly anisotropic. From preliminary work they give that the energy of activation is about 0.85 ev along the c axis and about 1.24 ev in the basal plane. It is customary to set the diffusion constant equal to $D_0e^{-Q/RT}$, where Q is the activation energy for diffusion and D_0 is the temperature independent factor. It is also found that the D_0 for the diffusion constant for the basal rate is larger by a factor of about 10^3 than for the corresponding quantity for diffusion along the hexagonal axis.

Because zinc is very far from a free-electron metal, such calculations as we have applied to copper are out of the question here. Nevertheless some qualitative remarks, based on consideration of a simple, central-force law, can be made concerning the relative probabilities that a vacancy is filled by an atom in the same basal plane, or by a neighboring atom in an adjoining plane. For a close-packed hexagonal lattice the atom which makes the jump to fill the vacancy, whether it stays in the same basal plane or not, must pass through an activation point where it is equidistant from four of its neighbors. The shortest distance of approach is $(\sqrt{3}/2)$ times the normal interatomic distance. For such a close-packed lattice one would expect nearly isotropic diffusion. Actually zinc departs from close-packing by a 14 percent elongation along the hexagonal axis. In

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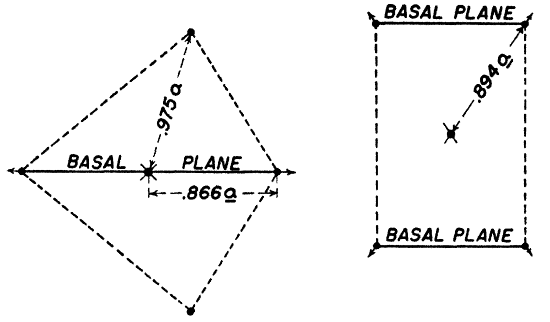
[6] J. Steigman, W. Shockley, and F. Nix, Phys. Rev. **56**, 13 (1939).

[7] Floyd R. Banks, Phys. Rev. **59**, 376 (1941); F. R. Banks and P. H. Miller, Phys. Rev. **59**, 943A (1941).



JUMP IN BASAL PLANE (a) NON-BASAL JUMP (b)

FIG. 5. Positions for diffusing atom in a zinc lattice. ✳ Diffusing atom. ● Neighboring atom. a Normal interatomic distance in the basal plane. In each case there are indicated the positions of the diffusing atom and its four nearest neighbors at the instant when the diffusing atom is halfway between vacancies. The plane section presented is that perpendicular to the path of the jump.

Fig. 5(a) the diffusing atom and its four nearest neighbors are shown in a cross section, perpendicular to the direction of diffusion, at the midpoint of a jump in the basal plane. The corresponding configuration for a jump from one basal plane to another is shown in Fig. 5(b).

If one calculates the activation energy for each case, the results turn out to be sensitive to the type of repulsive law chosen to represent the action of the ion-cores at close distances. For the exponential type, under certain conditions, the basal diffusion has a slightly higher activation energy than the non-basal diffusion. A curve of repulsion like Fuchs' would reverse the situation. Even with the exponential repulsion it seems hardly possible to account for the observed difference in activation energies, but there can be no doubt that such a treatment is far too simplified for the problem. This investigation does, however, throw some light on the reason for the larger D_0 for basal diffusion. In this case only the two neighbors in the same basal plane are near enough to obstruct the diffusing atom. For a jump from one adjoining plane to a vacancy in another, the moving atom is obstructed equally by four neighbors. It is evident that occasions propitious for a *basal* jump occur when *two* neighbors are favorably displaced from their equilibrium positions. On the other hand the *non-basal* jump is a more highly cooperative process since it depends on the favorable displacement of *four* neighboring atoms. One would expect that opportunities for the latter process would occur much more rarely.

To summarize the argument, then, one can remark the following: Self-diffusion rates in zinc appear to be markedly anisotropic. Were zinc strictly close-packed hexagonal, such a behavior would be difficult to explain on any model of diffusion. Taking into account the observed departure from close-packing and a rapidly increasing, close-range repulsive potential, one is able to show that the mechanism of vacancy diffusion predicts qualitatively at least the observed anisotropic behavior of the temperature-independent factor in the expression for the diffusion constant.

For the alkali metals the situation is to some extent reversed, in that they adhere quite closely to the free-electron model in their behavior, which greatly simplifies the theoretical problem. On the other hand no experiments have been performed to measure self-diffusion and there is little prospect that such experiments can be devised for some time to come.

When the results of the copper calculation are extrapolated to the alkalis with their larger lattice constants, the various kinetic and potential terms are decreased in size accordingly as their dependence on r_s indicates. The energy for the "extended lattice" can be taken from the analytic expression derived from free-electron consideration, or still better, from the sum of the ionization potential and heat of sublimation minus the work function, since Wigner and Bardeen[8] have shown that the two agree closely. The repulsions of the ion-cores can be treated with some assurance since the Born-Mayer formula has been well tested for its validity in dealing with these elements. The energies are, however, much smaller, of the order of 0.1 ev for an interstitial position, as contrasted to 6 ev for copper. In this way one can obtain crude values for the energies needed to form an interstitial atom, or a vacancy. Two clear deductions can be made. First, these energies range around one or two ev. Second, the interstitial and vacancy mechanisms are in much closer competition for the alkali metals than for copper, because here

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[8] E. P. Wigner and J. Bardeen, Phys. Rev. **48**, 84 (1935), see Fig. 1.

the ion-core repulsion is nearly negligible. A more detailed attack, perhaps along the lines of the foregoing self-consistent solution, is required, before one can state with definiteness which is the important mechanism for diffusion in the case of any given alkali.

The author wishes to express his very sincere thanks to Professor Frederick Seitz for suggesting this problem to him and for his many helpful suggestions and criticisms in the course of its development.

APPENDIX I. ESTIMATE OF THE SELF-ENERGY OF A HEMISPHERE

An estimate for the self-energy of a uniformly charged hemisphere was obtained by the two following simple lines of investigation. In each case it turned out to be about ten percent lower than the self-energy of the sphere with the same charge density and total charge.

Along the axis of the hemisphere the potential can be found directly by a simple integration in polar coordinates. For that part of the axis which lies inside the hemisphere the potential is given by

$$P_i(\alpha)=\frac{e}{2r_s}\left\{\frac{3}{2}+\frac{(1+\alpha^2)^{\frac{3}{2}}-1}{\alpha}-2\alpha^2\right\}, \tag{28}$$

where $\frac{1}{2}e$ is the total charge, r_s is the radius of the hemisphere and α is the ratio R/r_s. The distance between the field point and the center of the polar system of coordinates is measured by R, with the positive direction on the same side as the hemisphere. This potential has a maximum near the centroid of the hemisphere at $\alpha=\frac{3}{8}$. On substitution one gets $P(\frac{3}{8})=1.795$ in $e/2r_s$. The potential at the center of the equivalent sphere is $1.5e(2)^{\frac{1}{3}}/2r_s$, or 1.892 in $e/2r_s$. This shows that the potential plateau is five percent lower for the hemisphere than for the sphere. We may assume that the self-energy of the two bodies will differ by twice as much, or ten percent.

A more convincing line of argument is to consider a complete sphere sliced into two hemispheres. Since the self-energy of the sphere is known, the problem reduces to finding the potential interaction of one hemisphere with the other. We approximate this by the potential of one hemisphere at the centroid of the other. Along the negative direction of the axis of the hemisphere we have

$$P_-(\alpha)=\frac{e}{2r_s}\left\{\frac{3}{2}-\frac{(1+\alpha^2)^{\frac{3}{2}}-1}{\alpha}+\alpha^2\right\}. \tag{29}$$

Since $P_-(\frac{3}{8})=1.067\,e/2r_s$, the interaction of the hemispheres is approximated by $0.267\,e^2/r_s$. The self-energy for the sphere is $0.6\,e^2/r_s$, and there is left then for each hemisphere $0.167\,e^2/r_s$. For the equivalent sphere the self-energy is $0.6\,e^2(2)^{\frac{1}{3}}/4r_s$, or $0.189\,e^2/r_s$. The value for the hemisphere is about 12 percent below the corresponding self-energy for the sphere.

APPENDIX II. KINETIC ENERGY OF A SPHEROIDAL DISTRIBUTION

The kinetic energy associated with a wave function possessing spherical symmetry, say $F(r)$, is proportional to the integral,

$$\int F(r)\nabla^2F(r)dV=\int F(r)\left[F''(r)+\frac{2}{r}F'(r)\right]dV. \tag{30}$$

If a new wave function is obtained by a volume-conserving transformation, the normalization will be unaltered. The Laplacian of $F([x^2/\lambda^2+\lambda y^2+\lambda z^2]^{\frac{1}{2}})$ is, when developed in Cartesian coordinates,

$$\begin{aligned}&\left[\left(\frac{x}{\lambda^2\rho}\right)^2+\frac{\lambda^2}{\rho^2}(y^2+z^2)\right]F''(\rho)\\&\qquad+\left[\left(\frac{1}{\lambda^2}+2\lambda\right)-\frac{1}{\rho^2}\left\{\left(\frac{x}{\lambda^2}\right)^2+\lambda^2y^2+\lambda^2z^2\right\}\right]\frac{F'(\rho)}{\rho},\end{aligned} \tag{31}$$

where ρ has been written for the argument of F. If this expression is substituted in (30) and the inverse transformation, $x=\lambda\bar{x}$, $y=\lambda^{-\frac{1}{2}}\bar{y}$, $z=\lambda^{-\frac{1}{2}}\bar{z}$, and $\rho=\bar{r}$, is employed, then the integral becomes

$$\begin{aligned}\int F(\bar{r})\Bigg[&\frac{F''(\bar{r})}{(\bar{r})^2}\left\{\left(\frac{\bar{x}}{\lambda}\right)^2+\lambda(\bar{y}^2+\bar{z}^2)\right\}\\&+\frac{F'(\bar{r})}{\bar{r}}\left\{\frac{1}{\lambda^2}+2\lambda-\frac{1}{\bar{r}^2}\left(\frac{\bar{x}^2}{\lambda^2}+\lambda\bar{y}^2+\lambda\bar{z}^2\right)\right\}\Bigg]dV.\end{aligned} \tag{32}$$

The form of the integration is unaltered, because the transformation has left the size of the volume element unchanged and because the limits extend to infinity. If one now averages over angle, replacing $\bar{x}^2/\bar{r}^2$, etc. by $\frac{1}{3}$, the resulting expression is $\frac{1}{3}[(1/\lambda^2)+2\lambda]$ times the kinetic energy expression associated with the original, spherically symmetric wave function.