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Ring Diffusion in Metals*

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(*Received* 15 *December* 1949)

The concept of hole migration in metals as the mechanism of self-diffusion and of diffusion of substitution-solute atoms has arisen from the apparent failure of other reasonable mechanisms, such as direct interchange, to give heats of activation comparable to those observed. In the present paper it is pointed out that diffusion by direct interchange is only a special case of diffusion by the synchronized cyclic motion of a number of atoms, herein called ring diffusion. General arguments are presented demonstrating that a 4-ring has a lower potential-energy barrier for cyclic motion than has a 2-ring, which corresponds to direct interchange. These general arguments are supported by detailed calculations for the particular case of self-diffusion in copper. It is concluded that such ring diffusion is not excluded by energy considerations.

1. Introduction and results

In their study of the self-diffusion of copper, Huntington & Seitz (1942) found that in that metal an interchange of two neighboring atoms would require much more work than is represented by the observed heat of activation. They further found that this observed heat of activation is consistent with the concept that self-diffusion occurs by the mechanism of hole migration. That such migration does in fact occur in some appears (Smigelskas & Kirkendall, 1947) to be required by the Kirkendall experiment (R. Mehl, private communication). In the absence of any other mechanism of diffusion consistent with the observed heats of activation we would, therefore, be forced to accept hole migration as the primary mechanism responsible for self-diffusion in all metals as well as the diffusion of substitutional solute atoms. The purpose of this paper is to examine another possible mechanism.

Previous discussions of the mechanism of the diffusion of lattice atoms, as distinct from interstitial atoms, have started from the assumption that such diffusion must occur either by direct interchange of two neighboring atoms or by hole migration. While recognition has been indicated of the fact that disturbances involving the displacement or rotation of larger groups of atoms would also lead to diffusion (Le Claire, 1949, pp. 340–1), it has been implicitly assumed that the larger the group which participates in the elementary diffusion process the larger must be the work required to carry it over the free-energy barrier. The essential fallaciousness of this viewpoint is apparent once we recognize the smallness of the work per atom required to distort homogeneously a lattice to an unstable configuration midway between two stable configurations. Thus the author has shown (Zener, 1948, p. 36) that a work equivalent to only about 1600 cal./mole is required to strain homogeneously a copper lattice from one stable face-centered cubic (f.c.c.) configuration through an unstable body-centered cubic (b.c.c.) configuration on its way to a second f.c.c. configuration. This 1600 cal./mole is to be compared with the observed 60,000 cal./mole for the heat of activation for self-diffusion in copper. It is thereby apparent that the most appropriate region for an elementary diffusion act will be the most appropriate because of the smallness of its interaction with the surrounding lattice during the elementary diffusion act rather than because of the smallness of its size *per se*.

The interchange process discussed by Huntington & Seitz is represented in Fig. 1 as the rotation of a two-atom ring, hereafter abbreviated as a 2-ring. During this rotation the distance between the two-ring atoms, as well as the positions of the atoms in the surrounding lattice, must be regarded as adjusting themselves so as to minimize the work necessary to rotate the ring to its position of maximum free energy at the angle of $\frac{1}{2}\pi$. A possible 3-ring and 4-ring for f.c.c. lattices are illustrated in Figs. 2 and 3. These rings have been drawn so that each ring atom jumps into a nearest-neighbor position. It is anticipated that this nearest-neighbor requirement will be satisfied by that ring having the

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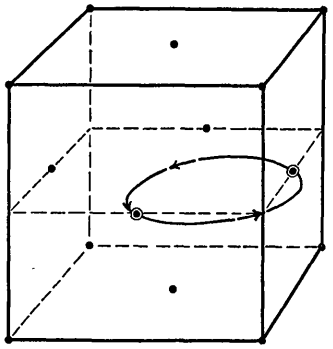
* This research has been supported in part by the Office of Naval Research under Contract No. N6ori-20-IV, NR 019 302.

lowest free energy of activation. A 3-ring cannot be drawn in a b.c.c. lattice satisfying this nearest-neighbor requirement. A possible 4-ring is illustrated in Fig. 4.

A computation of the free energy of activation for a ring diffusion can only be made upon the basis of some assumption regarding the interatomic forces. We start our analysis with the assumptions adopted by Huntington & Seitz. The measured 'heat of activation' is to be identified as the potential-energy barrier which a ring would have to overcome during an elementary diffusion act if the lattice were devoid of all thermal motion.



◉ ring atoms after Huntington & Seitz (1942)

Fig. 1. 2-ring diffusion in f.c.c. lattice.

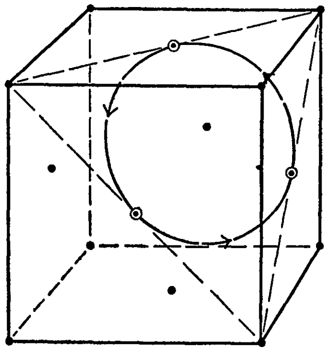


Fig. 2. 3-ring diffusion in f.c.c. lattice.

Under such conditions the energy of the lattice is represented as the sum of three terms:

$$E = \phi_c + \phi_{\text{ex.}} + \phi_v. \tag{1}$$

The first term represents the coulomb interaction of the positive ions on the assumption that the conduction electrons are uniformly distributed, and remain uniformly distributed irrespective of the movements of the positive ions during an elementary diffusion act. The second term represents the repulsive exchange interaction between the positive ions. It may be written as

$$\phi_{\text{ex.}} = \tfrac{1}{2}\Sigma_{ij} U(r_{ij}), \tag{2}$$

where $U(r_{ij})$ is the exchange interaction between two ions a distance r_{ij} apart. The implicit assumption is thus made that the exchange interaction between two ions is independent of the distances of these two ions from other neighboring ions. The interaction U is written explicitly as

$$U(r_{ij}) = A \exp[-\alpha(r_{ij} - r_0)/a], \tag{3}$$

where r_0 is the distance between nearest neighbors in the equilibrium configuration of the lattice, and a is the lattice constant. The two constants A and α are adjusted so as to give the observed shear elastic constants. The third term, ϕ_v, takes care of all other types of energy, and is assumed to be a function only of the volume of the lattice, and thereby to remain unaltered both during the elementary diffusion act and during the homogeneous shear strains considered in computing the two constants A and α.

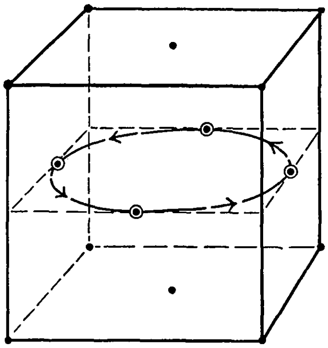


Fig. 3. 4-ring diffusion in f.c.c. lattice.

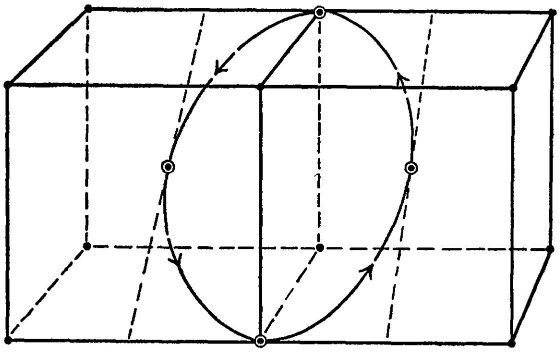


Fig. 4. 4-ring diffusion in b.c.c. lattice.

Again following Huntington & Seitz, we shall analyze separately the contributions of the coulomb and exchange interactions to the heat of activation for diffusion. In their original paper these authors estimated the contribution of the coulomb interaction, H_c, to be 250,000 cal./mole. This original estimate has later (Huntingon & Seitz, 1949) been reduced to 150,000 cal./mole when the surrounding lattice is considered as rigid, or to 110,000 cal./mole when the surrounding lattice is relaxed. In §2 we find that the coulomb interaction is an order of magnitude smaller for a 4-ring diffusion than for a direct interchange, being only 24,000 cal./mole as calculated before letting the surrounding lattice relax, 8000 cal./mole after relaxation of the first ten nearest neighbors. The coulomb interaction thus presents at most a relatively minor obstacle to 4-ring diffusion.

The exchange interaction is analyzed in § 3. Here the 4-ring diffusion does not show such a marked advantage over the 2-ring diffusion. Thus while Huntington & Seitz found the contribution $H_{\text{ex.}}$ of the exchange interaction to be 140,000 cal./mole in their original paper, and 125,000 in their refined computations, we find $H_{\text{ex.}}$ is 91,000 cal./mole for a 4-ring diffusion. No way is found of lowering this computed value of $H_{\text{ex.}}$ and still keeping within the general framework of our original assumptions regarding the nature of the exchange interaction between the ions. Our original assumption of the independence of the exchange interaction of two pairs of ions upon the presence of neighboring ions is in apparent contradiction to the findings of crystal chemistry in regard to the decrease in the effective size of ions as their co-ordination number decreases. It is found that a decrease in effective size of the ring atoms by 3·5 % at the saddle configuration, where the number of nearest neighbors is four as compared with twelve for the equilibrium configuration, is sufficient to reduce the computed value of $H_{\text{ex.}}$ to the empirically determined value of 60,000 cal./mole. Finally, in § 4 we present evidence that the coulomb energy term, ϕ_c, is much smaller than would be obtained on the assumption that the conduction electrons remain essentially undisturbed when the lattice is subject to a distortion involving no change in volume. We, therefore, feel justified in neglecting even the small contribution H_c which ϕ_c makes to the heat of activation based upon the above assumption.

The above results lead us to the conclusion that a 4-ring elementary diffusion act is energetically consistent with the observed heat of activation, and hence energy considerations do not force us to regard diffusion as arising from the migration of holes.

2. Coulomb interaction

Since the computation of the contribution of the coulomb interaction to the free energy of activation is quite tedious for any particular ring, it is desirable to have some easily applicable method of selecting those rings for which this contribution is a minimum, and of seeing why the contribution is larger for a 2-ring than for some higher-order rings. Towards this end we envisage a potential energy $V_n(s)$ associated with the rigid rotation of an n-ring, the surrounding lattice being regarded as held fixed. The argument s is the displacement of a ring atom from its original equilibrium position. The essential features of $V_n(s)$ are represented in Fig. 5. For an n-ring the equilibrium position $s = s_n$ will be identical with the equilibrium position $x = 0$. We shall attempt to gain some information about the relative magnitude of the potential energy barrier ΔV_n for various order rings from the behavior of $V_n(s)$ at small values of its argument.

For very small values of s, V_n may be written as

$$V_n(s) = \tfrac{1}{2} n C s^2 + \sum_{\text{pairs}} \frac{P^2}{r_{ij}^3} \{\mathbf{P}_i . \mathbf{P}_j - 3(\mathbf{r}_{ij} . \mathbf{P}_i)(\mathbf{r}_{ij} . \mathbf{P}_j)\}, \quad (4)$$

where C in the first term is the force constant which binds each atom to its equilibrium position, all other atoms being held fixed, and where the second term is the dipole–dipole interaction. In this second term, P is the magnitude of each dipole, namely es, while $\mathbf{P}_i$ is the unit vector pointing in the direction of the associated dipole. The quantities r_{ij} and $\mathbf{r}_{ij}$ have analogous interpretations. Upon expressing the curvature of V_n at its minimum in the form

$$V_n''(0) = a_n C - b_n e^2 / r_0^3, \quad (5)$$

where r_0 is the closest distance of approach between the atoms in the lattice, we construct Table 1 for 2-, 3-, 4- and 6-rings in a f.c.c. lattice. In evaluating the third row we have taken

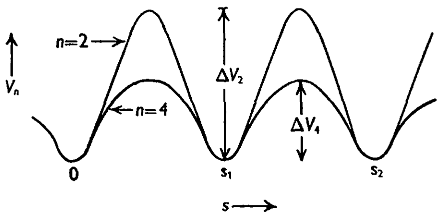


Fig. 5. Potential-energy function of ring.

$$C = (4\pi/3)\, e^2/\Delta, \quad (6)$$

where Δ is the atomic volume. This expression for C may be obtained directly from the definition

$$C = e(\partial^2/\partial x^2)\, \phi,$$

where the differentiation is to be taken at a lattice position, and ϕ is the electrostatic potential exclusive of the contribution due to the ion occupying this lattice position. The cubic symmetry of the crystal allows us to replace the operator $(\partial^2/\partial x^2)$ by $\frac{1}{3}\nabla^2$. We now obtain equation (6) by utilizing Poisson's equation to replace $\nabla^2\phi$ by $-4\pi\rho$, where ρ is the uniform charge density arising from the conduction electrons. From Table 1 we see that $V_n''(0)$ is practically constant as we pass from a 2- to a 6-ring. The linear increase in a_n with n is essentially compensated by the rapid rise in the dipole–dipole interaction as shown by the coefficient b_n.

Table 1. *Curvature of ring potential at minimum*

Order of ring	2	3	4	6
a_n	2	3	4	6
b_n	2	7·5	13·7	25·9
$V_n''(0)$ (in units of e^2/a^3)	27·9	29·0	28·4	27·5

The above simplified treatment of the interaction of the ring atoms as dipole–dipole interactions is sufficient to dispel our almost intuitive feeling that the larger the ring the larger the potential energy barrier ΔV_n. Higher approximations to the dipole–dipole interaction indicate that ΔV_2 is larger than the potential energy barrier for the rings of the next few higher orders. Thus when we retain the next terms in the dipole–dipole interaction, we find that for V_2 these form an oscillating series, while for V_4 and V_6 all terms have the same sign as the first. We thus anticipate the relative shapes of the potentials for the 2- and 4-rings to be in the same order as sketched in Fig. 5. The following quantitative analysis will be confined to a comparison of the 2-ring with the 4-ring, since consideration of the exchange interactions introduced in the next section indicates that the 4-ring is to be preferred over the other higher-order rings.

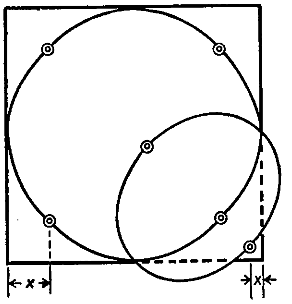


Fig. 6. Saddle parameter of ring.

While symmetry conditions give us lines along which the ring atoms must lie in the saddle configuration, they do not give their precise positions along this line. We therefore introduce the saddle configuration parameter x defined in Fig. 6. The height of the potential-energy barrier will then be calculated as a function of x. The appropriate value of x is that which minimizes this barrier. This calculation will proceed in two steps. In the first we calculate the work $n\Delta\phi$ required to transfer an ion from its equilibrium position to a position corresponding to a given x a long way from its original equilibrium position. We shall call $n\Delta\phi$ the energy of separation. In the second step we calculate the work which we gain back by bringing the n vacant lattice sites and the n displaced ions into a saddle configuration. We shall call the change in energy of the lattice associated with this second step the interaction energy. In calculating the energy of separation we have found it most convenient to use the Ewald method. The application of this method to our particular problem is discussed in the Appendix. The interaction energy is given by elementary coulomb interactions. The results of the computations are given in Figs. 7 and 8.

It is seen that the potential-energy barrier for the 4-ring in an unrelaxed lattice is one-fifth that for a 2-ring; in the case of copper it is 24,000 as compared to 115,000 cal./mole.

The calculated potential-energy barrier will, of course, be still further lowered when we allow the surrounding lattice atoms to relax. A relaxation of the first ten nearest neighbors lowers the potential energy barrier to $0{\cdot}08e^2/a$, or to 8000 cal./mole for copper, nearly one order of magnitude lower than the observed heat of activation for this metal.

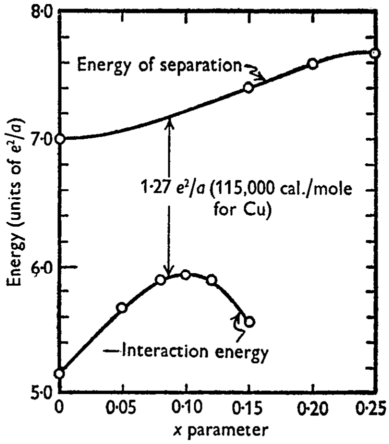


Fig. 7. Coulomb interaction in a 2-ring in f.c.c. lattice.

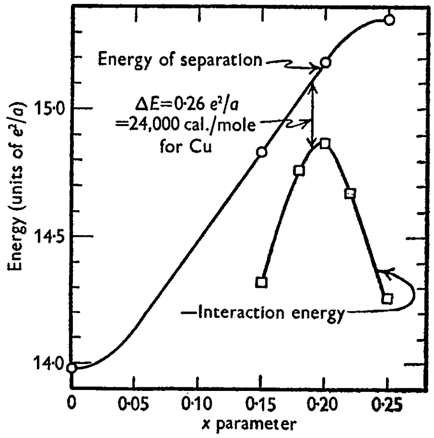


Fig. 8. Coulomb interaction in a 4-ring in f.c.c. lattice.

3. Exchange interaction

In this section we shall neglect the coulomb interaction between the positive ions, and shall study the contribution of the exchange interaction, acting alone, upon the potential-energy barrier for an elementary diffusion act. The lattice will have, in addition to the exchange energy, the term ϕ_v in equation (1) which is a function of the volume only, and which remains unaltered during an elementary diffusion act.

The characteristic feature of the exchange forces is their extreme shortness of range as compared with that of the coulomb forces. Thus, when an atom is in the equilibrium configuration of a f.c.c. lattice, its exchange interaction with its next nearest neighbors is only about one-quarter of 1 % of its exchange interaction with its nearest neighbors. We should, therefore, be able to judge the relative values of the potential-energy barriers for diffusion by 2-, 3- and 4-rings by a mere inspection of their respective saddle configurations. Since detailed calculations, to be given later, are required to determine the precise form of the saddle configuration, we shall at present consider those configurations obtained by merely rotating the rings without allowing for any relaxation either within the ring or in the surrounding lattice. Such saddle configurations are presented in Figs. 9 and 10 for a 2-ring and for a 4-ring, respectively. In the 2-ring each ring atom is at a distance of $0{\cdot}5a$, or $0{\cdot}71r_0$, from four lattice atoms, where r_0 is the distance between nearest neighbors in the equilibrium structure. Thus, in our present simplified picture the saddle configuration for a 2-ring is obtained by compressing eight links by 29 %. On the other hand, each atom of the 4-ring is at a distance of $0{\cdot}74r_0$ from two lattice atoms, and a distance of $0{\cdot}95r_0$ from two others. The saddle configuration of the 4-ring is thus attained by compressing eight links 26 %, and eight further links 5 %. If the energy of compression of the links is computed according to any reasonable model, we find the 4-ring requires less energy to attain its saddle configuration than does the 2-ring. Thus, if we regard the energy of compression as proportional to the square of the compression, the potential-energy barrier for the 4-ring will be only 83 % of that of the 2-ring. We can carry these qualitative considerations one stage further and show that if we now allow the surrounding lattice atoms to relax, such relaxation will reduce the potential-energy barrier by a relatively greater amount in the case of the 4-ring than in the case of the 2-ring. Thus, in the case of the 2-ring the relaxing lattice atoms are nearest neighbors of one another, and hence their relaxations mutually impede each other. On the other hand, the relaxing lattice atoms in the case of the 4-ring are not nearest neighbors of one another, and hence do not impede each other's relaxations.

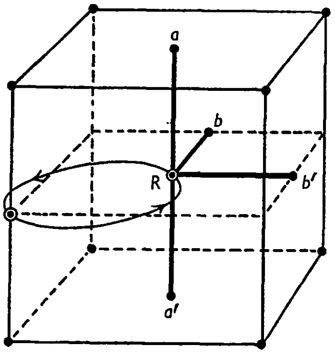


Fig. 9. Ring–lattice bonds for saddle configuration of a 2-ring in f.c.c. lattice.

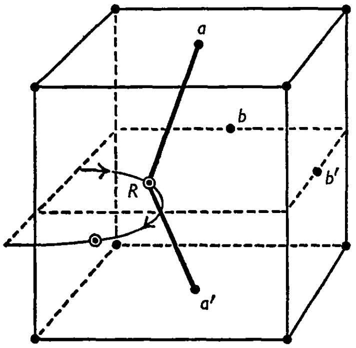


Fig. 10. Ring–lattice bonds for saddle configuration of a 4-ring in f.c.c. lattice.

We now turn to a quantitative calculation of the potential-energy barrier. Qualitative arguments along the line of the preceding paragraph indicate that the 4-ring has the lowest potential-energy barrier of all possible rings, and hence our quantitative discussion will be confined to a 4-ring, and to its comparison with a 2-ring. The author is aware that such qualitative arguments may be misleading, and that another type of ring could possibly have a lower potential-energy barrier.

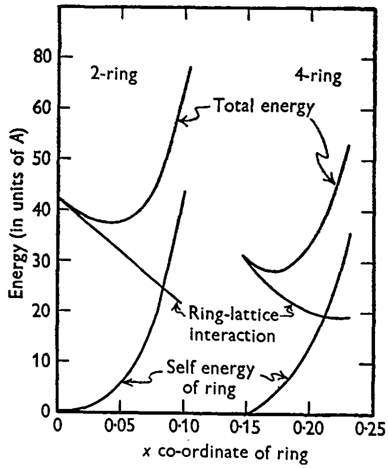


Fig. 11. Exchange interaction of a 2-ring and 4-ring in f.c.c. lattice.

In making a quantitative comparison of the 2-ring and 4-ring we shall take essentially the same exchange interaction as was used by Huntington & Seitz (1942), namely, that given by equation (3) with α equal to 13·5. (Huntington & Seitz took α as 12·5.) We allow the ring to relax by contracting, at the same time allowing the lattice to relax by the movement of those lattice atoms adjacent to the ring atoms. The potential-energy barrier was calculated for each ring as a function of the saddle parameter x defined in Fig. 6. The results are presented in Fig. 11. Here the potential-energy barrier has been separated into two terms:

$$V(x) = V_R(x) + V_L(x).$$

The first term, the self-energy of the ring, is the change in the bonds linking the ring atoms with one another. The second term is the change in the energy of all other links, and has been called the ring–lattice interaction energy. We note that if we compare the 2-ring and the 4-ring at the same value of the parameter x, the ring–lattice interaction energy for the 4-ring is essentially twice that for the 2-ring. The advantage of the 4-ring over that of the 2-ring lies in the circumstance that in the 4-ring the x parameter may assume a much larger value before the self-energy of the ring begins to rise appreciably. Thus, before any contraction of the ring the x parameter of the 2-ring is 0, while that of the 4-ring is 0·145. We observe that at the optimum value of the ring relaxations the potential-energy barrier for the 4-ring is 75 % that of the 2-ring.

Having established the superiority of the 4-ring, we next perform a more precise calculation for the 4-ring in order to see if our present model of diffusion is capable of yielding a potential-energy barrier for copper as low as the observed heat of activation of 60,000 cal./mole. Towards this end two modifications are made in the above-mentioned calculations. First, the constants A and α are so chosen as to reproduce the observed shear elastic constants. Secondly, relaxation in the lattice is allowed of next and of next next nearest neighbors to the ring atoms.

The exponent α is completely determined by the anisotropy ratio

$$\mathfrak{A} = C_{44}/\tfrac{1}{2}(C_{11} - C_{12}).$$

An explicit relation between $\mathfrak{A}$ and α is obtained by utilizing the following relations given by Fuchs (1936):

$$C_{44} = \tfrac{1}{2}N\{r^2U'' + 3rU'\}_{r=r_0}, \tag{7}$$

$$C_{11} - C_{12} = \tfrac{1}{2}N\{r^2U'' + 7rU'\}_{r=r_0}. \tag{8}$$

Here N is the number of atoms per unit volume. We find

$$\alpha = 2^{\frac{1}{2}}(7\mathfrak{A} - 6)/(\mathfrak{A} - 2). \tag{9}$$

Upon substituting into this equation the value of 3·2 for the anisotropy ratio of copper, we obtain for α the value of 19. We may now solve equation (7) for A, obtaining

$$A = 4C_{44}/N\alpha(\alpha - 2^{\frac{1}{2}}.3). \tag{10}$$

Upon substituting into this equation the constants appropriate to copper we obtain

$$A = 1800\ \text{cal./mole}.$$

The procedure adopted for the calculation of the potential-energy barrier was as follows. We tentatively took the saddle parameter x to be the optimum value given in the preliminary calculations reproduced in Fig. 11. This value was 0·17. Each of the eight lattice atoms which are close to the ring atoms may then be regarded as being subjected to a perturbation energy V_P defined by

$$V_P = U(r') - 2U(r''), \tag{11}$$

where r' and r'' are defined by Fig. 12, and hence to an externally applied vertical force f equal to

$$f(h) = -\partial V_P/\partial h, \tag{12}$$

where h is its vertical displacement. In order to calculate the equilibrium value of h, we must first find the effective force constant $C_{\text{eff.}}$, which relates h to the applied force. Denoting by C the force constant which binds an atom to its equilibrium position under conditions where all neighboring atoms are held fixed, we find

$$C_{\text{eff.}} = 0{\cdot}76C. \tag{13}$$

Those atoms which suffer the largest displacements are shown in Fig. 12. The relative displacements are given by

$$h'' = \tfrac{1}{2}h', \quad h' = 0{\cdot}35\,h.$$

The force constant C is obtained from the general equation for a cubic lattice

$$C = \tfrac{1}{3}n\,\nabla^2 U,$$

where n is the number of nearest neighbors. For a bond energy U of the type given by equation (3) we obtain

$$C = 4A\alpha(\alpha - 2^{\frac{1}{2}}.2)/a^2,$$

or, upon using the constant appropriate for copper,

$$Ca^2 = 2{,}250{,}000\ \text{cal./mole}.$$

With this value of C substituted into (13), we now obtain h by the numerical solution of

$$f(h) = C_{\text{eff.}}h. \tag{14}$$

This solution gives h as 0·08a. The potential-energy barrier calculated in this manner was found to be 101,000 cal./mole.

Attempts to lower this potential-energy barrier by further relaxations resulted in only a slight decrease. Allowing the eight a-type atoms to relax horizontally lowered the energy 6000 cal./mole. Further miscellaneous relaxations accounted for a lowering of 4000 cal./mole. The originally estimated value of 0·17 for the x parameter was found to be correct, since the ring atoms were found to be under no net force. On the model herein adopted it thus appears that the potential-energy barrier for diffusion is about 91,000 cal./mole, 50 % higher than the observed value.

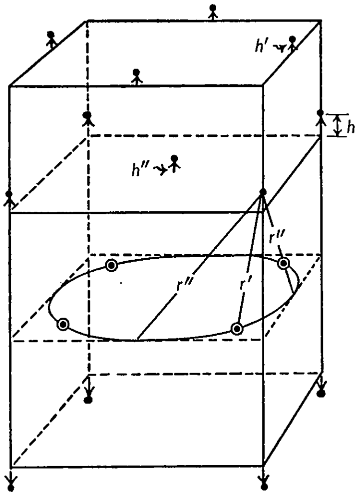


Fig. 12. Relaxation in copper lattice surrounding a 4-ring.

An attempt was made to lower the calculated potential-energy barrier by allowing the ring to rotate as a ring dislocation rather than for all four atoms to rotate in synchronism, as was implicitly assumed above. It was found that if one atom was placed at a saddle point, the potential energy was a minimum when all other ring atoms were also at saddle points. Rotation does not, therefore, occur as a ring dislocation.

Any further attempts at lowering the calculated potential-energy barrier must, therefore, consist in a relaxation in the assumptions made regarding the atomic interactions. The first attempt in this direction lay in testing the possibility that the coefficient α decreases with decreasing interatomic distance. Such a variation of α would lead to a bulk modulus which increases with pressure less rapidly than if α were to remain constant. Upon adopting Bridgman's notation for compressibility data,

$$-(V-V_0)/V_0=aP-bP^2, \tag{15}$$

we obtain

$$P=-\{(V-V_0)/(aV_0)\}.\{1-(b/a^2)(V-V_0)/V_0\}.$$

Upon expressing P in terms of δr, the change in the distance between nearest neighbors, we find

$$P=-\frac{3}{a}\{(\delta r/r_0)+(1-3b/a^2)(\delta r/r_0)^2\}.$$

We now utilize equations (1)–(3) to obtain a second power series of P in $\delta r/r_0$. In so doing we neglect the second derivative of ϕ_c and of ϕ_v with respect to r in comparison with the second derivative of $\phi_{\text{ex.}}$. Comparison of coefficients in these two power series for P leads to

$$(1-3ba^{-2})=(\tfrac{1}{2}\beta^2+2\beta+3)(/(\beta+2), \tag{16}$$

where $$\beta=2^{-\frac{1}{2}}\alpha.$$

From Table 2 we see that the assumption of a constant α is in complete agreement with the compressibility data and hence one would not be justified in letting α decrease with decreasing distance of separation. This conclusion of constancy of α had previously been reached by Huntington & Seitz (1949).

Table 2. *Compressibility data*

Source	b/a^2
Equation (16)	7·8
Bridgman	6·53 (Lazarus, 1949)
Lazarus	8·09 (Lazarus, 1949)

We shall make one further attempt at relaxing our assumptions regarding atomic interactions. Whereas in the equilibrium configuration each lattice atom has 12 nearest neighbors, in the saddle configuration each ring atom has only two nearest neighbors, two neighbors at a somewhat further distance, two atoms at a still further distance, etc. The distances of the first few neighbors are given in Table 3.

Table 3. *Neighbors at saddle configuration*

Number	2	2	2	2
Distance (in units of r_0)	0·89	0·935	0·965	1·01

In his study of the radii of metallic atoms Pauling (1947) starts from the assumption that metallic binding is due to valence bonds. According to this viewpoint, the smaller the co-ordination number, i.e. the number of nearest neighbors, the larger will be the number of valence electrons which contribute to the binding with a given nearest neighbor, and hence the tighter will be the binding between each pair of adjacent atoms. Pauling argues that the tighter binding associated with a smaller co-ordination number will be reflected in a smaller atomic radius, and conversely that the observed decrease in interatomic distance with decreasing co-ordination number is due solely to a tighter binding. His empirical formula for the radius R_z associated with a co-ordination number z is

$$R_{12}-R_z=0{\cdot}300A\log_{10}(12/z). \tag{17}$$

The contraction, as given by this equation, of the radii of copper atoms having a co-ordination number less than 12 is given in Table 4. A change in the radii of the ring atoms may be formally incorporated into our theory through a corresponding change of the parameter r_0 appearing in the exchange interaction of equation (3).

Table 4. *Influence of co-ordination number upon radii of copper atoms* (*according to equation* (17))

Co-ordination no.	12	8	6	4	2
$(R_{12}-R_z)/R_{12}$	0	0·04	0·07	0·11	0·18

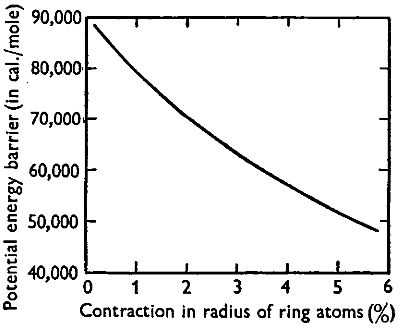


Fig. 13. Effect of contraction of ring atoms upon potential-energy barrier of a 4-ring in copper.

Thus if we assume a 6 % decrease in the radii of the ring atoms at their saddle configuration, the parameter r_0 in equation (3) must be decreased 3 % for the interaction energy between ring atoms. The effect of such a decrease upon the calculated potential-energy barrier is shown in Fig. 13. Comparison of Tables 3 and 4 with Fig. 13 shows that an uncritical acceptance of Pauling's viewpoint would lead to a potential-energy barrier much less than the observed 60,000 cal./mole. Thus, if we were to take 6 as a conservative estimate of the co-ordination number of a ring atom at the saddle configuration, the potential-energy barrier would be less than 45,000 cal./mole.

The success of equation (17) in reproducing the observed change in atomic radii with co-ordination number does not necessarily imply a related change in atomic interactions. As has already been discussed by Zachariasen (1931), the distance between nearest neighbors will be different in structures having different co-ordination numbers merely because of energy requirements. We are, therefore, led to investigate that relation between closest distance of approach and co-ordination number which is demanded by energy requirements. In conformity with our original assumptions we write as follows the energy of an undeformed lattice of N atoms having a co-ordination number of z:

$$E = \tfrac{1}{2}NzBe^{-\gamma r} + \phi(v). \tag{18}$$

The equilibrium distance between nearest neighbors will be that value of r, r_z, which minimizes E. This equilibrium distance is obtained by equating dE/dr to zero. If we are to compare the equilibrium distances associated with different values of z, some assumption must be made regarding $\phi'(v)$. In recognition of the fact that the exchange energy varies with r much more rapidly than do the other energy terms, we shall take $\phi'(v)$ as being identical in the two structures. We thereby obtain for the equilibrium values r_z and r'_z:

$$r_z - r'_z = \{r_z/(r_z\gamma - 2)\}\ln(z/z'). \tag{19}$$

Upon using the values of R_{12} and γ appropriate to copper, we obtain for the radius R_z:

$$R_{12} - R_z = 0{\cdot}25A\log_{10}(12/z). \tag{20}$$

When we now compare this equation with Pauling's empirical equation (17), we see that our general assumptions (1)–(3) lead us to the conclusion that the major part of the observed contraction of the radii of metallic atoms with decreasing co-ordination number arises because of energy requirements and is, therefore, not associated with a change in the interatomic forces, as has been assumed by Pauling.

The above considerations prevent us from adjusting the parameter r_0 in the exchange energy (3) in accordance with Pauling's formula (17). They detract in no way, however, from Pauling's general thesis that the exchange interaction between two metallic atoms will be more attractive, or less repulsive, the smaller the co-ordination number of each atom. Such a thesis may also be arrived at from considerations based upon the Thomas–Fermi model of an atom. When, in this model, an atom has only two nearest neighbors, the exchange repulsive interaction between each pair of atoms will be reduced by an angular redistribution of charge. An angular redistribution of charge would not take place if the co-ordination number were high. As yet, however, the theory of interatomic forces has not advanced to a stage where we may quantitatively evaluate the effect of a change of co-ordination number. We must at present, therefore, be content with the knowledge that theoretical considerations show that a decrease in co-ordination number will lead to a decrease in the parameter r_0 in the exchange energy (3), and that a decrease in r_0 of 3·5 % for ring–ring interaction, of 1·75 % for ring–lattice interaction, is sufficient to reduce the computed value of the potential energy barrier for diffusion to the observed value.

4.

In §2 we found that coulomb interactions, in the absence of all exchange interactions, would give rise to a potential-energy barrier for 4-ring diffusion at least one order of magnitude smaller than the observed heat of activation. From this result we cannot deduce, *a priori*, that when exchange interaction is present the contribution of the coulomb interaction will still be negligible. Such would not be the case if the saddle configuration corresponding to the coulomb forces acting alone were considerably different from the saddle configuration corresponding to the exchange forces acting alone. The two saddle configurations are, however, very similar. Thus in the two extreme cases where the coulomb forces act alone and where the exchange forces act alone, the x parameter of the saddle configuration is $0{\cdot}19a$ and $0{\cdot}18a$, respectively, while the vertical displacement of the a-type atoms (see Fig. 12) are $0{\cdot}04a$ and $0{\cdot}07a$, respectively. We anticipate, therefore, that in the actual copper lattice the coulomb forces will make at most a very small contribution to the potential-energy barrier.

An attempt to make a consistent calculation in which both types of forces are taken into account has led to the conclusion that when a copper lattice is distorted the copper ions do not move through an undistorted essentially uniform distribution of conduction electrons, but rather that the distribution of the conduction electrons becomes distorted so as to shield the positive ions from the major part of their coulombic interaction. In the absence of such shielding equations (7) and (8) for the exchange parameter α must be modified. The left members of these equations must then represent only that contribution to the elastic coefficients arising from the exchange interaction, i.e. they must equal the actual elastic coefficients minus the coulombic contributions. Upon using the coulombic contributions calculated by Fuchs (1936), one obtains for α the value 25 in place of our original value 19. Two independent considerations lead us to the belief that the original value is the better of the two. First, we anticipate that the exchange interaction will vary with interatomic distance approximately as the product of the charge densities of the two atoms at their midpoint. Upon using the charge densities (Hartree & Hartree, 1936) computed by the Hartree–Fock equations, we find that this product is $\exp(-20r/a)$, in agreement with our original value for α of 19. Secondly, we have found in §3 our original value of α to be in complete agreement with the empirical data on the pressure variation of compressibility. We must therefore conclude that, at least in the case of copper, during a lattice distortion the conduction electrons must suffer such a redistribution as to shield the positive ions from the major part of their coulombic interaction.

APPENDIX

In the calculations referred to in § 2 the author has made extensive use of the Ewald method of evaluating the potential within a crystal lattice (Ewald, 1916*a*, *b*, 1921 *a*, *b*). In our present case of a f.c.c. lattice where the positive ions have all the same charge, and the negative charge is uniformly distributed, the Ewald formula may be expressed in a particularly simple manner. The potential at an arbitrary point with the position vector **r** is given by

$$V(\mathbf{r}) = -(eq/\pi\Delta) + (e\pi q^{-\frac{1}{2}})\,S_1 + (eq/\pi\Delta)\,S_2'. \qquad (1)$$

The quantity q is a parameter with dimensions of $(\text{length})^2$ which may be given any arbitrary positive value. For small values the first sum S_1 is rapidly convergent, the second sum S_2 is slowly convergent. For large values of q, S_1 converges slowly, S_2 converges rapidly. In actual computations q is assigned such a value as to minimize the labor in evaluating these two sums. For reasons explained below, q has been given the value

$$q = \pi\Delta^{\frac{2}{3}} \qquad (2)$$

in the present calculations. With this value it has rarely been necessary to retain more than the first two terms in S_1 and S_2 in order to obtain V to an accuracy of one part in 10,000. The quantity Δ is the atomic volume. The first sum is given by

$$S_1 = \sum_{\sigma} \frac{F\{\pi q^{-\frac{1}{2}}\,|\,\mathbf{r}-\mathbf{r}_\sigma\,|\}}{\pi q^{-\frac{1}{2}}\,|\,\mathbf{r}-\mathbf{r}_\sigma\,|}, \qquad (3)$$

where the sum is over all lattice positions $\mathbf{r}_\sigma$, and where

$$F(x) = 2\pi^{-\frac{1}{2}} \int_x^\infty e^{-s^2}\,ds. \qquad (4)$$

The quantity $1 - F(x)$ is simply the error function, tables of which may be found in many places. A table in which x varies in steps of 0·001 over the range of interest in our present work has been given by Burgess (1897–8). The second sum is given by

$$S_2' = \sum_{\mathbf{k}}{}' \exp[2\pi i\mathbf{k}.\mathbf{r}]\exp[-q\,|\,\mathbf{k}\,|^2]/q\,|\,\mathbf{k}\,|^2. \qquad (5)$$

Here the sum is over all points of the reciprocal lattice exclusive of the origin. Thus the sum is over all values of the vector

$$\mathbf{k} = (l, m, n)/a \qquad (6)$$

for which l, m, n assume integer values satisfying the equation

$$1 + \exp[i\pi(l+m)\,a] + \exp[i\pi(m+n)] + \exp[i\pi(n+l) \neq 0. \qquad (7)$$

In order to obtain the potential energy of an ion at a lattice point, we place the origin of co-ordinates at this lattice point, and subtract from $V(\mathbf{r})$ the potential $e/|\,\mathbf{r}\,|$ due to the lattice ion itself. For very small values of $|\,\mathbf{r}\,|$ one then finds

$$V(\mathbf{r}) - e/|\,\mathbf{r}\,| = -e\{(q/\pi\Delta) + 2(\pi/q)^{\frac{1}{2}}\} + \{(e\pi q^{-\frac{1}{2}})\,S_1' + (eq/\pi\Delta)\,S_2'\}. \qquad (8)$$

Here S_1 has been replaced by S_1', in which the lattice point at the origin is excluded from the sum. We now note that the first term is negative, while the two sums are positive. The contribution of the sums will, therefore, be minimized by so choosing the parameter q as to minimize the first term. This value is given by equation (2). It is interesting to note that with this value of q the argument of F in S_1 for a f.c.c. lattice assumes the same values as does the argument of the exponential function in S_2 in the case of a b.c.c. lattice, and vice versa.

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