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Effect of Screening on Solute Diffusion in Metals*

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A simple atomistic theory of solute diffusion in metals for cases of negligible chemical concentration gradients is discussed. Calculations are made, using a Thomas-Fermi approximation, of the influence of the presence of impurity atoms on the Fermi electrons of the lattice. The results are applied to the case of diffusion of Sb in Ag, and indicate that the screening terms are sufficient to explain the magnitude and direction of the observed deviation from self-diffusion in Ag for a vacancy mechanism for diffusion.

INTRODUCTION

THE recent work of Sonder, Slifkin, and Tomizuka[1] on the diffusion of Sb^{124} into pure monocrystalline Ag has demonstrated conclusively that the solute Sb atoms diffuse at a rate markedly different from the rate of self-diffusion[2] of Ag under conditions of negligible chemical concentration gradients. The magnitude of the effect proved much smaller than that previously reported.[3] The previous work had been the basis for a considerable amount of speculation on the nature of the solute diffusion process, and a number of mechnisms[4] had been proposed to explain the large differences between the rates of solute diffusion and self-diffusion in metals, which required the assumption of strong coupling forces between a diffusing solute atom and a lattice imperfection.

It is apparent from a consideration of the kinetics of the diffusion process[5] that the true diffusion characteristics of relatively isolated solute atoms in a lattice can easily be masked by large unidirectional currents of imperfections which result from gradients in chemical composition. Such currents give rise to the measurable volume changes and porosity associated with the Kirkendall effect.[6] Since all of the original work on solute diffusion[7] was done under conditions of strong chemical gradients, the interpretation of much of the old data is open to question.

In the present paper, an attempt is made to adopt an atomistic approach to the diffusion problem, in contrast to some of the current thermodynamic theories,[8] in order to account quantitatively for the observed effects. The computations are confined to a consideration, using a Thomas-Fermi model, of the effects of screening of the solute ions on the Fermi electrons of the solvent lattice. The additional terms arising from this interaction are evaluated and applied to the particular case of Sb diffusing in Ag.

CALCULATIONS

In order to form a simple atomistic theory for solute diffusion, a number of assumptions have been made dealing with I, the nature of the diffusion process, and II, the nature of the solute atom, as follows:

I. (A) Diffusion is presumed to occur by means of imperfections, either vacancies or interstitials; the probability of an elementary diffusion jump P_D is then related to the probability of existence of an appropriate imperfection at an adjacent lattice site P_E and the probability of jump of the diffusing atom into the imperfection P_J by the relation $P_D=(P_E)(P_J)$.

(B) Thermal equilibrium is presumed to be established at all stages of the diffusion process, the formation and destruction of imperfections being effected at dislocations or surfaces by mechanisms not of immediate concern which represent an infinite potential reservoir of imperfections. One may then assume that the above probabilities may be treated using Boltzmann statistics, and that the diffusion process is adequately described by the relation

$$D=r_0^2\nu \exp[-(E_f+E_m)/kT], \tag{1}$$

where D is the diffusion coefficient, r_0 the interatomic distance, ν the vibrational frequency of the atom in the lattice, E_f the energy required to form an imperfection (analogous to P_E), E_m the energy required for motion of an atom into an adjacent imperfection (analogous to P_J), k Boltzmann's constant, and T the absolute temperature.

II. (A) The assumption is made that a solute atom may be represented as a solvent atom differing only in nuclear charge and numbers of valence electrons, that is inserted into the lattice in place of a solvent atom. The limitations of this assumption are considered later.

(B) It is assumed that the change in energy of the lattice resulting from replacement of a solvent atom by an isolated solute atom is small compared to the binding energy of the solvent atom in the lattice. This assump-

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[1] Sonder, Slifkin, and Tomizuka, this issue [Phys. Rev. 93, 970 (1954)].

[2] Slifkin, Lazarus, and Tomizuka, J. Appl. Phys. 23, 1032 (1952).

[3] W. Seith and E. Peretti, Z. Elektrochem. 42, 570 (1936).

[4] R. P. Johnson, Phys. Rev. 56, 814 (1939); G. Wyllie, Proc. Phys. Soc. (London) 59, 694 (1947).

[5] E.g., F. Seitz in *Phase Transformations in Solids* (John Wiley and Sons, Inc., New York, 1951).

[6] A. Smigelskas and E. Kirkendall, Trans. Am. Inst. Mining Met. Engrs. 171, 130 (1947).

[7] E.g., W. Seith, *Diffusion in Metallen* (Julius Springer, Berlin, 1939); C. J. Smithells, *Metals Reference Book* (Butterworth Scientific Publications, London, 1949).

[8] E.g., C. Zener, J. Appl. Phys. 22, 372 (1951); G. J. Dienes, Phys. Rev. 89, 185 (1953); A. D. LeClaire, Acta Metallurgica 1, 438 (1953).

tion is shown to lead to self-consistent results. The calculations will therefore be confined to a consideration of the changes in the various quantities of Eq. (1) by insertion of the solute atom into the lattice.

The procedure follows that developed by Mott[9] in a calculation of the effect of impurities on electrical resistivity. The solvent atom is assumed to be monovalent, while the solute atom has $1+Z$ valence electrons. The limits on the electrostatic potential $\phi(r)$ around the solute atom are

$$\begin{aligned} &\phi \rightarrow Ze/r && \text{as } r\rightarrow 0, \\ &\phi \rightarrow 0 && \text{as } r \text{ becomes infinite.} \end{aligned}$$

A Thomas-Fermi model is assumed, the density of the electron gas being given by

$$N(r)=(8\pi/3h^3)[2me(\phi+\phi_0)]^{\frac{3}{2}},$$

where $e\phi_0$ is the maximum energy of electrons in the Fermi gas

$$e\phi_0=(h^2/2m)(3N_0/8\pi)^{\frac{2}{3}}.$$

The density of the negative charge is then

$$\rho(r)=-eN(r),$$

and the total excess charge density is $e(N_0-N)$. Poisson's equation can be written as

$$\nabla^2\phi=-4\pi e(N_0-N)=\alpha[(\phi+\phi_0)^{\frac{3}{2}}-\phi_0^{\frac{3}{2}}],$$

where $\alpha=2^{13/2}\pi^2m^{3/2}e^{5/2}/3h^3$.

Under the conditions $\phi\ll\phi_0$, the expression can be expanded to first terms only. Then,

$$\nabla^2\phi=\tfrac{3}{2}\alpha\phi_0^{\frac{1}{2}}\phi=q^2\phi,$$

where $q^2=4me^2(3N_0/\pi)^{\frac{1}{3}}/h^3$. Solving, one obtains a value for $\phi(r)$,

$$\phi(r)=\frac{Ze}{r}\exp(-qr).$$

Using this value of the electrostatic potential, one may estimate the additional Coulomb energy, E_c, considering dipole terms only, as

$$E_c(r)=e\phi(r)=\frac{Ze^2}{r}\exp(-qr). \qquad (2)$$

E_c is a repulsive contribution to the total lattice energy, so that the change in energy of formation of an imperfection at the nearest-neighbor distance r_0 will be given by

$$\Delta E_f=\pm E_c(r_0), \qquad (3)$$

where the positive sign applies to formation of an interstitial and the negative sign for formation of a vacancy.

In evaluating the change in energy of motion E_m it will be assumed that this barrier can be represented entirely in terms of the elastic shear strain energy involved during the jump of the diffusing atom into the imperfection site. Following the method of Fuchs,[10] two shear deformations will be considered. The first of these is equivalent to an equal and opposite tension and compression on two orthogonal axes of the unit cell, such that the volume of the cell remains unchanged. The modulus of this deformation, A, is related to the macroscopic (110) shear modulus $\frac{1}{2}(C_{11}-C_{12})$ by

$$A/V_0=(C_{11}-C_{12}),$$

where V_0 is the volume of the unit cell. The second deformation is the familiar "pure shear," the atomic modulus B being related to the macroscopic (100) shear modulus by

$$B/V_0=\tfrac{1}{2}C_{44}.$$

The atomic moduli A and B are defined in the usual way in terms of the second derivatives of the lattice energy E with respect to the appropriate shear strain, evaluated at r_0, the equilibrium interatomic distance. They can be written for a face-centered cubic lattice in terms of derivatives with respect to distance as

$$\begin{aligned} A&=\tfrac{1}{2}r^2d^2E/dr^2+(7/2)rdE/dr, \\ 2B&=\tfrac{1}{2}r^2d^2E/dr^2+(3/2)rdE/dr. \qquad (4) \end{aligned}$$

The changes in these moduli due to the additional term $E_c(r)$ defined by Eq. (3) can be calculated by substitution of E_c for E in Eq. (4). Then

$$\begin{aligned} \Delta A_c&=\tfrac{1}{2}E_c(q^2r^2-5qr-5), \\ \Delta B_c&=\tfrac{1}{4}E_c(q^2r^2-qr-1). \qquad (5) \end{aligned}$$

For many metals, and in particular for Ag, the (110) shear modulus $\frac{1}{2}(C_{11}-C_{12})$ is much smaller than the (100) modulus C_{44}. For such materials one may assume that the strain energy of motion E_m arises almost entirely from (110) strains, and that E_m should be about equal to $A/2$ (the factor of 2 entering because Fuch's moduli are energies per ion *pair*). Using experimental values of the elastic constants for Ag, E_m for self-diffusion in Ag would then be 0.84 ev/atom, which is about the value expected from other theoretical considerations.[11]

For such anisotropic materials, one may then directly relate ΔA_c with ΔE_m, the change in energy of motion, by

$$\Delta E_m=\tfrac{1}{2}\Delta A_c. \qquad (6)$$

In estimating the other factors which would be expected to change for diffusion of solute atoms compared to self-diffusion, one must consider the usual thermodynamic expression for the diffusion coefficient

$$D=D_0\exp(-H/RT), \qquad (7)$$

where the frequency factor D_0 and enthalpy or heat of activation H are assumed to be temperature-independent, and R is the gas constant. This relation is obeyed

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[9] N. F. Mott, Proc. Cambridge Phil. Soc. **32**, 281 (1936).

[10] K. Fuchs, Proc. Roy. Soc. (London) **151**, 585 (1935); **153**, 622 (1936); **157**, 444 (1936).

[11] H. B. Huntington and F. Seitz, Phys. Rev. **61**, 315, 325 (1942).

experimentally to high precision,[1] any residual temperature dependence of D being negligible within the limits of error. In correlating Eq. (7) with the atomistic diffusion Eq. (1), it is obviously sufficient to define

$$(E_m+E_f)=H/N_0+Td(E_m+E_f)/dT,$$
$$D_0=r_0^2\nu\exp[-d(E_m+E_f)/kdT], \tag{8}$$

where N_0 is Avogadro's number. Higher derivatives of E_m and E_f with respect to temperature are assumed negligible because of the observed consistency of the experimental measurements with Eq. (7).

One must consider the energies E_m and E_f as functions of temperature both explicitly and implicitly through the distance parameter r, as shown in previous work[12] on a study of the variation of elastic constants of cubic materials with pressure. The derivatives in Eq. (8) may then be expanded as

$$d(E_m+E_f)/dT=[\partial(E_m+E_f)/\partial r]_T dr/dT + [\partial(E_m+E_f)/\partial T]_r. \tag{9}$$

The second term on the right of Eq. (9) is not amenable to analytical solution without a complete knowledge of $E(r,T)$, but might be presumed to arise from the variation in amplitude of the lattice vibrations with temperature. Such a variation might be expected to produce a large effect in E_m but a negligible change in E_f. It will be assumed that the explicit temperature dependence of E_m is proportional to the implicit term, as indicated by the high-pressure measurements for shear moduli. Then, the temperature variation may be written as

$$d(E_m+E_f)/dT=r_0\alpha[(\partial E_f/\partial r)_T+C(\partial E_m/\partial r)_T], \tag{10}$$

where α is the linear thermal expansion coefficient and the constant C will be evaluated from the observed value of D_0 for self-diffusion.

In evaluating C the assumption is made that the dominant terms in $(\partial E/\partial r)_T$ for self-diffusion arise from the closed-shell repulsion energy, W_r, given by the Born-Mayer approximation

$$W_r(r)=k\exp(-r/\rho), \tag{11}$$

and, as above, that E_m will be equal to $A/2$, as defined by Eq. (4) with W_r in place of E. Then

$$r_0(\partial E/\partial r)_T=r_0(\partial E_m/\partial r)_T=-r_0E_m/\rho. \tag{12}$$

The value of the constant C can now be estimated by comparison of the observed value of D_0 for self-diffusion with that defined by Eq. (8). Using the same value for C for the case of solute diffusion, one can then easily compute the change in D_0, from Eqs. (3), (5), and (6), since

$$r_0(\partial\Delta E_f/\partial r)_T=-(qr_0+1)E_c(r_0),$$
$$r_0(\partial\Delta E_m/\partial r)_T=-\tfrac{1}{4}E_c(r_0)[2q^2r_0^2-5qr_0 - (qr_0+1)(q^2r_0^2-5qr_0-5)]. \tag{13}$$

RESULTS AND DISCUSSION

By substituting appropriate parameters for Ag and Sb, the changes in D_0 and H for diffusion of Sb in Ag compared with self-diffusion in Ag can now be calculated. The following values are assigned to the parameters:

$r_0=2.88$A (from x-ray data),

$\nu=0.9\times10^{13}$ sec^{-1} (from ratio of velocity of sound to r_0),

$q=1/0.58$A (from Mott[9]),

$\rho=0.345$A (from Fuchs[10]),

$\alpha=1.9\times10^{-5}$ deg C^{-1} (from *Handbook of Chemistry and Physics*),

D_0(self-diffusion of Ag)$=0.72$ cm^2/sec (from reference 2),

H(self-diffusion of Ag)$=45.5$ kcal/mol (from reference 2).

The excess valence of Sb, Z, is taken as 4, and E_m for self-diffusion in Ag is taken as 0.84 ev from the (110) shear modulus. The constant C, from Eqs. (12) and (8) and the observed value of D_0 for self-diffusion, is evaluated as 3.

If a vacancy mechanism for diffusion is assumed, ΔE_f is defined by using the negative sign in Eq. (3), and the calculated expression for diffusion of Sb in Ag is

$$D_{\text{calc}}=0.16\exp(-38\,100/RT)\text{ cm}^2/\text{sec},$$

while the experimental value[1] is

$$D_{\text{exp}}=0.167\exp(-38\,320/RT)\text{ cm}^2/\text{sec}.$$

If an interstitial mechanism is assumed, the calculated value of H is 44.7 kcal/mol, in substantial disagreement with the observed value.

The extremely close agreement between the calculated and observed results can only be regarded as fortuitous, particularly in the case of the D_0 term, where a considerable approximation has been made in estimating the numerical constant in the exponent. However, it is noteworthy that the screening effects alone appear to be sufficient to explain the magnitude and direction of the measured effect, without requiring the introduction of any detailed models.

The derived dependence of the terms D_0 and H of Eq. (7) on the excess valency Z and screening parameter q is given by:

$$D_0(\text{solute})=D_0(\text{solvent})\exp\left\{-\frac{\alpha E_c}{k}[(qr_0+1) + (\tfrac{1}{4}C)(-q^3r_0^3+6q^2r_0^2+5qr_0+5)]\right\},$$

$$H(\text{solute})=H(\text{solvent})-[1-\tfrac{1}{4}(q^2r_0^2-5qr_0-5)]N_0E_c,$$

where E_c is $(Ze^2/r_0)\exp(-qr_0)$.

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

The functional form of these relationships is strongly influenced by the approximations made in the Thomas-Fermi model. Friedel[13] has recently shown by a more exact Hartree-Foch calculation of screening that the Thomas-Fermi model is approximately correct for large even values of Z, but that a relatively larger screening effect would probably be observed for $Z=1$, and possibly also for $Z=3$.

One of the most questionable approximations made in the present treatment is II(A), concerning the nature of the solute atom. One can estimate the magnitude of terms neglected by ignoring the possible difference in closed-shell radii of solute and solvent atoms by writing the closed-shell repulsion energy as

$$W_r(r)=K' \exp[(r_1+r_2-r)/\rho],$$

where r_1 and r_2 are radii of the solvent and solute ions, respectively. The calculated value of ΔE_f will be approximately unchanged since the exponent vanishes for $r=r_0$ in a close-packed lattice. The calculated value of ΔE_m, however, will be modified by the addition of a repulsive term ΔA_r given by

$$\Delta A_r=W_r(r_0)[(r_2-r_1)/\rho](r_0/\rho-7/2).$$

The sign of this term is that of r_2-r_1, since $r_0/\rho>7/2$. For an atom such as Sb of intrinsically larger size than Ag, ΔA_r might be presumed to be small and positive, tending to decrease the magnitude of the calculated value of ΔE_m.

In considering the motion of the solute atom into the imperfection site, the degree of randomness of the process must be evaluated, as shown by Bardeen and Herring.[14] It will be sufficient here to consider the difference in probability of return P_r of the atom to its initial position after a second jump for self-diffusion and solute diffusion. For the former case, P_r is of the order of the reciprocal of the number of nearest neighbors. For solute diffusion, one must consider as especially favored in the second jump both the solute atom and the solvent atoms which are nearest neighbors of both the imperfection and the solute atom. The energy required for motion of any of these atoms will be changed by an amount ΔE_m because of the symmetry of the Coulomb potential. Thus for a face-centered cubic lattice the probability of return P_r is of the order $b/5(1+b)$, where $b=(5/7)\exp[-(\Delta E_m/kT)]$. For the case of Sb in Ag, this probability is about 0.16, which is only a factor two larger than that for self-diffusion. The increase in correlation arising from the change in P_r should be expected to change the calculated effect by only a few percent, and can be neglected in the present approximation.

It is also evident that a solute-vacancy complex, in the sense of the Johnson mechanism,[4] is not expected to play an important role in the solute diffusion process, since the probability that a vacancy will remain as a nearest neighbor of the solute atom after a second jump is $b/(1+b)=0.8$ for the present case. The mean lifetime of the complex is thus only about 5 jump times. However, this effect should produce an appreciable change in the rate of self-diffusion of the solvent atoms if the solute is present as an impurity of the order of one percent concentration.

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[13] J. Friedel, Phil. Mag. 43, 153 (1952).

[14] J. Bardeen and C. Herring, in *Imperfections in Nearly Perfect Crystals* (John Wiley and Sons, Inc., New York, 1952), p. 281 ff.