

incident on the face containing the group V atoms. Other directions were not investigated.

In regard to the formation of displacement spikes: I agree that there very well may be a contraction around such a region which would be in striking contrast to the expansions seen here.

Vavilov, V.S.: Can effects investigated by you be used to solve the question as to which of the theories: the cascade theory or the thermal spike theory of Brinkman is nearer the truth?

Vook, F.L.: Length change measurements can be used to distinguish between the cascade and spike theories if we know the sign of the volume change for a spike as compared with that for a cluster of point defects. It might be expected that the volume change for a spike region in semiconductors is a contraction since the liquid phase is denser than the solid. Contractions have been reported by Gonser for low temperature deuteron irradiation of InSb and GaSb. For InSb and GaAs we see large expansions on electron irradiation, and therefore we believe effects due to point defects are in many cases strikingly different than for spikes. For germanium we see a much greater *expansion* per defect for deuteron irradiation than for electron irradiation. This may imply that clusters exist in germanium with overlapping strains which enhance the expansion rather than spikes having a true phase change.

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Kinetic Interpretation of the Thermodynamic Theory of Impurity Diffusion in Solids*

R. E. HOWARD** AND A. B. LIDIARD

*Theoretical Physics Division, Atomic Energy Research
Establishment, Harwell, England*

A kinetic interpretation is given of the phenomenological equations describing diffusion in a dilute solid solution. It is found, in particular, that the Onsager relation between cross-coefficients of the phenomenological equations is satisfied. The thermodynamic phenomenological formulae are shown to be consistent with previous results on impurity diffusion in metals and on the electromigration of ions in an ionic crystal.

1. Introduction

One may describe the diffusion of atoms through solids either by thermodynamic or by kinetic equations. The thermodynamic description is useful when no detailed information is available about how the atoms diffuse. The atom fluxes are related to thermodynamic "forces", which are functions

of chemical potentials and of external forces, by so-called Onsager coefficients. These coefficients are, in a purely thermodynamic description, unknown. However, the physical content of the theory is provided by the Onsager theorem, which states that if the fluxes and forces satisfy certain conditions, then the cross-coefficients relating pairs of fluxes and forces are equal.

Specifically, consider a crystal consisting of $N-1$ atomic species and suppose that diffusion in this crystal takes place by a vacancy mechanism. Further, consider the vacancies as the N th component. We assume with

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** Permanent address: National Bureau of Standards, Washington 25, D.C., U.S.A.

others¹⁾ that isothermal diffusion and mass transport properties can be described phenomenologically by the equations

$$J_i = \sum_{k=1}^{N-1} L_{ik}(X_k - X_N), \quad (1)$$

where J_i is the flux of species i relative to the local crystal lattice and X_k is the thermodynamic force on species k . If the external force per atom of k is F_k (e.g. electrical force on the ions in an ionic crystal) then

$$X_k = F_k - (\nabla \mu_k)_T \quad (k=1 \cdots N) \quad (2)$$

where μ_k is the chemical potential of species k . The coefficients L_{ik} , in general, depend on temperature and the concentrations of k but are independent of gradients of the concentrations. The Onsager relations are

$$L_{ik} = L_{ki} \quad (3)$$

(absence of magnetic fields).

The above description has been taken over from the non-equilibrium thermodynamics of diffusion in fluids²⁾. For these systems (3) is well grounded. However, it is not clear without further discussion that (3) is also valid in solid systems, particularly when lattice vacancies are treated as an independent component. (The use of the Onsager relations for diffusion in solids has recently been questioned by Allnatt and Jacobs³⁾.) We note that a full discussion of this point does not seem to have been given although it is not our purpose to give such a general discussion here. Rather we examine some existing kinetic calculations⁴⁾⁻⁷⁾ of diffusion and ionic transport to see if they are consistent with the thermodynamic formalism. We have found that it is possible to express the currents (relative to the crystal lattice) in the form of Eq. (1) with detailed expressions for the coefficients L_{ik} . The validity of the Onsager relations (3) is then verified by inspection. Previous results on diffusion of solutes present in small concentration and on departures from the Einstein relation in ionic crystals are also found to be consistent with the thermodynamic formalism.

2. Chemical Potentials

We consider a dilute solid solution. Let there be N_A solvent atoms, N_B solute atoms and N_v vacancies with $N_B, N_v \ll N_A$. Diffusion is assumed to take place by a vacancy mechanism. We wish to express the currents of A and B relative to the crystal lattice in

the form (1) and for this we need the chemical potentials μ_A , μ_B and μ_v . The Gibbs free energy of the system is then made up of non-configurational terms plus⁴⁾

$$G = -kT \ln (\Omega_1 \Omega_2 \Omega_3) + N_v g_v + N_B p \Delta g, \quad (4)$$

where

$$\Omega_1 = \frac{(z)^{N_B p}}{(N_B p)!} \prod_{s=0}^{N_B(p-1)} (N_A + N_B + N_v - 2s), \quad (5)$$

$$\Omega_2 = \frac{[N_A + N_v + N_B(1-2p)]!}{[N_B(1-p)]! [N_A + N_v - N_B p]!}, \quad (6)$$

$$\Omega_3 = \frac{[N_A + N_v - N_B(p+z(1-p))]!}{[N_A - zN_B(1-p)]! [N_v - N_B p]!}. \quad (7)$$

Here g_v is the free energy to form a vacancy at a site surrounded by only A atoms and $(g_v + \Delta g)$ is the free energy to form a vacancy at a site which is nearest neighbour of a B atom. The number of nearest neighbours is denoted by z ($=12$ for the face-centred cubic lattice). The fraction of B atoms which are paired with vacancies is p . We neglect any interactions of B atoms with vacancies in the second or higher co-ordination shells.

The equilibrium value of the degree of association p is given by

$$\left(\frac{\partial G}{\partial p} \right)_{N_A, N_B, N_v} = 0, \quad (8)$$

which is found from Eqs. (4)-(7) to be

$$\frac{p}{(1-p)} = \left[\frac{z(N_v - pN_B)}{N_s} + O(\text{conc}^2) \right] \exp \left(-\frac{\Delta g}{kT} \right), \quad (9)$$

where $N_s = N_A + N_B + N_v$ is the total number of lattice sites in the crystal. We now find the chemical potentials of A , B and v from

$$\mu_i = \left(\frac{\partial G}{\partial N_i} \right), \quad (10)$$

assuming that the association of vacancies and B atoms is in equilibrium. Apart from terms which are independent of concentration, and therefore unimportant for Eq. (1), these are

$$\mu_A = -kT \left[\left(\frac{n_B + n_v + N_B p}{N_s} \right) + O(\text{conc.}^2) \right], \quad (11)$$

$$\mu_B = kT \left[\ln \left(\frac{n_B}{N_s} \right) + \left(\frac{zn_v + N_B p}{N_s} \right) + O(\text{conc.}^2) \right], \quad (12)$$

$$\mu_v = g_v + kT \left[\ln \left(\frac{n_v}{N_s} \right) + \left(\frac{zn_B + N_B p}{N_s} \right) + O(\text{conc.}^2) \right], \quad (13)$$

where n_v and n_B are the numbers of unassociated vacancies and B atoms respectively. The thermodynamic forces follow from Eqs. (2), (9) and (11)–(13).

3. Phenomenological Coefficients, L_{ij}

A number of kinetic and random walk calculations of diffusion in dilute solid solutions have now been made^{(5)–(9)} and it is possible to compare these with Eq. (1). We shall here limit ourselves to the pair association model of a dilute face-centred cubic alloy as discussed in reference (5)*. We use the following notation for the jump frequencies of the vacancies. Five jump frequencies are distinguished: that of a vacancy from one unassociated position to another (w_0); from one associated position to another *via* an exchange with an A atom (w_1); from one associated position to another *via* an exchange with a B atom (w_2); from an associated to an unassociated position (w_3); from an unassociated to an associated position (w_4). A careful comparison of the results of the kinetic calculation with Eq. (1) using forces derived as in Section 2 shows that the results can be expressed in the form (1) and that the L coefficients are,

$$L_{AA} = -\frac{a^2 N_B \dot{p}}{3kT} \times \left[\frac{-(40w_3w_1 + 40w_3^2 + 14w_2w_3 + 4w_1w_2)}{w_1 + w_2 + 7w_3/2} + \frac{7w_3w_0}{w_4} \right] + \frac{4a^2 w_0 n_v}{kT}, \quad (14)$$

$$L_{BB} = \frac{a^2 N_B \dot{p}}{3kT} \frac{w_2(w_1 + 7w_3/2)}{(w_1 + w_2 + 7w_3/2)}, \quad (15)$$

$$L_{AB} = \frac{a^2 N_B \dot{p}}{3kT} \frac{w_2(-2w_1 + 3w_3)}{(w_1 + w_2 + 7w_3/2)}, \quad (16a)$$

$$= L_{BA}. \quad (16b)$$

In arriving at these results, terms of the order of the vacancy and B atom concentrations in J_A and J_B have been omitted, since the pair association theory does not give these

* We may note an error in the equation (3.13) in this paper. In the notation of the paper the following terms should be added to the r.h.s. to give j_v correctly

$$w_0 a^2 \left[28 \frac{m_i}{N_+} \frac{\partial m_v}{\partial x} - 52 \frac{m_v}{N_+} \frac{\partial m_i}{\partial x} \right].$$

Subsequent equations dependent on (3.13) are also in error. Corrected expressions are given in §6.

terms correctly. Eqs. (16) show that the Onsager relations are verified for this model.

In the case of tracer diffusion (where $B=A^*$ represents tracer atoms of A) the cross-term L_{AB} may be written as

$$L_{AA}^* = \frac{a^2 N_B \dot{p}}{3kT} \left(\frac{2}{11} \right) w_2.$$

The correlation factor f for tracer diffusion in an f.c.c. crystal is found to be 9/11 when computed on the pair-association model (5), so that this equation may be written as

$$L_{AA}^* = \frac{a^2 N_B \dot{p}}{3kT} (1-f) w_2.$$

The proportionality between L_{AB} and $(1-f)$ displayed here is an exact result independent of the details of a kinetic model or of crystal structure. That a non-vanishing of the cross-term in tracer diffusion is due to correlation effects was first stated by Bardeen and Herring in their classic article⁽¹⁾.

4. Inter-diffusion Coefficients

These are defined by the equation

$$J_{A,B} = -D_{A,B} \frac{\partial N_{A,B}}{\partial x}, \quad (X_v=0). \quad (17)$$

In the low concentration limit, the phenomenological equations supplemented by (14)–(16) give

$$D_B = \frac{a^2 \dot{p}}{3} \frac{w_2(w_1 + 7w_3/2)}{(w_1 + w_2 + 7w_3/2)}, \quad (18)$$

as obtained previously, and

$$D_A = \frac{4a^2 n_v w_0}{N_s} \left[1 - \frac{N_B \dot{p}}{12n_v w_0 (w_1 + w_2 + 7w_3/2)} \right]. \quad (19)$$

These equations imply that

$$D_A = D_A^* \left[1 + \left(\frac{2}{9} - \frac{(3w_3 - 2w_1)}{(w_1 + 7w_3/2)} \frac{D_B}{D_A^*} \right) \right], \quad (20)$$

where D_A^* is the diffusion coefficient of tracer atoms of A . The term in parenthesis is the correction to the Darken assumption which is

$$D_A = D_A^* \left(1 + \frac{\partial \ln \gamma_A}{\partial \ln c_A} \right) = D_A^*,$$

in the low concentration limit where the activity coefficient $\gamma_A \rightarrow 1$.

5. Departures from the Einstein Relation

As another application consider that component B represents cation impurities of charge q_B in an ionic crystal the host cations of which have charge q_A . The currents of A and B atoms are now given from (1) by the equations

$$J_A = -L_{AA}\mathcal{F}(\mu_A - \mu_v)_T - L_{AB}\mathcal{F}(\mu_B - \mu_v)_T + (L_{AA}q_A + L_{AB}q_B)E, \quad (21)$$

$$J_B = -L_{BA}\mathcal{F}(\mu_A - \mu_v)_T - L_{BB}\mathcal{F}(\mu_B - \mu_v)_T + (L_{BA}q_A + L_{BB}q_B)E, \quad (22)$$

where E is the electric field. The electrical mobility $m_{A,B}$ of an A or B ion is defined by the equation

$$m_{A,B} = \left| \frac{J_{A,B}}{N_{A,B}E} \right|, \quad (\mathcal{F}(\mu_A - \mu_v)_T = \mathcal{F}(\mu_B - \mu_v)_T = 0). \quad (23)$$

The ratio of the impurity ion mobility to its zero field diffusion coefficient (defined by (17) with $E=0$) is now easily shown to be given by the expression

$$\frac{\mu_B}{D_B} = \frac{|L_{BB}q_B + L_{BA}q_A|}{kTL_{BB}}. \quad (24)$$

We observe that the usual form of the Einstein relation is only obtained if $L_{AB}=0$. It has recently been stated⁽¹⁰⁾ in connection with diffusion in ionic melts (where the phenomenological equations are identical to those for a solid) that departures from the Einstein relation imply the operation of different microscopic mechanisms for diffusion and for electrical migration. This is, in fact, incorrect. In the system we are considering both diffusion and electrical conduction processes take place by a vacancy mechanism. However, a departure from the Einstein relation occurs as L_{AB} is non-vanishing because of *correlation* effects. From (15) and (16) we find for a *monovalent* cation in an alkali halide

$$\frac{\mu_B}{D_B} = \frac{e}{kT} \left(\frac{-w_1 + 13w_3/2}{w_1 + 7w_3/2} \right), \quad (25)$$

while for a divalent cation

$$\frac{\mu_B}{D_B} = \frac{e}{kT} \frac{10w_3}{(w_1 + 7w_3/2)}, \quad (26)$$

as obtained previously by extension of the kinetic theory^{(7), (9)}.

6. The Nernst Field

A concentration gradient of impurities in an ionic crystal will in general give rise to an internal electric field because of the tendency for charge separation. The internal field corresponding to the condition of zero charge transfer is called the Nernst field and is calculated from the equation

$$q_A J_A + q_B J_B = 0. \quad (27)$$

In the case of a divalent cation diffusing in

a monovalent cation lattice this gives

$$eE = \{ (L_{AA} + 2L_{AB})\mathcal{F}(\mu_A - \mu_v)_T + (L_{AB} + 2L_{BB})\mathcal{F}(\mu_B - \mu_v)_T \} / \{ L_{AA} + 4(L_{AB} + L_{BB}) \}. \quad (28)$$

If we assume that the anion lattice of the crystal is perfect, then the condition that the crystal be electrically neutral is

$$N_A + 2N_B = N_s, \quad (29)$$

where here N_s is the number of anion or cation sites. Since $N_s = N_A + N_B + N_v$ this equation may be written as

$$N_B = N_v. \quad (30)$$

Evaluating the gradients of the chemical potentials under this condition gives easily

$$\mathcal{F}(\mu_B - \mu_v)_T = 0 \quad (31)$$

and

$$-\mathcal{F}(\mu_A - \mu_v)_T = \frac{kT}{(1+p)} \frac{\partial \ln N_B}{\partial x}. \quad (32)$$

This gives for the Nernst field E the equation

$$\frac{eE}{kT} = \alpha \left(\frac{1}{1+p} \right) \frac{\partial \ln N_B}{\partial x}, \quad (33)$$

where

$$\alpha = \frac{L_{AA} + 2L_{AB}}{L_{AA} + 4(L_{AB} + L_{BB})}. \quad (34)$$

From (21), (22), (27) and (33) the current of B atoms under conditions of zero charge flow is given by

$$J_A = D_B^{(N)} \frac{\partial N_B}{\partial x} \quad (35)$$

with $D_B^{(N)}$, the diffusion coefficient of B in the presence of the Nernst field equal to

$$D_B^{(N)} = \frac{a^2}{3} \frac{p}{1+p} w_2 \left(\frac{2w_1 - 3w_3 + 10w_3\alpha}{w_1 + w_2 + 7w_3/2} \right). \quad (36)$$

The limiting forms of $D_B^{(N)}$ for $p \gg 1$, $p \ll 1$ and for $w_2 \ll w_1$ are the same as those given in reference (5) and the reader is referred to the discussion of that paper.

7. Conclusion

We have compared the predictions of the detailed pair association theory of mass transport in dilute solid solutions with the thermodynamic formalism. We have verified the Onsager reciprocal relation and have verified that the thermodynamic formalism gives a correct description of ionic migration in an electric field. Attention is drawn to the general form of the Einstein relation for ionic crystals. This form also applies to *molten* ionic salts.

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DISCUSSION

Girifalco, L. A.: Could you clarify the relation between the assumptions necessary in the statistical mechanical derivation and the kinetic derivation of the Onsager reciprocal relation? Have you any comment as to why only detailed balance is needed in the kinetic approach while this is not true in the thermodynamic method?

Lidiard, A. B.: I think we must presume that the general requirements for the demonstration of the Onsager reciprocal relations, such as microscopic reversibility and the assumptions about regression of fluctuations, are implicit in the model of vacancies following a random walk. But I must confess that I am not myself completely clear on this matter. Nevertheless I believe the result, which we have verified in our vacancy model of a face-centered cubic alloy, to be true more generally for defect models of mass transport phenomena.

Beeler, J. R.: A comment pertinent to Dr. Girifalco's question is that the probabilities considerations involved in constructing vacancy jump models were discussed by Wood and Parker in the J. Chem. Phys. (1953).

Iida, Y.: According to your result, the term $kT\mu_B/D_B$, which is constant in the simple Einstein theory, has a temperature dependence of Arrhenius type. Now Chemla's results say nothing about it. Do you know other experiments which may serve as the crucial test of your theory?

Lidiard, A. B.: The ratio μ/D depends on temperature through the *quotient* of two functions which are made up of Arrhenius terms. It does not itself depend rapidly on temperature. The early results of Chemla were not made over a very extended range of temperature. I do not know of other experiments of this kind at the present time, but I think such measurements would be valuable.