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POINT DEFECTS IN SILVER HALIDES.

Kinetics and thermodynamics of the migration of interstitial defects

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Résumé. — On présente les résultats d'une étude théorique de la cinétique du transport d'atomes et d'ions au moyen des défauts interstitiels. En particulier, on discute un modèle dans lequel les défauts interstitiels forment des liaisons binaires. Les résultats sont en bon accord avec les équations phénoménologiques de la thermodynamique des processus irréversibles. On vérifie la relation réciproque d'Onsager et on démontre que les formes mathématiques des coefficients phénoménologiques, L_{ij} , ressemblent à celles des solides qui contiennent les lacunes.

Abstract. — This paper presents the results of a theoretical study of the kinetics of atomic and ionic transport *via* interstitial defects for a particular model in which interstitial pairing occurs. These are compatible with the phenomenological equations suggested by the thermodynamics of irreversible processes. The Onsager reciprocal relation is verified and the forms of the phenomenological coefficients, L_{ij} , show broad similarities with those for systems containing vacancies.

1. Introduction. — Over 20 years ago one of us presented a kinetic method for describing the diffusion of atoms *via* the agency of vacancies in crystalline solids and applied it, in particular, to solids having the face-centred cubic structure [1]. Manning [2] later indicated how it could be extended and one such development for the diamond lattice was made by Yoshida [3]. The method has been used to a limited extent for other vacancy problems (e.g. Howard [4], Reiss [5] and Howard and Manning [6]). But for most calculations in diffusion theory, especially those concerned with correlation effects, methods derived from the theory of random walks [2, 7] have generally been preferred. One reason for this may be the less developed formal structure of the kinetic method and its apparently greater algebraic complexity. Despite these limitations the method does have the advantage that it can conveniently provide insight into the generalized phenomenological description provided by the thermodynamics of irreversible processes [8]. The expressions for the generalized phenomenological coefficients L_{ij} in terms of the vacancy properties depend upon the crystal lattice but not upon solid type (e.g. they are the same for atomic transport in a f.c.c. metal as for ionic transport in one sub-lattice of an ionic compound with the rocksalt or zincblende structure). The convenience of this is apparent in treatments of vacancy transport problems as diverse as the effects of vacancy fluxes in metals [9], the diffusion of foreign ions in alkali halides [10], ionic mobility and thermotransport [8]. For other

more general discussions of this formalism see also [11, 12].

Recently one of us has used the same kinetic approach to discuss defect diffusion and thermomigration in certain interstitial alloys with the f.c.c. structure ([13, 14] and unpublished work by McKee). Two particular defect models were examined. The first allowed solute atoms to be in both interstitial and substitutional positions and stable solute interstitial-vacancy pairs to form (a so-called *dissociative* alloy; see e.g. Warburton and Turnbull [15]). The second allowed pairs of interstitial solute atoms to form; these could be made up of either solvent (AA) or solute (BB) atoms or both (AB). These models provide a means for understanding site exclusion and defect correlation effects in both metals and polar compounds. In view of the occurrence of interstitial defects in various ionic compounds (e.g. AgCl, AgBr and compounds with the CaF₂ structure) it therefore seemed of interest to re-express the results of these calculations for interstitial alloys in terms of the more general thermodynamic formalism which would allow their transfer to equivalent ionic systems. In this paper we report some results obtained on the model of interstitial pairing. The dissociative model (e.g. for Cu⁺ ions in AgCl and AgBr) will be described later elsewhere.

2. Calculation and results. — The model for the defect movements is shown in figure 1. We consider only the case where the two ions of the pair are che-

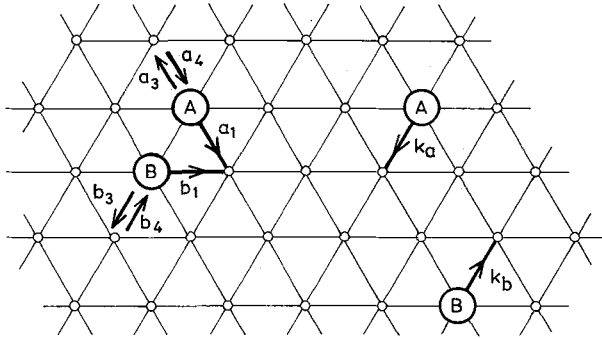


Fig. 1. — Schematic diagram of a (111) plane of a f.c.c. interstitial lattice showing available interstitial positions (small circles), isolated A and B interstitials and an A-B interstitial pair. The various jump frequencies are as indicated.

mically different since ions of the same type (e.g. two anions or two cations) will normally be strongly repulsive and will not form stable pairs. The model could therefore correspond to anti-Schottky disorder.

We suppose that there are n_a and n_b unpaired interstitial ions of species A and B respectively and that there are n_{ab} A-B interstitial pairs in a solid offering a fixed number N of interstitial sites on an f.c.c. lattice. We expect therefore to obtain isothermal phenomenological flux equations of the form

$$J_a = L_{aa} X_a + L_{ab} X_b, \quad (1a)$$

$$J_b = L_{ba} X_a + L_{bb} X_b, \quad (1b)$$

in which J_a and J_b are the fluxes of ions A and B in the presence of thermodynamic forces X_a and X_b :

$$X_i = -(\nabla \tilde{\mu}_i)_T \quad (i = A, B)$$

where $\tilde{\mu}_i$, the electrochemical potential of species i is the sum of the chemical potential, μ_i , and the potential energy of ion i in an electrical potential, ϕ ,

$$\tilde{\mu}_i = \mu_i + q_i \phi \quad (i = A, B)$$

in which q_i is the charge carried by ion i .

In general we may obtain expressions for the L_{ij} by using kinetic theory to give the J_i and statistical thermodynamics to give the corresponding X_i . The simplest procedure, however, is to consider a uniform system subject to a uniform electric field, $E = -\nabla\phi$. The L_{ij} are then readily identified from the coefficients of q_a and q_b in J_a and J_b . We have however verified that identical results are obtained if we consider instead gradients of concentration, although in this procedure some care is necessary to ensure that both sides of eqs. (1) are obtained to the same order in the concentrations of the distinct defects.

We obtain the following results.

(i) We obtain equations for the fluxes J_a and J_b which can be put into the form (1). This confirms that the thermodynamic formalism applies to interstitial

as well as to vacancy systems. We anticipate therefore that for non-isothermal systems we shall have in place of (1)

$$\begin{aligned} J_a &= L_{aa}(X_a + Q_a^* X_q) + L_{ab}(X_b + Q_b^* X_q), \\ J_b &= L_{ba}(X_a + Q_a^* X_q) + L_{bb}(X_b + Q_b^* X_q), \end{aligned} \quad (2)$$

in which

$$X_q = -\frac{1}{T} \nabla T, \quad (3)$$

but where the heats of transport will be composite quantities (Howard [4], Howard and Manning [6], McKee [13]).

(ii) The expressions for the phenomenological coefficients correct to first order in the concentrations of the distinct defects (free interstitials and interstitial pairs) are

$$\begin{aligned} \frac{L_{aa}}{(4 d^2/kT)} &= k_a n_a + \\ &+ \frac{n_{ab}}{12} \left\{ \frac{2(2 a_1 + 7 a_3)(2 b_1 + 7 b_3)}{\Omega} \right. \\ &\left. + \frac{80 a_3(a_1 + a_3)}{\Omega} - 7 k_a \left(\frac{b_3}{b_4} \right) \right\}, \end{aligned} \quad (4)$$

$$\begin{aligned} \frac{L_{ab}}{(4 d^2/kT)} &= \frac{n_{ab}}{6} \frac{(2 a_1 - 3 a_3)(2 b_1 - 3 b_3)}{\Omega} \\ &= \frac{L_{ba}}{(4 d^2/kT)}, \end{aligned} \quad (5)$$

in which

$$\Omega = 2 a_1 + 2 b_1 + 7 a_3 + 7 b_3. \quad (6)$$

The expression for L_{bb} is similar to that for L_{aa} except that a_1 and a_3 are everywhere replaced by b_1 and b_3 respectively, and *vice versa* (but note that b_3/b_4 , which gives the reaction constant for pairing, is necessarily equal to a_3/a_4). We observe that the Onsager equality is satisfied, i.e. $L_{ab} = L_{ba}$ (5). We also observe that there is some similarity between the structure of (4) and (5) and that of the corresponding expressions for vacancy defects [8]: similar numerical coefficients and similar combinations of jump frequencies occur. The generalization of these results to the case where several types of ion, i , and corresponding pairs, $i-j$, are present is straightforward.

(iii) As with vacancy defects the ionic electrical mobilities are

$$\lambda_a = \frac{1}{N_a} |q_a L_{aa} + q_b L_{ab}|, \quad (7a)$$

$$\lambda_b = \frac{1}{N_b} |q_b L_{bb} + q_a L_{ab}| \quad (7b)$$

in which the L_{ij} are as above and N_a and N_b are the total number of interstitial A and B ions respectively (i.e. $N_a = n_a + n_{ab}$ and $N_b = n_b + n_{ab}$).

(iv) If we suppose that the A ions are intrinsic

defects (e.g. of Frenkel type) and that they are therefore everywhere present in local equilibrium (i.e. $\nabla n_a = 0$) then we find that the diffusion coefficient of the B ions is

$$D_b = \frac{kTL_{bb}}{N_b}. \quad (8)$$

As with vacancies however a different and more complex result holds when the introduction of B ions leads to changes in the population of A interstitials for reasons of charge compensation.

(v) When (7) and (8) apply the simple form of the

Nernst-Einstein relation between λ_b and D_b is no longer valid. This is because the off-diagonal term $L_{ab} \neq 0$, which in turn is a direct consequence of the pairing of the defects.

3. Conclusion. — We have presented some of the initial results of a study of the kinetics of atomic and ionic transport *via* interstitial defects. We have shown that these are compatible with the phenomenological equations suggested by the thermodynamics of irreversible processes and that there are broad similarities with vacancy systems.

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