

Diffusion of Interstitial Solute-Vacancy Pairs in a Dilute Alloy

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It has been proposed that the diffusion of cadmium in lead, which is inconsistent with the vacancy mechanism of solute diffusion, occurs by means of an interstitial migration which is strongly correlated because of an attraction between interstitial cadmium ions and vacancies. It is plausible that cadmium, like the noble-metal solutes, should dissolve in lead by the dissociative mechanism, but interact strongly with vacancies by a screened electrostatic interaction. A thermodynamic model of a dilute dissociative solid solution is developed, and expressions for the equilibrium fractions of substitutional, interstitial, and interstitial solute-vacancy close-pair solute states are derived. Following the method of Lidiard, the solute diffusivity and linear enhancement of self-diffusion in this dissociative fcc alloy are calculated. It is shown that in the limit of tightly bound close pairs, the linear-enhancement factor is $b_{11} = f_0(D_2^0/D_1^0)$, in close agreement with the observed linear enhancement of lead self-diffusivity by cadmium additions. It is, therefore, inferred that cadmium diffuses in lead by means of this bound-close-pair mechanism. It is also shown that the solute correlation factor, and therefore the isotope effect for solute diffusion must be very small for this mechanism of diffusion.

I. INTRODUCTION

IT has been shown¹ that the diffusivity D_2^0 of cadmium in lead and the linear enhancement of lead self-diffusion by additions of cadmium solute are not in accord with solute diffusion by the simple vacancy, interstitial, or ring mechanisms. The self-diffusivity linear-enhancement factor b_{11} is correlated with the solute-to-self-diffusivity ratio D_2^0/D_1^0 according to the simple relation

$$b_{11} = D_2^0/D_1^0 \quad (1)$$

over a wide temperature range. That the kinetics of solute and self-diffusion in the alloy are so directly and simply related suggests the possibility of the direct interchange mechanism, for which

$$b_{11} = f_0 D_2^0/D_1^0. \quad (2)$$

This possibility was considered unlikely, however, primarily because such a process should require a higher activation energy than the vacancy mechanism.² It was proposed instead¹ that cadmium, like the noble-metal solutes,³ dissolves in lead by the dissociative mechanism,⁴ i.e., both substitutionally and interstitially. It was suggested that the fast diffusion of cadmium results from migration of the interstitial solute, but that a strong attractive interaction between interstitial solute ions and vacancies has a correlating effect on the interstitial migration and also gives rise to a linear enhancement of the self-diffusion.

The linear enhancement of lead self-diffusion by additions of cadmium indicates that there is a strong attractive interaction between cadmium solute and vacancies. On the basis of the screened electrostatic interaction model developed by Lazarus,⁵ the effective

charge of a substitutional cadmium ion in lead is $Z_{\text{eff}} = -2$, so that the interaction with the negative charge of a vacancy should be repulsive. Since a repulsive interaction leads to a larger activation energy for solute diffusion than for self-diffusion, one would then expect the diffusivity of substitutional cadmium to be slow. More recent calculations by March and Murray⁶ show that the first node of the electronic potential occurs at greater than nearest-neighbor distance for many monovalent solvents, but approximately at the nearest-neighbor distance for many polyvalent solvents. This suggests that the impurity-vacancy interaction at nearest-neighbor distance may be very small in a polyvalent metal.⁷ It is then to be expected that substitutional impurities diffuse in lead at very nearly the rate of self-diffusion. The diffusivity of thallium in lead⁸ is in agreement with this expectation.

Interstitial solute ions may interact strongly with vacancies in a polyvalent metal lattice, however. The interstice-to-lattice-site distances are much smaller than the nearest-neighbor distance, so that the electrostatic interaction is only partially screened. The effective charge of an interstitial solute ion is simply the ionic charge, so that $Z_{\text{eff}} = +2$ for interstitial cadmium in lead. The interaction of this interstitial with an adjacent vacancy therefore is attractive, as proposed, and leads to a positive linear enhancement of the self-diffusion, as observed. The interaction should be much stronger for interstitial cadmium ions than for the interstitial noble-metal ions, for which $Z_{\text{eff}} = +1$. The stronger interaction may produce a significant correlation of the interstitial migration, effecting a reduction in solute diffusivity. It would then be expected, as is

¹ J. W. Miller, Phys. Rev. **181**, 1095 (1969).

² C. Zener, Acta Cryst. **3**, 346 (1950).

³ B. F. Dyson, T. Anthony, and D. Turnbull, J. Appl. Phys. **37**, 2370 (1966).

⁴ F. C. Frank and D. Turnbull, Phys. Rev. **104**, 617 (1956).

⁵ D. Lazarus, Phys. Rev. **93**, 973 (1954).

⁶ N. H. March and A. M. Murray, Proc. Roy. Soc. (London) **A261**, 119 (1961).

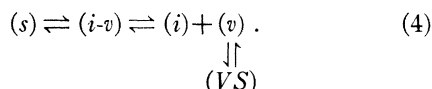
⁷ N. L. Peterson and S. J. Rothman, Argonne National Laboratory Annual Progress Report, Metallurgy Division, No. 249, 1965 (unpublished).

⁸ H. A. Resing and N. H. Nachtrieb, J. Phys. Chem. Solids **21**, 40 (1961).

observed, that

$$D(\text{Pb} \rightarrow \text{Cd}) < D(\text{Pb} \rightarrow \text{Ag}), \\ D(\text{Pb} \rightarrow \text{Au}), D(\text{Pb} \rightarrow \text{Cu}). \quad (3)$$

Let us now consider the implications of an attractive interstitial solute-vacancy interaction with respect to the dissociative mechanism of dissolution. The first step in the formation of an interstitial solute atom is the jump of a substitutional solute atom to an adjacent interstitial site, creating for the moment an interstitial-vacancy pair. If the interaction of this close pair is attractive, as predicted for interstitial cadmium in lead, this defect will then be present in the lattice in significant numbers, in equilibrium with substitutional solute, interstitial solute, and free vacancies. The dissociative mechanism should then be modified to include the interstitial-vacancy close pair as a distinct equilibrium defect,



Here (s) denotes a substitutional solute atom, (i-v) is an interstitial solute-vacancy close pair, (i) is a free interstitial solute atom, (v) is a free vacancy, and (VS) are vacancy sources and sinks.

It is considered that thermodynamic equilibrium is maintained during a metallic-diffusion experiment, so that we are concerned only with the equilibrium case. There is, of course, a difference in free energy between these three dissolved states of solute atoms. Equilibrium is maintained among these states by means of a variety of distinct atomic jumps of solute and solvent atoms, and the independent action of vacancy sources and sinks in maintaining an equilibrium fraction of free vacancies in the crystal. The effective solute-diffusion constant $(D_2^0)_{\text{eff}}$ may then be written

$$(D_2^0)_{\text{eff}} = X_s D_s + X_p D_p + X_i D_i. \quad (5)$$

Here X_s , X_p , and X_i are the respective equilibrium fractions of the total solute concentration X_2 in the substitutional, close pair, and free interstitial states, and D_s , D_p , and D_i are the respective solute diffusivities associated with these states. Although X_s may be large for a dissociative solution, we shall consider that D_s is approximately equal to the self-diffusivity. The diffusivities D_p and D_i both result from interstitial solute atomic jumps, however, and may be very large. In the general dissociative solid solution, both X_p and X_i may then be sufficiently large that $X_p D_p$, $X_i D_i \gg X_s D_s$, so that

$$(D_2^0)_{\text{eff}} \simeq X_p D_p + X_i D_i. \quad (6)$$

It is considered that the interstitial noble-metal solutes interact only weakly with vacancies in the polyvalent metals, so that $X_i D_i \gg X_p D_p$. It follows that $(D_2^0)_{\text{eff}} \simeq X_i D_i$.

If the observed linear enhancement of self-diffusion by cadmium additions is due to the binding of interstitial cadmium ions to vacancies in lead, the close relation (1) between the kinetics of the enhancement effect and the solute diffusivity strongly suggests that the interstitial solute-vacancy pair defect also plays a major role in the diffusion of solute. The interaction of interstitial cadmium ions with vacancies may be sufficiently strong that $X_p D_p \gg X_i D_i$, in which case $(D_2^0)_{\text{eff}} \simeq X_p D_p$. It is, therefore, important to determine analytically the role of interstitial-vacancy pair defects in the diffusion of both solute and solvent.

II. SIMPLE MODEL OF CLOSE-PAIR DIFFUSION

Before proceeding to develop a detailed thermodynamic and kinetic model for the diffusion of interstitial solute-vacancy pairs in an fcc alloy, let us consider the diffusion of both solute and solvent resulting from such defects in a qualitative sense. Having assumed that the interstitial solute-vacancy pair is an equilibrium defect, we realize that any solute atom in a substitutional site may frequently be activated by statistical fluctuations of its vibrational energy to this close-pair state, and will thus spend a certain fraction of its time in this state. While in this state, several types of subsequent solute and solvent atomic jumps are possible. The solute atom may jump to adjacent interstices so as to either dissociate or reorient the close pair, or may merely jump back to the substitutional site, annihilating the pair. Adjacent solvent atoms may also jump so as to either dissociate or reorient the pair.

If the close pairs are tightly bound, the dissociative jumps are energetically disfavored. The frequencies of solute reorientation and annihilation jumps should be characteristic of interstitial jump frequencies, i.e., very very fast compared to vacancy jump frequencies. On the scale of times required for a vacancy jump, we may then consider the interstitial to be randomly positioned with respect to its associated vacancy. In order to clarify the kinetics of a single diffusive step, we shall associate its position with the lattice site of the associated vacancy.

It is clear that no effective diffusion of either solute or solvent may occur unless a solvent atom exchanges with the associated vacancy, effecting a reorientation of the pair. Before another vacancy jump can occur, interstitial solute reorientation, annihilation, and creation jumps have again effected randomization of the solute atom's position with respect to the new lattice site. The solute atom has thus completed one diffusive step, and a solvent atom has also completed a diffusive step in the opposite direction. It is easily deduced from this approximate model that the kinetics of both solute and solvent diffusion are formally identical to those for a direct interchange mechanism, so that the linear-enhancement factor for self-diffusion is given by Eq. (2). This deduction is in good agreement with the

observed linear enhancement of lead self-diffusion by cadmium [Eq. (1)]. It is anticipated that the linear-enhancement factor which we shall derive more rigorously will be very similar to Eq. (2).

An atomic model of a dilute dissociative fcc alloy will now be developed in order to describe the diffusivity of solute and solvent resulting from the presence of interstitial solute-vacancy pair defects. The model and the thermodynamic and kinetic derivations are formally analogous to those of Lidiard⁹ for the dilute substitutional fcc alloy. His results, together with the refinements of Howard and Manning,¹⁰ have provided a quantitative explanation of the linear enhancement of self-diffusion in dilute substitutional fcc alloys. The agreement of experimental results with the predictions of Lidiard's model are evidence that the assumption of nearest-neighbor interactions only is a good approximation for the diffusive behavior of metallic solutions. Since the screening by conduction electrons is necessarily much less effective at interstice-to-lattice-site distances than at nearest-neighbor distance, we shall neglect nearest-neighbor substitutional solute-vacancy interactions in favor of interstitial solute-vacancy close-pair interactions. This is justified in view of the preceding discussion, and permits considerable simplification.

III. EQUILIBRIUM-DEFECT CONCENTRATIONS

In order to describe the general dissociative solid solution, three impurity defects must be included in the formulation—substitutional solute atoms, free interstitial solute atoms, and bound interstitial solute-vacancy pairs. The interaction of substitutional solute atoms with vacancies is neglected, while that of interstitial solute atoms with vacancies is explicitly included. Consideration is restricted to the fcc lattice, and it is further assumed that the interstitial solute atoms occupy only the interstices of octahedral symmetry.

The alloy is assumed to be composed of N_1 solvent and N_2 solute atoms. These solvent atoms and the substitutional solute atoms are to be randomly distributed on the lattice sites. There are n_v free vacancies, also randomly distributed, whose standard Gibbs free energy of formation is g_v . There are N_2q free interstitial solute atoms having a formation energy I . The total number of interstitial solute atoms associated with vacancies is N_2p , and the free energy of this defect is taken to be $(g_v + I + B)$. The binding energy of interstitial to vacancy is then $-B$. Exclusive of configurational entropy contributions, which are to be calculated, the free energy of the crystal is

$$n_v g_v + N_2 q I + N_2 p (g_v + I + B). \quad (7)$$

The total number of substitutional lattice sites in

the crystal is given by

$$N_s = N_1 + N_2(1 - p - q) + N_2 p + n_v. \quad (8)$$

Since there is a one-to-one correspondence between the substitutional sites and interstitial sites of octahedral symmetry, Eq. (8) is also the number of interstitial sites in the crystal. The number of ways in which the $N_2(1 - p - q)$ substitutional solute atoms may be randomly distributed on the lattice sites is

$$(N_1 + N_2 - N_2 q + n_v)! / [N_2(1 - p - q)]! \times (N_1 + N_2 p + n_v)!. \quad (9)$$

The number of vacancies which are associated with interstitial solute atoms $N_2 p$ may now be arranged among the remaining $(N_1 + N_2 p + n_v)$ substitutional sites in the following number of ways:

$$(6)^{N_2 p} (N_1 + N_2 p + n_v)! / (N_2 p)! (N_1 + n_v)!. \quad (10)$$

The six distinct orientations of this defect give rise to the multiplicative factor $(6)^{N_2 p}$. There now remain $N_1 + n_v$ substitutional sites in the lattice, but in considering the arrangement of vacancies among these sites, we must exclude sites adjacent to free interstitial solute atoms. There are, of course, $6N_2 q$ such sites. The number of ways in which the n_v free vacancies may be arranged among the remaining $N_1 + n_v - 6N_2 q$ sites is

$$(N_1 + n_v - 6N_2 q)! / n_v! (N_1 - 6N_2 q)!. \quad (11)$$

Finally, we must calculate the number of ways in which the $N_2 q$ free interstitial solute atoms may be arranged on the allowable interstitial sites. From the total number of interstitial sites, we must exclude all of the $6N_2 p$ interstitial sites associated with the interstitial-vacancy pair defects and the $6n_v$ interstitial sites next to free vacancies. The number of ways in which the free interstitials may be arranged among the allowed sites is

$$\frac{(N_1 + N_2 - N_2 q - 6N_2 p - 5n_v)!}{(N_2 q)! (N_1 + N_2 - 2N_2 q - 6N_2 p - 5n_v)!}. \quad (12)$$

The total free energy G of this dissociative-alloy crystal relative to a crystal containing no vacancies or interstitials is

$$G = -kT \ln[\text{product of Eqs. (9)-(12)}] + n_v g_v + N_2 q I + N_2 p (g_v + I + B). \quad (13)$$

To obtain the thermodynamic-equilibrium numbers of the various defects it is necessary to minimize the free energy G ,

$$\frac{\partial G}{\partial p} = \frac{\partial G}{\partial q} = \frac{\partial G}{\partial n_v} = 0. \quad (14)$$

We may use Stirling's approximation and simplify further by assuming that both p and q are small compared to unity. With neglect of higher-order effects, the resulting expressions for the equilibrium values of

⁹ A. B. Lidiard, *Phil. Mag.* **5**, 1171 (1960).

¹⁰ R. E. Howard and J. R. Manning, *Phys. Rev.* **154**, 561 (1967).

N_2p , N_2q , and n_v are

$$N_2p = 6N_2e^{-(\sigma v + I + B)/kT}, \quad (15)$$

$$N_2q = N_2e^{-I/kT}, \quad (16)$$

$$n_v = N_s e^{-\sigma v/kT}. \quad (17)$$

In arriving at (17), we have neglected a factor $(1 - 6X_2q)$ multiplying the right-hand side because $6X_2q \ll 1$. This factor arises from the exclusion of sites discussed above. Since we have neglected substitutional solute vacancy interactions, those vacancies which are nearest neighbors to substitutional solute atoms are considered to be free vacancies.

IV. DIFFUSION OF SOLUTE

We have postulated that close interstitial vacancy pair defects are formed by the creation jump of a substitutional solute atom to a nearest-neighbor interstice. We shall specify this creation jump frequency as v_1 , and the frequency of the reverse annihilation jump as v_2 . The total jump frequency for each of these may be calculated by multiplying the total number of solute atoms in the appropriate configuration for a particular jump by the probability per unit time that such a jump occurs from that configuration. In order that equilibrium be maintained, it is necessary that these total jump frequencies be equal. The following relation, derived from this condition, is useful in simplification of further results:

$$v_1/v_2 = e^{-(\sigma v + I + B)/kT}. \quad (18)$$

Let us postulate that the interstitial atom may also jump from one interstice surrounding the associated vacancy to another, and specify the jump frequency of these reorientation jumps as k_2 . The activation barrier for such a jump may be very small. If only v_1 , v_2 , and k_2 solute jumps are allowed, it is evident that each solute atom remains associated with the same lattice site, and no real diffusion occurs. The various atomic jumps, and their respective jump frequencies, are shown in Fig. 1.

There is a finite probability, however, that after a given initial creation or reorientation jump of a solute atom, the vacancy may make an exchange jump with one of its nearest-neighbor solvent atoms. We shall specify the jump frequency of such solvent-vacancy exchanges which retain the association as w_2 and those which dissociate the pair as w_1 . If an initial k_2 jump is followed by a w_2 jump, subsequent solute jumps result in a calculable nonzero correlation factor for solute diffusion. Considering the combined effect of only k_2 and w_2 jumps, it is obvious that the interstitial may simply move along with its associated vacancy. The interstitial may also make dissociative jumps, at a frequency k_1 , but since we are primarily interested in the migration of tightly bound close pairs, we may assume that dissociative jumps of either the associated

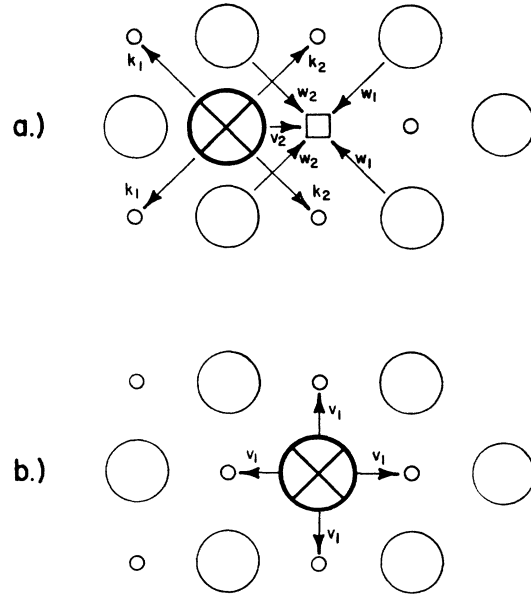


FIG. 1. Interstitial solute-vacancy pair configuration (a) and substitutional solute ion (b) are viewed in the (100) plane of the fcc lattice so as to identify the jump frequencies described in the text. Solvent ions are shown as large open circles, and solute ions as large crossed circles; both are shown approximately to scale as Pb^{4+} solvent ions and Cd^{2+} solute ions. The small circles indicate vacant octahedral interstitial sites, and the square indicates a vacant lattice site.

interstitial or the vacancy occur infrequently, i.e., $k_1 \ll k_2$ and $w_1 \ll w_2$. Free interstitial solute jumps from one interstice to another will be considered to occur at the frequency k_0 . Since solute-vacancy interactions are to be neglected at distances equal to or greater than the nearest-neighbor distance s , associative jumps of a free interstitial so as to form a close pair will be assumed to occur with the same frequency.

The solute diffusion constant may be derived from^{10,11}

$$D = \frac{1}{6} \lim_{n \rightarrow \infty} \frac{1}{t_n} \left(\sum_{i=1}^n \langle \mathbf{r}_i \cdot \mathbf{r}_i \rangle + 2 \sum_{i=1}^n \langle \mathbf{r}_i \cdot \mathbf{r}_{i+1} + \mathbf{r}_i \cdot \mathbf{r}_{i+2} + \dots \rangle \right). \quad (19)$$

This result for the diffusion constant applies to the three-dimensional random walk of a single tracer atom by means of n discrete vector steps \mathbf{r}_i for a total time t_n . The effect of correlation of successive jump directions are included in the second summation. In the limit $n \rightarrow \infty$, each solute atom spends an equilibrium fraction of its time in each of the solute states previously defined, so that the diffusion constant calculable from this result applies to all solute atoms.

To perform the first summation in (19), we first note

¹¹ P. G. Shewmon, in *Diffusion in Solids* (McGraw-Hill Book Co., New York, 1963), pp. 47-48.

that

$$\lim_{n \rightarrow \infty} \frac{1}{t_n} \sum_{i=1}^n \langle \mathbf{r}_i \cdot \mathbf{r}_i \rangle = \lim_{n \rightarrow \infty} \frac{1}{t_n} \sum_{i=1}^n r_i^2 = \sum_j \Gamma(j) r^2(j). \quad (20)$$

Here the fractional jump frequency $\Gamma(j)$ is obtained by dividing the total solute jump frequency for atomic jumps of the distinct type j by the total number of solute atoms, and $r(j)$ is the corresponding jump distance. Only creation jumps v_1 may occur from the substitutional solute states, of which there are $N_2(1-p-q)$. Since there are six possible creation jumps to the surrounding interstices, and the jump distance is $s/\sqrt{2}$, where s is the nearest-neighbor distance,

$$\Gamma(v_1) r^2(v_1) = \frac{1}{2}(1-p-q)(6v_1)s^2. \quad (21)$$

From each of the close-pair configurations, numbering $N_2 p$, there are four possible reorientation jumps of distance s , eight possible dissociative jumps of distance s , and a single annihilation jump of distance $s/\sqrt{2}$. It follows that

$$\Gamma(k_2) r^2(k_2) + \Gamma(k_1) r^2(k_1) + \Gamma(v_2) r^2(v_2) = p(4k_2)s^2 + p(8k_1)s^2 + \frac{1}{2} p v_2 s^2. \quad (22)$$

Assuming that both p and q are small compared to unity, i.e., $(1-p-q) \simeq 1$, using (18) to simplify, and including the contribution of free interstitial jumps, the result for the first summation is

$$\lim_{n \rightarrow \infty} \frac{1}{t_n} \sum_{i=1}^n \langle \mathbf{r}_i \cdot \mathbf{r}_i \rangle = s^2 p (v_2 + 4k_2 + 8k_1) + s^2 q (12k_0); \quad (23)$$

exclusive of correlation effects, the solute diffusion constant is then

$$D_2^0 = \frac{1}{6} s^2 p (v_2 + 4k_2 + 8k_1) + 2s^2 q k_0. \quad (24)$$

We must now determine the modification of this result resulting from the correlation of successive solute jumps. These effects are contained in the second summation of Eq. (19), which may be expressed as

$$\lim_{n \rightarrow \infty} \frac{2}{t_n} \sum_{i=1}^n \langle \mathbf{r}_i \cdot \mathbf{r}_{i+1} + \mathbf{r}_i \cdot \mathbf{r}_{i+2} + \dots \rangle = 2 \sum_j \Gamma(j) \sum_k \sum_l p_l(k) \langle \mathbf{r}(j) \cdot \mathbf{r}_l(k) \rangle. \quad (25)$$

Here $p_l(k)$ is the probability that the l th succeeding atomic jump of a tracer atom, following the initial jump of type j , is of the distinct type k , which has a jump vector $\mathbf{r}_l(k)$. Associated vacancy jumps may, of course, occur between successive solute jumps, and such terms must be included in the summation over l . These terms make a null contribution. For initial k_2, v_1 , and v_2 jumps, the contribution for $l > 1$ is null, while for initial k_1 and k_0 jumps, the total contribution is of second order, and considered negligible. The only significant contribution to correlation effects result from the jump sequences $v_1 - v_2, v_1 - k_2, v_1 - k_1, k_2 - k_2, k_2 - k_1$, and $k_2 - v_2$. The

final result of this summation, as well as that for the first summation, are then substituted in Eq. (19) to give the solute diffusion constant

$$D_2^0 = \frac{1}{6} s^2 p (4k_2 + v_2) \left(\frac{4w_2 + 8w_1 + 12k_1}{4w_2 + 8w_1 + 4k_2 + 8k_1 + v_2} \right) + \frac{1}{6} s^2 p (8k_1) + 2s^2 q k_0. \quad (26)$$

If the binding of interstitial solute ions to vacancies is very strong, the fraction of free interstitials may be sufficiently small that the diffusivity of free interstitial solute, given by the term $2s^2 q k_0$, is negligible compared to the diffusivity of associated solute. Neglecting this latter term of Eq. (26), the solute diffusion constant attributable to close-pair defects may be expressed as

$$D_2^0 = \frac{1}{6} s^2 p (4k_2 + v_2) \times \left(\frac{4w_2 + 8w_1 + 12k_1}{4w_2 + 8w_1 + 4k_2 + 8k_1 + v_2} + \frac{8k_1}{4k_2 + v_2} \right). \quad (27)$$

The term in parentheses is the effective correlation factor for diffusion by means of k_2 and v_2 jumps. If the close pairs are strongly bound, the dissociative jump frequency k_1 must be energetically disfavored, so that $k_1 \ll k_2, v_2$. In addition, the interstitial jump frequencies k_2 and v_2 are considered to be much larger than vacancy jump frequencies, so that $k_2, v_2 \gg k_1, w_2, w_1$. Thus, the solute correlation factor is very small. Making this approximation in (27), and substituting for the fraction of close pairs p according to the result (15), we may write the solute diffusion constant

$$D_2^0 = 4s^2 e^{-(g_v + I + B)/kT} (w_2 + 2w_1 + 5k_1). \quad (28)$$

It may easily be seen from Eq. (26) that if only v_1, v_2 , and k_2 jumps are allowed, the solute diffusion constant $D_2^0 = 0$, as previously anticipated. We should note also that solute diffusion by means of tightly bound close pairs, unlike the simple vacancy, interstitial, and simple interchange mechanisms of diffusion, actually requires that the solute correlation factor be very small. The explicit dependence of solute diffusion by this mechanism on the vacancy jump frequencies w_2 and w_1 is made clear in Eq. (28), as is also the tendency of increasing dissociative solute jump frequencies to decrease the extreme correlation effects and to eventually lead to a dominantly interstitial mechanism of diffusion.

Since we shall later wish to compare a result for the linear enhancement of solvent diffusion due to such close pair defects with the ratio D_2^0/D_1^0 , it is convenient to calculate this ratio. Using the result (28) for the solute diffusivity, and dividing by the self-diffusivity,¹² we obtain

$$D_2^0/D_1^0 = [2(w_2 + 2w_1 + 5k_1)/w_0 f_0] e^{-(I+B)/kT}. \quad (29)$$

¹² A. D. LeClaire, Phil. Mag. 7, 141 (1962).

V. LINEAR ENHANCEMENT OF SOLVENT DIFFUSION

The solvent diffusivity for this model of a dilute dissociative alloy may also be derived from Eq. (19). Equations (20) and (25) are used to perform each of the summations in the limit that $n \rightarrow \infty$. The fractional solvent atom jump frequency $\Gamma(j)$ is obtained by dividing the total solvent jump frequency for atomic jumps of the distinct type j by the total number of solvent atoms.

We shall first determine the solvent diffusivity exclusive of correlation effects by calculating the contribution of the first summation, (20), to the diffusion constant (19). Since all solvent atomic jumps are of the same distance s , the quantity s^2 is common to all terms of the sum, and the fractional jump frequencies $\Gamma(j)$ are simply additive. There are four possible w_2 jumps and eight possible w_1 jumps of solvent atoms into the N_2p associated vacancies in the crystal, so that

$$\Gamma(w_2) + \Gamma(w_1) = (N_2p/N_1)(4w_2 + 8w_1). \quad (30)$$

Free vacancies may jump so as to associate with free interstitials. This jump frequency is designated w_3 . There are 32 distinct orientations of these two defects at the associative separation, and thus a total of

$$32N_2qn_v/N_s \quad (31)$$

configurations from which a vacancy may make an associative jump. From these configurations, there are a total of 48 possible w_3 jumps, so that

$$\Gamma(w_3) = (N_2q/N_1)(n_v/N_s)(48w_3). \quad (32)$$

In calculating $\Gamma(w_0)$, it must be noted that there are a total of 336 possible w_0 jumps from the above associative configurations, in addition to the contribution from the remainder of the intrinsic vacancies. Since we have assumed that substitutional solute atoms do not interact with vacancies, the fraction N_1/N_s of the atoms surrounding the remainder of intrinsic vacancies are, in fact, solvent atoms. We may then write

$$\Gamma(w_0) = \frac{N_2q}{N_1} \frac{n_v}{N_s} (336w_0) + \frac{N_1}{N_s} \frac{n_v}{N_1} \left(1 - \frac{32N_2q}{N_s}\right) (12w_0). \quad (33)$$

The first summation is then given by the sum of Eqs. (30), (32), and (33), multiplied by s^2 . As the fraction of free interstitials q is considered very small, we neglect terms of the order X_2q . The result is substituted into (19) to give the solvent diffusivity in the absence of correlation effects

$$D_1(X_2) = 2s^2w_0e^{-u_v/kT} + 4X_2s^2(w_2 + 2w_1) \times e^{-(u_v + I + B)/kT}. \quad (34)$$

In performing the second summation, (25), to determine the correlation effects, we need only include those terms for the initial solvent jumps of types w_0 , w_2 , and w_1 . It is easily shown that the contribution for initial w_0 jumps results in a simple numerical modification of the first term in (34); this term becomes $2s^2w_0f_0e^{-u_v/kT}$, where $f_0 = 0.78146$, as calculated by Compaan and Haven,¹³ is the correlation factor for self-diffusion in a pure fcc crystal. Because interstitial jump frequencies are so much larger than vacancy jump frequencies, many associated interstitial jumps follow a w_2 or w_3 vacancy jump before another vacancy jump may occur. We may then assume that there is an equal probability of finding the associated interstitial in any one of its six sites at the time of a subsequent vacancy jump. This assumption has been used to calculate the solvent correlation effects for initial w_2 and w_1 jumps. Following an initial tracer-vacancy exchange, the vacancy may, of course, make several additional jumps before returning to effect a subsequent tracer jump, and the appropriate probabilities $p_l(k)$ and averages $\langle \mathbf{r}(j) \cdot \mathbf{r}_l(k) \rangle$ must be included in the summation over l . The calculation was performed so as to include such terms for a maximum of four successive vacancy jumps. Although the resultant correlation effects are a very complex function of the vacancy jump frequencies, an effective numerical correlation factor may be estimated by making various reasonable approximations among the vacancy jump frequencies. For all such approximations, the correlation effects determined in this way modify the second term of (34) by a numerical factor $f \approx f_0$. This is a consequence of the rapid randomization of the interstitial position with respect to its associated vacancy. We may finally express the solvent diffusivity in this dilute dissociative alloy

$$D_1(X_2) = 2s^2w_0f_0e^{-u_v/kT} \times \left[1 + \left(\frac{2(w_2 + 2w_1)}{w_0} e^{-(I+B)/kT} \right) X_2 \right]. \quad (35)$$

This result is formally similar to the result of Lidiard⁹ since it is of the form

$$D_1(X_2) = D_1^0(1 + b_{11}X_2). \quad (36)$$

Here D_1^0 is the self-diffusivity in a pure fcc crystal, while $D_1(X_2)$ is that in the dilute dissociative fcc alloy. The linear enhancement of self-diffusion effected by the migration of bound interstitial solute-vacancy pairs is then described by the linear-enhancement factor

$$b_{11} = (2(w_2 + 2w_1)/w_0)e^{-(I+B)/kT}. \quad (37)$$

Noting the great similarity between this result and that for D_2^0/D_1^0 , Eq. (29), we may express b_{11} as a function

¹³ K. Compaan and Y. Haven, Trans. Faraday Soc. **52**, 786 (1956).

of D_2^0/D_1^0 :

$$b_{11} = f_0(D_2^0/D_1^0)[1 + 5k_1/(w_2 + 2w_1)]^{-1}. \quad (38)$$

VI. DISCUSSION

In the limit that solute diffusion occurs purely by a tightly bound interstitial solute-vacancy pair mechanism, interstitial dissociative jumps k_1 are disallowed. In this case, the linear-enhancement factor for self-diffusion is

$$b_{11} = f_0(D_2^0/D_1^0). \quad (39)$$

In addition, the interstitial jump frequencies k_2 and v_2 are expected to be much larger than the vacancy jump frequencies w_2 and w_1 , so that the correlation factor for solute diffusion, in the parentheses of (27), may be written, within these approximations,

$$f_2 = (4w_2 + 8w_1)/(4k_2 + v_2). \quad (40)$$

The correlation factor for solute diffusion must, therefore, be very small.

Screening of the electrostatic solute-vacancy interaction by the conduction electrons may be very ineffective at the interstice-lattice-site separation, so that the binding energy $-B$ may be rather large. If this is so, there will result a significant fraction p of bound close pairs, and the solute diffusivity will be much larger than the self-diffusivity. If D_2^0/D_1^0 is sufficiently large, the linear-enhancement factor for self-diffusivity may be less than the minimum consistent with solute diffusion by the simple vacancy mechanism¹

$$b_{11} = f_0(D_2^0/D_1^0) < (b_{11})_{\min}^{\text{vac}} \\ = -18 + 1.9448(D_2^0/D_1^0). \quad (41)$$

The diffusivity of the solute cadmium in lead is unusually large,¹ and the magnitude and temperature dependence of the linear-enhancement factor b_{11} [Eq. (1)] agree well with the analytical result (39) and furthermore, are inconsistent with solute diffusion by the simple vacancy mechanism. It is, therefore, proposed that cadmium dissolves dissociatively in lead, and that the interstitial solute binds strongly to vacancies, so that cadmium solute diffuses primarily by the bound close-pair mechanism described herein. Since solute diffusion by this mechanism requires that the solute correlation factor be very small, the isotope effect¹⁴ for

diffusion of cadmium in lead should be unusually small. This isotope effect has been measured by Miller and Edelstein¹⁵ as a further test of the proposed mechanism of diffusion; the effect is very small, as predicted. All of the experimentally measurable parameters of cadmium solute diffusion are thus in direct accord with this model for diffusion of tightly bound interstitial-vacancy pairs.

If other solutes dissolve dissociatively in lead, but the interstitial fraction interacts more weakly with vacancies, as is expected for the noble-metal solutes, the binding energy $-B$ is much smaller, and the dissociative interstitial jump frequency k_1 much larger. We may then deduce from Eq. (26) that the solute diffusivity may be much larger than for the bound close-pair mechanism, and that the correlation factor for solute diffusion must also be larger. In the limit that the free interstitial fraction q is sufficiently large, solute diffusion occurs primarily by the interstitial mechanism, i.e., by means of free interstitial k_0 jumps, and the correlation factor is unity. We may also predict, from Eq. (38), that the linear-enhancement factor for self-diffusion in such an alloy system must be less than the quantity $f_0(D_2^0/D_1^0)$.

In accord with these deductions, noble-metal solute diffusivities in lead³ are much faster than the diffusivity of cadmium, and noble-metal solute additions produce no observable enhancement of the lead self-diffusivity.^{3,16} A measurement of the isotope effect for noble-metal diffusion in lead is desirable to confirm the proposed interstitial mechanism.³

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¹⁵ J. W. Miller and W. A. Edelstein, following paper, Phys. Rev. **188**, 1081 (1969).

¹⁶ W. Seith and A. Keil, Z. Physik Chem. **B22**, 350 (1933).

¹⁴ N. L. Peterson, Solid State Phys. **22**, 409 (1968).