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Correlation Factors for Diffusion in Nondilute Alloys

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Correlation factors for diffusion in binary and multicomponent alloys are calculated for a random-alloy model with diffusion by a vacancy mechanism. This model, which should apply best for nondilute alloys, assumes that atoms and vacancies are randomly distributed and that suitable average values can be used to represent the actual atom and vacancy jump frequencies in the crystal. In alloys, both atoms and vacancies follow correlated walks. Also, the atom correlation factors are influenced by the nonrandom motion of the vacancies. Thus, in order to treat correlation effects in concentrated alloys properly, one must consider not only the correlation factors f_i for diffusion of atoms but also the correlation factor f_v for diffusion of vacancies. In specific calculations, one also must find the partial correlation factors f_v^i for diffusion of vacancies by exchange with atoms of the particular species i . Analytic expressions for all of these correlation factors are calculated. These equations can be expressed directly in terms of the measurable tracer-diffusion-coefficient ratios D_i^*/D_k^* with no unknown jump frequencies appearing. The calculations also yield a forbidden region in the plot of diffusion-coefficient ratio as a function of alloy composition, with correlation factors going to zero at the boundary of this region. Specific applications to binary alloys are discussed.

INTRODUCTION

When diffusion occurs by a random walk, the diffusion coefficient D_i^* for species i in a cubic crystal is given by

$$D_i^* = \frac{1}{6} \lambda^2 \nu_i, \quad (1)$$

where λ is the jump distance and ν_i is the jump frequency for species i . When there is a correlated

walk, this expression becomes

$$D_i^* = \frac{1}{6} \lambda^2 \nu_i f_i, \quad (2)$$

where f_i is the correlation factor for species i . Here f_i takes into account the correlation between the directions of successive atom jumps. In crystals having sufficient symmetry and with diffusion by a vacancy mechanism, the general expression for f_i is^{1,2}

$$f_i = H_i / (2w_i + H_i), \quad (3)$$

where w_i is the jump frequency for exchange of a vacancy with a neighboring atom of species i and H_i is the effective escape (or randomization) frequency for vacancies which neighbor an atom of species i .

In the present paper, a random-alloy model will be used to evaluate f_i for multicomponent alloys. This requires the evaluation of H_i in such alloys.

The probability that a vacancy will reexchange with atom i and introduce a correlation between succeeding jumps of atom i depends not only on the jump frequency w_i but also on the competing jump frequencies for exchange of the vacancy with atoms other than atom i . H_i in Eq. (3) gives the dependence of f_i on these competing vacancy jump frequencies. To a first approximation, H_i is just the sum of the competing vacancy jump frequencies available immediately after an exchange with i . To completely avoid a nonrandom reexchange with i , however, the vacancy must not only refrain from exchanging with i on its first subsequent jump but also must not come back and exchange from a nonrandom direction at a later time. Thus, H_i does not simply equal the sum of the competing jump frequencies but instead is somewhat smaller than this.

The physical measurement of H_i is most easily visualized by considering diffusion along a $\langle 100 \rangle$ direction in a simple-cubic crystal and introducing the concept of a randomization plane. A vacancy which arrives on the same $\{100\}$ plane as atom i is in a random position with respect to i so far as diffusion along the $\langle 100 \rangle$ direction normal to this plane is concerned, since such a vacancy is just as likely to cause a jump of i in the positive $\langle 100 \rangle$ direction as in the negative $\langle 100 \rangle$ direction. This plane can be called the randomization plane. H_i equals the jump frequency with which a vacancy on site α neighboring on the impurity will exchange with an atom other than atom i and begin a path which leads it either permanently away from site α or to a site on the randomization plane before it returns to site α . Jump paths where the vacancy returns to site α without reaching the randomization plane do not contribute to H_i . Thus, H_i is related directly to the rate at which vacancies move from sites neighboring on atom i to sites on the boundary of a specified crystal space, with the randomization plane forming one boundary of this space. The remaining boundaries in practice are formed by the crystal surfaces and physical vacancy sinks such as grain boundaries and dislocations. In calculations, usually only a small error is introduced if it is approximated that these other boundaries are an infinite distance from atom i .

In the following discussion, the fact that H_i de-

pends linearly on the rate at which a vacancy diffuses away from site α will be used to calculate the effect of vacancy correlations on H_i . This result applies not just to the simple-cubic structure discussed above but more generally to all cubic crystals and to diffusion in certain directions in some noncubic crystals where a randomization plane can be defined.

VACANCY CORRELATION FACTORS

The preceding discussion of f_i has described correlation factors for atom diffusion. In addition, the vacancies themselves can follow correlated walks. As in Eq. (2), one can write for cubic crystals

$$D_v = \frac{1}{6} \lambda^2 \nu_v f_v. \quad (4)$$

Subscript v here and in subsequent equations indicates that vacancies are the diffusing species under consideration. Also, f_v is the vacancy correlation factor and

$$\nu_v^0 = \nu_v f_v, \quad (5)$$

where ν_v^0 is the effective frequency of random vacancy jumps.

In pure crystals, each vacancy does pursue a random walk, so in this case f_v equals unity. In alloys on the other hand, f_v usually does not equal unity. Even in a dilute alloy, the equations for vacancy motion are much less simple than in a pure crystal. For example, there are several different atom-vacancy exchange frequencies, and also in the vicinity of an impurity the vacancy does not follow a random walk. In a nondilute alloy, with each atom species having a different atom-vacancy exchange frequency, the situation is even more complex. Then, there are no regions where a vacancy will pursue a random walk.

The total vacancy jump frequency ν_v in Eq. (4) can be expressed as a sum over all species i ,

$$\nu_v = z \sum_i w_i N_i = \sum_i \nu_v^i, \quad (6)$$

where z is the number of nearest-neighbor sites to which a vacancy can jump, w_i is the average jump frequency for the vacancy jump to a site occupied by an atom of species i , and N_i is the fraction of nearest-neighbor sites occupied by i atoms. Also ν_v^i is the total vacancy jump frequency from jumps with species i and

$$\nu_v^i = z w_i N_i. \quad (7)$$

Because of correlation effects, not all w_i jumps will be effective in causing random diffusion of the vacancy. For each type of jump, the correlation effect can differ. Thus, one must define a partial correlation factor f_v^i for each species i , with

$$\nu_v^{ie} = \nu_v^i f_v^i = z w_i N_i f_v^i, \quad (8)$$

where ν_v^{ie} is the effective frequency of random vacancy jumps involving species i . Since

$$\nu_v^e = \sum_i \nu_v^{ie}, \quad (9)$$

one finds with Eqs. (5), (6), and (8),

$$f_v = \sum_i w_i N_i f_v^i / \sum_i w_i N_i. \quad (10)$$

Here, f_v is the average correlation factor for diffusion of vacancies and the f_v^i are partial vacancy correlation factors applying to each individual species i .

In principle, the f_v^i and hence f_v could be calculated in a straightforward manner in terms of the detailed correlations between successive vacancy jumps. In a nondilute alloy, this would be a very complex task. Thus, in the present paper a different approach is used, taking advantage of the relations in a random-alloy model between the atom correlation factor f_i and the partial vacancy correlation factor f_v^i .

RANDOM-ALLOY MODEL

The model which will be used assumes that (a) the jump frequency w_i for exchange of a vacancy with an atom of species i depends only on i and does not depend on the identity of other neighboring atoms nor on the site, and (b) the vacancy jump frequency to a neighboring site containing an atom of unspecified or unknown species equals W , with

$$W = \sum_i N_i w_i, \quad (11)$$

where N_i is the mole fraction of species i and W is the average vacancy jump frequency in the crystal. Thus, the vacancy jump frequency for exchange with an i atom whose diffusion is being followed equals w_i , but other jumps are assumed to occur with the average frequency W .

This alloy model will apply best to random alloys where there are no energetically preferred sites for vacancies or for atoms of particular species. Treating each site as an average site is then most reasonable. In such an alloy, there would be zero vacancy binding energy and no atom ordering or clustering. Also, it is assumed in the present treatment that all atom sites are crystallographically equivalent and all jumps by i atoms are geometrically the same. Thus, a single atom correlation factor f_i and partial vacancy correlation factor f_v^i can be associated with each species, and a single average vacancy correlation factor f_v can be applied to all W jumps. In the case of nonequivalent sites, a separate partial correlation factor would be needed for each geometrically different type of w_i or W jump.

In actual concentrated alloys, a large variety of local atom configurations can occur, with each

configuration allowing a different characteristic jump frequency. Thus, in real alloys, a spectrum of jump frequencies for jumps by the various atoms of species i would be expected. The present model simplifies the situation by replacing this spectrum of frequencies by a single average frequency w_i . As a further simplification, the model then treats each atom as being in identical surroundings. Each i atom whose diffusion is being followed (as is necessary to calculate its correlation factor) is assumed to have jump frequency w_i characteristic of the particular species i , but a vacancy diffusing away from this i atom is treated as encountering only average atoms, all having the average jump frequency W . The introduction of the average frequencies w_i and W introduces an approximation into the model. Nevertheless, in a random alloy, effects from these averaging approximations should be small.

Mathematically, the random-alloy model makes the correlation problem amenable to calculation without detailed statistical analysis. This not only simplifies the equations but also allows H_i to be calculated without introducing a "near-boundary" approximation, where it is assumed that a vacancy which has reached a site only a short distance from atom i , for example a second-nearest-neighbor site, will not further affect the diffusion of i . By contrast, a near-boundary approximation often is necessary when more detailed statistical calculations are attempted.

The random-alloy model should provide a good approximation for any reasonably random nondilute alloy and should show any major effects arising in such an alloy. Also, the resulting equations contain no unknown jump frequencies but instead can be expressed in terms of experimentally measurable tracer-diffusion coefficients. This is especially important in allowing direct comparison with experiment.^{3,4}

EFFECTIVE ESCAPE FREQUENCY IN ALLOY

The effective escape frequency H_i in the random-alloy model will be closely related to a basic escape frequency H_0 , where H_0 is the effective escape frequency in a pure crystal having the same crystal structure as the random alloy but containing only one type of atom, whose atom-vacancy exchange frequency is W . In a pure crystal, H can be calculated from the known values of the correlation factor. If f_0 is the correlation factor in a pure crystal of the cubic structure under consideration, one finds from Eq. (3) that

$$f_0 = H_0 / (2W + H_0). \quad (12)$$

Since f_0 for any such crystal will be a pure number, it follows that

TABLE I. Values of the correlation factor f_0 are those quoted by K. Compaan and Y. Haven [Trans. Faraday Soc. 54, 1498 (1958)]. Values of M_0 are calculated from Eq. (15).

Crystal structure	f_0	M_0
Diamond	$\frac{1}{2}$	2
Simple cubic	0.6531	3.77
bcc	0.7272	5.33
fcc	0.7815	7.15

$$H_0 = M_0 W, \quad (13)$$

where M_0 is a numerical constant. Substituting Eq. (13) into Eq. (12) yields

$$f_0 = M_0 / (2 + M_0) \quad (14)$$

or

$$M_0 = 2f_0(1 - f_0)^{-1}. \quad (15)$$

Values of f_0 and M_0 for several cubic structures are listed in Table I.

In practice, the effective escape frequency H_i for a vacancy neighboring on an i atom in an alloy will differ from H_0 somewhat because a vacancy in an alloy does not follow a random walk as does one in a pure crystal. The correlations between successive vacancy jumps do not change the over-all vacancy concentrations nor do they change the locations of the sites to which a vacancy must move to "escape" from the diffusing atom. However, the correlations do change the rate at which vacancies will diffuse and hence the rate at which a vacancy will move to an escape site, such as a vacancy sink or a site on the randomization plane. With a constant concentration of diffusing vacancies, vacancies will arrive at escape sites less frequently if the effective rate of vacancy motion is decreased. A vacancy correlation factor f_v which is smaller than unity decreases the vacancy diffusion rate. Therefore, it also decreases the effective escape frequency H_i . If correlation effects were neglected, H in the random-alloy model would equal H_0 . Thus, in this model when vacancy correlations are included, one finds

$$H_i = f_v H_0. \quad (16)$$

The derivation above uses a continuum approach in that it does not include specific jump frequencies. Explicit consideration of effective jump frequencies yields this same result on an atomic scale. This latter approach, presented in the following paragraph, is particularly pertinent when the vacancy reaches the randomization plane in only one jump or a very few jumps.

On an atomic scale, one can consider the first jump in a series of jumps which take the vacancy

to an escape site. Without correlations, this first jump to a neighboring site in a random alloy occurs on the average with jump frequency $\sum_i N_i w_i$, with H_0 being proportional to this sum. When there are correlation effects, the effective jump frequency for random exchange of vacancies with neighboring A atoms becomes $N_A w_A f_v^A$, with neighboring B atoms $N_B w_B f_v^B$, and so on. Thus, in a random alloy, H_i will be proportional to the sum $N_A w_A f_v^A + N_B w_B f_v^B + \dots$. Since randomly directed effective jump frequencies are assumed, the constant of proportionality will be the same here as in the calculation of H_0 . Therefore, one obtains

$$\frac{H_i}{H_0} = \frac{N_A w_A f_v^A + N_B w_B f_v^B + \dots}{N_A w_A + N_B w_B + \dots} = f_v, \quad (17)$$

which is the same result as in Eq. (16). The right-hand equality in Eq. (17) follows from Eq. (10).

It may be noted that the right-hand sides of Eqs. (16) and (17) do not depend on i . This is a consequence of the assumption that all vacancy jumps other than with specified tracer atoms whose diffusion is being studied occur with jump frequency W . Since H_i depends only on the frequency of these nontracer jumps, it is the same for all species and is independent of i .

If each H_i equals the value given in Eqs. (16) and (17), Eq. (3) becomes

$$f_i = H_0 f_v / (2w_i + H_0 f_v). \quad (18)$$

Thus, in order to calculate the atom correlation factor f_i , one must know something about the vacancy correlation factor f_v .

RELATION BETWEEN ATOM AND VACANCY CORRELATION FACTORS

In Ref. 5, a relation between the f_i and the f_v^i was obtained for a binary random alloy. In the present paper, similar relations are derived for the more general case of a multicomponent random alloy. The method is to calculate contributions to the vacancy flux J_v in two separate ways: one directly in terms of the vacancy drift velocities and the second indirectly by calculating the atom fluxes J_i and using the equation

$$J_v = -\sum J_i. \quad (19)$$

The partial vacancy correlation factors f_v^i enter into the direct calculation of J_v , whereas the atom correlation factors enter into the calculation of the J_i .

With vacancies in equilibrium, the vacancy flux which might result from the vacancy concentration gradient $\partial c_v / \partial x$ or chemical potential gradient $\partial \mu_v / \partial x$ disappears.^{5,6} Thus, the vacancy flux J_v in a system with vacancy concentration maintained at equilibrium equals the vacancy concentration c_v multiplied by an average vacancy drift velocity

$\langle v_F \rangle_v$ resulting from forces other than $\partial\mu_v/\partial x$. When there are several atom species i , vacancy exchanges with each atom species should be treated separately and the results summed over all atom species to obtain the total vacancy drift velocity. Thus

$$J_v = c_v \langle v_F \rangle_v = c_v \sum_i \langle v_F \rangle_v^i. \quad (20)$$

Here $\langle v_F \rangle_v^i$ is the contribution to the vacancy drift velocity arising from the driving force F_v^i (other than $\partial\mu_v/\partial x$) influencing the atom exchange frequency for exchange of vacancies with atoms of the particular species i and $\langle v_F \rangle_v$ is the total vacancy drift velocity from these forces F_v^i .

For any randomly diffusing entity, the drift velocity $\langle v_F \rangle$ is proportional to the driving force F multiplied by the random jump frequency ν^e . In cubic crystals if there is a single random jump frequency²

$$\langle v_F \rangle = DF/kT = \frac{1}{6} \lambda^2 \nu^e F/kT, \quad (21)$$

where k is Boltzmann's constant, T is the absolute temperature, and the random-walk expression in Eq. (1) has been used for D . In the present case, Eq. (21) becomes

$$\langle v_F \rangle_v^i = \frac{1}{6} \lambda^2 (kT)^{-1} \nu_v^i F_v^i, \quad (22)$$

where F_v^i is the force influencing i -type vacancy jumps. With Eq. (8) this yields

$$c_v \langle v_F \rangle_v^i = \frac{1}{6} \lambda^2 z w_i c_v (kT)^{-1} f_v^i N_i F_v^i. \quad (23)$$

To obtain a final compact equation for J_v , it may be noted that in a random alloy the atom jump frequency ν_i is given by

$$\nu_i = z w_i N_v, \quad (24)$$

where N_v is the mole fraction of vacancies in the crystal. Also, for atoms i and vacancies v , the mole fractions N and the concentrations c per unit volume are related by

$$c_i = N_i C, \quad (25)$$

$$c_v = N_v C, \quad (26)$$

where C is the number of sites per unit volume. Combining Eqs. (23)–(26) with Eqs. (2) and (20) yields

$$J_v = \sum_i (c_i D_i^* / kT) (f_v^i / f_i) F_v^i. \quad (27)$$

Here f_i enters in the denominator since it appears in Eq. (2) for the atom diffusion coefficient D_i^* but does not appear in Eq. (23). By contrast, f_v^i enters in the numerator since it appears in the kinetic expression for $\langle v_F \rangle_v^i$ through Eq. (8), substituted into Eq. (22).

The forces F_v^i which arise from chemical concentration gradients equal the negatives of the chemical-potential gradients,

$$F_v^i = - \frac{\partial \mu_i}{\partial x}. \quad (28)$$

When these are the only forces present, Eq. (27) can be expressed as

$$J_v = - \sum_i L_{vi} \frac{\partial \mu_i}{\partial x}, \quad (29)$$

where

$$L_{vi} = (c_i D_i^* / kT) (f_v^i / f_i). \quad (30)$$

Here, Eq. (29) has the form of the general thermodynamic diffusion equation for diffusion of vacancies, where the mobility coefficient L_{vi} is the proportionality constant relating the flux J_v to the driving force $\partial\mu_i/\partial x$.

Equations similar in form to Eq. (29) can be written for the fluxes J_j of the various atom species j . When the only driving forces are those from the atom chemical-potential gradients $\partial\mu_i/\partial x$, one can write

$$J_j = - \sum_i L_{ji} \frac{\partial \mu_i}{\partial x}. \quad (31)$$

A detailed kinetic calculation of J_j with the random-alloy model used here has previously been performed.^{7,4,2} In a multicomponent alloy, this analysis yields an equation having the form of Eq. (31) with

$$L_{ii} = (c_i D_i^* / kT) (1 + 2c_i D_i^* / M_0 \sum_m c_m D_m^*), \quad (32)$$

$$L_{ji} = L_{ij} = (2c_i c_j D_i^* D_j^* / M_0 kT \sum_m c_m D_m^*) \text{ for } i \neq j. \quad (33)$$

Here, the summation over m includes all atom species in the crystal and M_0 is a numerical constant given by Eqs. (13) and (15).

We now are in a position to compare the vacancy flux calculated directly in Eqs. (27) and (29) with that obtained from the kinetic calculation of the atom fluxes J_j . Since in general the driving forces $\partial\mu_i/\partial x$ are independent of one another, it follows from Eqs. (19), (29), and (31) that

$$L_{vi} = - \sum_j L_{ji}. \quad (34)$$

Inserting values of L_{ii} and L_{ji} from Eqs. (32) and (33) then yields

$$L_{vi} = \frac{c_i D_i^*}{kT} \left(1 + \frac{2}{M_0} \right) = \frac{c_i D_i^*}{kT f_0}, \quad (35)$$

where f_0 is the atom correlation factor for self-diffusion in a pure crystal, given by Eq. (14). Values of f_0 are given in Table I. Comparison of Eqs. (30) and (35) yields

$$f_i = f_0 f_v^i. \quad (36)$$

This equation is valid for every atom species i even

in a multicomponent alloy under the random-alloy model used here.

This equation is reasonable. For example, in the limit where all atom species have the same jump frequency, one obtains a random walk for the vacancies, making all f_v^i equal unity. In this limit, it also is obvious that all f_i equal f_0 . The resulting relation between f_v^i in this special case is exactly that given by Eq. (36).

ATOM CORRELATION FACTORS

In the present random-alloy model, the probability N_v of any particular site being occupied by a vacancy is independent of the identities of neighboring atoms. With Eq. (24) substituted into Eq. (2), one obtains

$$D_v^* = \frac{1}{6} \lambda^2 N_v z w_i f_i. \quad (37)$$

Here D_v^* depends on i only through the factors w_i and f_i since there is no dependence of N_v on i . This equation along with previous equations derived for a random alloy relating H_i to H_0 and f_v^i to f_i allows f_i in such an alloy to be expressed in a simple analytic form in terms of diffusion-coefficient ratios.

Substitution of Eq. (10) for f_v into Eq. (18) with f_v^i being given by Eq. (36), H_0 by Eq. (13), and W by Eq. (11) yields

$$f_i = M_0 f_0^{-1} \sum_m N_m w_m f_m / (2w_i + M_0 f_0^{-1} \sum_m N_m w_m f_m). \quad (38)$$

After some algebra and substitution of Eq. (14) for f_0 , this becomes

$$f_i = [-2w_i f_i + (M_0 + 2) \sum_m N_m w_m f_m] / (M_0 + 2) \sum_m N_m w_m f_m. \quad (39)$$

Finally, the products $w_i f_i$ and $w_m f_m$ can be replaced by the appropriate tracer diffusion coefficients from Eq. (37) to yield

$$f_i = [-2D_v^* + (M_0 + 2) \sum_m N_m D_m^*] / (M_0 + 2) \sum_m N_m D_m^*. \quad (40)$$

This expresses f_i in terms of the experimentally measurable quantities D_v^* , D_m^* , and N_m .

Equation (40) shows that, when D_v^* is zero, f_i equals unity. Since D_v^* cannot be negative, a non-zero D_v^* will always make f_i be smaller than unity. The deviation of f_i from unity, which measures the strength of the correlation effect, increases as D_v^* increases, being largest for the fastest-diffusing species. Also f_i itself is smallest for this fastest-diffusing species.

ATOM CORRELATION FACTORS IN BINARY ALLOYS

In a binary alloy containing species A and B , Eq. (40) becomes

$$f_A = \frac{M_0}{M_0 + 2} \left(\frac{(M_0 + 2)(N_A D_A^* + N_B D_B^*) - 2D_v^*}{M_0(N_A D_A^* + N_B D_B^*)} \right), \quad (41)$$

$$f_A = f_0 \left(1 - \frac{2N_B(D_A^* - D_B^*)}{M_0(N_A D_A^* + N_B D_B^*)} \right). \quad (42)$$

Similarly, we have

$$f_B = f_0 \left(1 + \frac{2N_A(D_A^* - D_B^*)}{M_0(N_A D_A^* + N_B D_B^*)} \right). \quad (43)$$

When D_A^* equals D_B^* , one obtains simply $f_A = f_B = f_0$, since $(D_A^* - D_B^*)$ appears as a factor in the last term in Eqs. (42) and (43). When the two tracer-diffusion coefficients differ, the correlation factor calculated from these equations for the faster-diffusing species will be smaller than f_0 whereas that for the slower-diffusing species will be larger than f_0 . Figures 1 and 2 give values of f_A and f_B in a fcc crystal (where $M_0 = 7.15$ and $f_0 = 0.78$) as a function of composition and of D_A^*/D_B^* . For purposes of this presentation, A is taken to be the faster-diffusing constituent and B the slower-diffusing constituent. It may be noted that in Figs. 1 and 2 the maximum value of f_B is unity and the minimum value of f_A is zero, with there being a strong dependence of the correlation factors on both N_A and D_A^*/D_B^* .

It might appear from Eq. (42) that f_A could become negative when $D_A^* \gg D_B^*$. Negative values of f_A are not allowed by Eq. (3), however. This forbidden region is discussed further in a subsequent section.

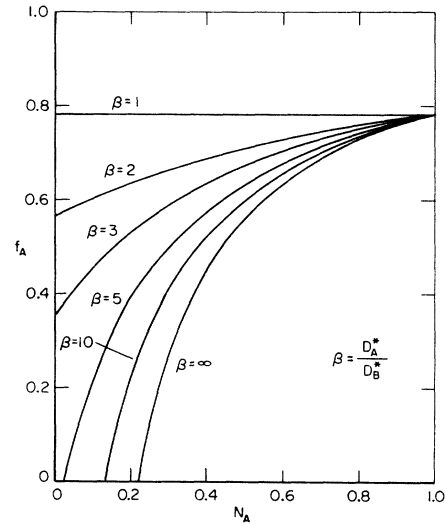


FIG. 1. Correlation factor f_A of faster-diffusing atom species A in random binary fcc A - B alloy with diffusion by vacancy mechanism. Similar curves for other crystal structures can be obtained from Eq. (42) by using the appropriate M_0 values quoted in Table I.

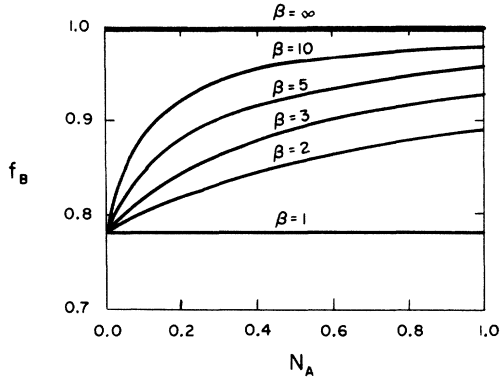


FIG. 2. Correlation factor f_B of slower-diffusing atom species B in random binary fcc alloy with diffusion by vacancy mechanism. Here $\beta = D_A^*/D_B^*$. Similar curves for other crystal structures can be obtained from Eq. (43) by using the appropriate M_0 values quoted in Table I.

DIFFUSION-COEFFICIENT RATIOS RELATED TO JUMP-FREQUENCY RATIOS

The fact that f_i can be expressed directly in terms of the D_i^* makes it particularly easy to derive an analytic expression relating the ratio w_i/w_k to the ratios D_i^*/D_k^* . Because of the correlation factor, D_i^*/D_k^* in a random alloy equals w_i/w_k only when w_i/w_k equals unity and $f_i = f_k$. When w_i and w_k are unequal, the correlation factor of the slower-diffusing species will be larger than that of the faster-diffusing species.

Equation (37) for the random-alloy model yields

$$D_i^*/D_k^* = w_i f_i / w_k f_k. \quad (44)$$

In a multicomponent alloy, one finds from Eqs. (40) and (44) that

$$w_i/w_k = (D_i^*/D_k^*) \left[-2D_k^* + (M_0 + 2) \sum_m N_m D_m^* \right] / \left[-2D_i^* + (M_0 + 2) \sum_m N_m D_m^* \right] \quad (45)$$

or

$$w_i/w_k = (D_i^*/D_k^*) \left\{ 1 + 2(D_i^* - D_k^*) / \left[-2D_i^* + (M_0 + 2) \sum_m N_m D_m^* \right] \right\}. \quad (46)$$

These equations can also be expressed in terms of f_0 by using the equation

$$1 - f_0 = 2 / (M_0 + 2). \quad (47)$$

For example, Eq. (45) reduces to

$$w_i/w_k = (D_i^*/D_k^*) \left[\sum_m N_m D_m^* - (1 - f_0) D_k^* \right] / \left[\sum_m N_m D_m^* - (1 - f_0) D_i^* \right]. \quad (48)$$

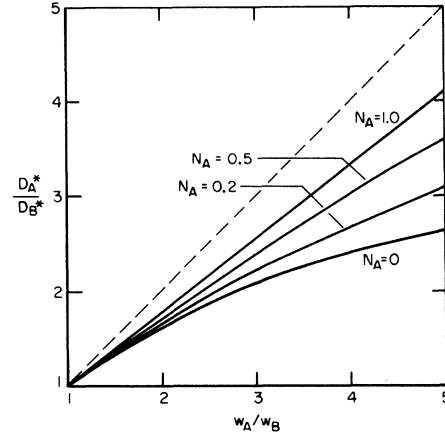


FIG. 3. Relation in fcc structure between jump frequency ratio w_A/w_B and diffusion-coefficient ratio D_A^*/D_B^* in random binary $A-B$ alloy with diffusion by vacancy mechanism. Note that for D_A^* greater than D_B^* all curves lie below the dashed line, which indicates the locus where $w_A/w_B = D_A^*/D_B^*$. Relations for larger values of w_A/w_B are given in Fig. 4.

In a binary alloy, this becomes

$$\frac{w_A}{w_B} = \frac{D_A^*}{D_B^*} \left(\frac{(N_A D_A^* + N_B D_B^*) - (1 - f_0) D_B^*}{(N_A D_A^* + N_B D_B^*) - (1 - f_0) D_A^*} \right). \quad (49)$$

Figures 3 and 4 were obtained from Eq. (49) with $(1 - f_0)$ in a fcc structure set equal to 0.219. The graph for other cubic crystal structures will be similar, the only difference being in the value of M_0 or f_0 .

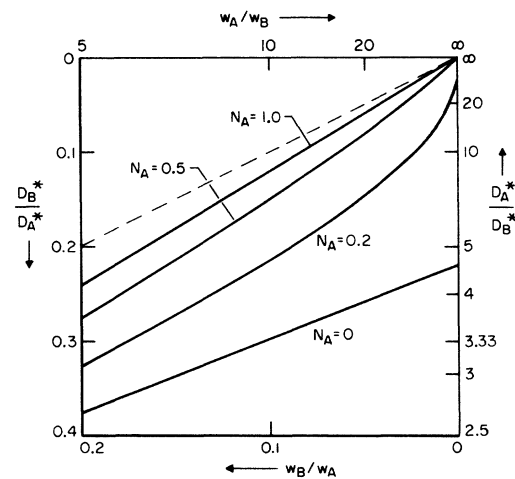


FIG. 4. Relation in fcc structure between jump frequency ratio w_A/w_B and diffusion-coefficient ratio D_A^*/D_B^* in random binary $A-B$ alloy with diffusion by vacancy mechanism. The dashed line indicates the locus where $w_A/w_B = D_A^*/D_B^*$. Relations for smaller values of w_A/w_B are given in Fig. 3.

In structures where correlation effects are larger, so that f_0 is smaller and $(1 - f_0)$ larger than in a fcc crystal, a larger deviation from the condition $D_A^*/D_B^* = w_A/w_B$ will be found. The line where these ratios are equal is indicated as a dashed line in Figs. 3 and 4. At large or even moderate values of w_A/w_B , deviations from this line are appreciable.

In a random multicomponent alloy, the deviation of w_i/w_k from unity will always be greater than the deviation of D_i^*/D_k^* from unity. This statement is valid for all values of w_i/w_k , both large and small, either greater than unity or smaller than unity. In addition, if one of the two ratios D_i^*/D_k^* or w_i/w_k is larger than unity, the other also will be larger than unity. Similarly, if one is smaller than unity, the other will be smaller than unity. These results can be obtained directly from Eqs. (3) and (44). According to Eq. (3), if w_i is greater than w_k , then f_i is smaller than f_k , since in our random alloy it is assumed that H does not depend on the diffusing species. It then follows from Eq. (44) that w_i/w_k is larger than D_i^*/D_k^* if $w_i/w_k > 1$ and that w_i/w_k is smaller than D_i^*/D_k^* if $w_i/w_k < 1$.

FORBIDDEN REGION

In Fig. 4, w_B/w_A and D_B^*/D_A^* are used as coordinates in order to show what happens when w_A/w_B goes to infinity (or w_B/w_A goes to zero). It may be noted that for $N_A = 0$ and $N_A = 0.2$, the ratio D_B^*/D_A^* never goes to zero, not even when w_B/w_A goes to zero. Thus, for particular values of N_A , there are certain values of D_B^*/D_A^* which are not allowed by the random-alloy model. There are minimum values allowed for D_B^*/D_A^* and maximum allowed values for D_A^*/D_B^* .

The limits of the region of allowed values can be deduced from Eq. (40). Physically, the jump frequencies w_i and H_i cannot be negative. Thus, one concludes from Eq. (3) that the correlation factors f_i cannot be negative and, from Eq. (40), for a multicomponent random alloy that

$$-2D_i^* + (M_0 + 2) \sum_m N_m D_m^* \geq 0 \quad (50)$$

or

$$D_i^* \leq \frac{1}{2}(M_0 + 2) \sum_m N_m D_m^* \quad (51)$$

Species i is included in the sum over m . If the i term is removed from the sum, one obtains

$$D_i^* [1 - \frac{1}{2}(M_0 + 2)N_i] \leq \frac{1}{2}(M_0 + 2) \sum_{m \neq i} N_m D_m^* \quad (52)$$

where the summation is over all atom species m except $m = i$. This inequality obviously is obeyed whenever $\frac{1}{2}(M_0 + 2)N_i$ is greater than or equal to unity. Thus for $N_i \geq 2/(M_0 + 2) = 1 - f_0$, there is no restriction on D_i^* . However, if

$$N_i < 1 - f_0 \quad (53)$$

it must be true that

$$D_i^* \leq (1 - f_0 - N_i)^{-1} \sum_{m \neq i} N_m D_m^* \quad (54)$$

In a binary alloy with $N_A + N_B = 1$ and with the faster-diffusing species i being identified as species A , Eq. (54) becomes

$$D_B^*/D_A^* \geq 1 - f_0/N_B \quad (55)$$

This equation applies in the region $N_A \leq 1 - f_0$, which is also the region where

$$N_B \geq f_0 \quad (56)$$

An equation giving the boundary of the region of allowed values

$$[1 - (D_B^*/D_A^*)_{\text{min}}](1 - N_A) = f_0 \quad (57)$$

can be obtained from Eq. (55). This equation has the form of a hyperbola. At the boundary line defined in Eq. (57), the equality sign in Eq. (55) applies. This line also corresponds to the locus where w_A/w_B goes to infinity, as can be seen from Eq. (49) by noting that the denominator on the right-hand side goes to zero when the equality sign in Eq. (55) is used but remains positive if the inequality is used.

The graph of Eq. (57) for a fcc crystal with $f_0 = 0.781$ is shown in Fig. 5. The intercepts on the N_A and D_B^*/D_A^* axes are at $1 - f_0$. The region below this curve is a forbidden region, which contains values of D_B^*/D_A^* smaller than allowed by the random-alloy model for these values of N_A .

COMPARISON WITH EXPERIMENT

The present random-alloy model contains several simplifying assumptions. In particular, the model is consistent with zero vacancy binding energy. Consequently, results obtained from this model will not apply to all alloys. For example, they usually will not be valid for dilute alloys having appreciable vacancy-impurity binding. However, in a more concentrated alloy, which contains 10% or more atom fraction of impurity, each lattice site has a large probability of neighboring on at least one impurity. Then, the vacancy binding energy will be more nearly equal at all sites in the crystal. In the absence of ordering or clustering, the random-alloy model then can be expected to provide a very reasonable approximation.

It would be of interest to compare experimental results in nondilute alloys with those predicted by the present model. This could help to ascertain the range of validity of the model. This model may apply well even to some alloys with less than 10% impurity.

Isotope-effect experiments yield estimates (or at least upper limits) for the atom correlation factors f_i .⁸ These experimental figures can be compared

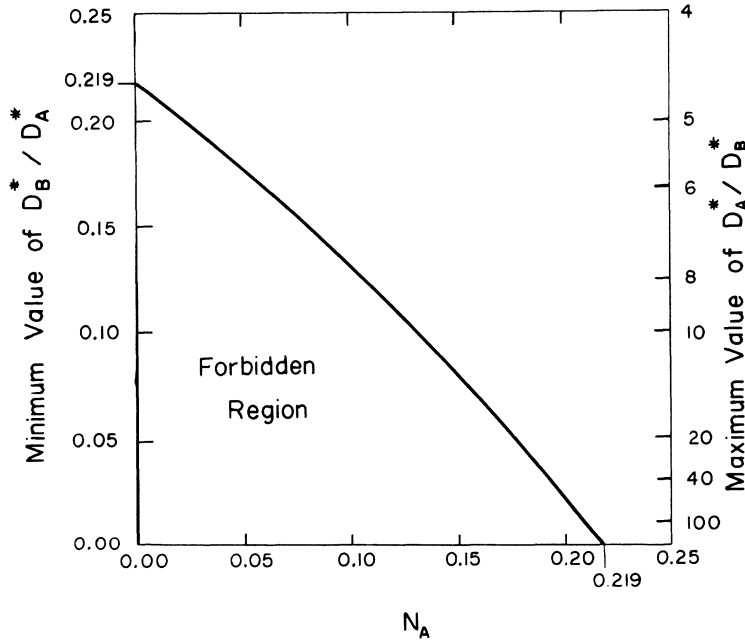


FIG. 5. Forbidden region for diffusion by vacancy mechanism in random binary fcc alloy. Values of D_A^*/D_B^* in the forbidden region are not allowed in the random-alloy model.

with theoretical values given by Eqs. (40)–(43), some of which are displayed in Figs. 1 and 2.

Heumann and Reerink⁹ measured in an interdiffusion experiment the strength of the isotope effect E for Cr^{50} and Cr^{54} diffusing in fcc Ni–Cr (0–20% Cr) at 1245 °C, where $D_{\text{Cr}^{50}}^*/D_{\text{Cr}^{54}}^* \approx 2$. As discussed in Ref. 8, E should equal $f\Delta K$, where f is the atom correlation factor of the diffusing isotopes and ΔK is related to the number of atoms moving during the jump, probably being nearly unity for a simple vacancy mechanism in fcc crystals. Heumann and Reerink's value of $E \approx 0.5$ thus leads to the estimated value $f_{\text{Cr}} \approx 0.5$. This value is smaller than 0.78, as expected for the faster-diffusing constituent in an fcc alloy. Detailed comparison with Fig. 1 probably is not justified since the critical data in determining the E value were taken mainly in the range 2–5% Cr, where the random-alloy model used for Fig. 1 perhaps is not valid. However, the value of $f_{\text{Cr}} \approx 0.6$ from Fig. 1 is in reasonable agreement with the measured value and its possible experimental error.

A similar interdiffusion experiment by Johnson¹⁰ for Ni^{58} , Ni^{60} , and Ni^{62} diffusing in fcc Cu–Ni (0–100% Ni) at 1053 °C yielded results which indicate an E of 1.0 ± 0.2 . Here the critical data were those in the range 2–13% Ni. Since $D_{\text{Cu}}^*/D_{\text{Ni}}^* \approx 3$ in this range,¹¹ this measurement is consistent with the result ($f_{\text{Ni}} \approx 0.9$) predicted by Fig. 2.

Tracer measurements made by Peterson and Rothman¹² of Zn^{65} and Zn^{69} diffusing in ordered (411 °C) and disordered (560 °C) β -phase CuZn (approximately 48% Zn) yielded E values of 0.20 and 0.24, respectively. These alloys are bcc with¹³ $D_{\text{Zn}}^*/D_{\text{Cu}}^* \approx 2$. Thus, the predicted value of f_{Zn} from

Eq. (42) is ≈ 0.6 , which is appreciably larger than 0.20 or 0.24. The discrepancy here may arise from a very small ΔK or from short-range-ordering phenomena which persist even in the “disordered” alloy.

Similar measurements¹⁴ on the diffusion of Cu^{64} and Cu^{67} gave values of E for copper diffusing in β -CuZn which were larger than these for zinc, as would be expected from the present equations. For the disordered β -CuZn, the ratio $E_{\text{Zn}}/E_{\text{Cu}}$ was very close to that predicted from Eqs. (42)–(43) for the ratio $f_{\text{Zn}}/f_{\text{Cu}}$, with $E_{\text{Zn}}/E_{\text{Cu}} = 0.738$ compared to $f_{\text{Zn}}/f_{\text{Cu}} = 0.732$. This is consistent with the supposition that ΔK is nearly the same for copper and zinc in these alloys. For ordered β -CuZn, the agreement between $E_{\text{Zn}}/E_{\text{Cu}}$ and the value of $f_{\text{Zn}}/f_{\text{Cu}}$ predicted for the random alloy was less good (0.615 vs 0.721), which is not surprising since a theory designed for random alloys might not apply well to ordered alloys.

In α -phase CuZn, Peterson and Rothman's measurements¹⁴ of $E_{\text{Zn}}/E_{\text{Cu}}$ showed rather poor agreement with predicted $f_{\text{Zn}}/f_{\text{Cu}}$ values from Eqs. (42)–(43) at 4-at. % zinc (0.557 vs 0.456) but better agreement at 30-at. % zinc (0.706 vs 0.650). Agreement in the disordered β -CuZn at nearly 50-at. % zinc was best of all (0.738 vs 0.732). Thus, as might be expected, the random-alloy model seems to apply increasingly well as one moves from the dilute range toward a 50-50 alloy. In all cases, the E values were less than the corresponding random-alloy correlation factors, as would be expected if $\Delta K < 1$.

Measurements of E_{Fe} and E_{Co} by Fishman, Gupta,

and Lieberman¹⁵ in disordered equiatomic FeCo also show good agreement with the present predictions if allowance is made for a ΔK which is less than unity. In all cases, the measured E values are slightly less than the f values calculated from the present equations (for example, $E_{F_e} = 0.66$ compared to $f_{F_e} = 0.75$); and, at the one temperature (1060°C) where both E_{C_o} and E_{F_e} were measured, the ratio E_{F_e}/E_{C_o} agrees very well with the random-alloy ratio for f_{F_e}/f_{C_o} from Eqs. (42) and (43), being 0.92 compared to 0.95.

The results described above are all consistent with results from the present random-alloy calculations. To further test these equations, additional tracer isotope experiments would be especially useful.

A second experimental quantity which can be compared with theory is D_A^*/D_B^* for alloy compositions where there is a forbidden region, such as shown in Fig. 5. In binary alloys, the present random-alloy model predicts an upper limit on possible values of D_A^*/D_B^* whenever N_A is less than $1 - f_0$. This restriction is strongest at the limit $N_A \rightarrow 0$, where the theory yields $D_A^*/D_B^* \leq 4.57$ in fcc crystals, or 3.67 in bcc crystals. The random-alloy model usually is not valid in this dilute limit, so one expects frequent violations of the forbidden region in very dilute alloys. At $N_A = 0.1$, the forbidden region is somewhat less restrictive ($D_A^*/D_B^* \leq 7.59$ in fcc crystals, or 5.21 in bcc crystals). The alloy compositions where the random-alloy model should be most valid are those between $N_A = 0.1$ and $N_A = 0.9$. In this range, there do not appear to be any examples where the forbidden-region restriction is violated.

VALUE OF VACANCY CORRELATION FACTOR

The partial correlation factors f_v^i for diffusion of vacancies are very simply related to the atom correlation factors f_i in the present model by Eq. (36) with f_v^i equaling merely f_i times f_0^{-1} . In the present model, the atom correlation factors are restricted to being less than or equal to unity. This restriction does not apply to the f_v^i , which often are larger than unity. According to Eqs. (12), (13), and (18), a slow-diffusing species with jump frequency w_i smaller than Wf_v , where W is the average vacancy jump frequency and f_v is the average vacancy correlation factor, will have an atom correlation factor which is larger than f_0 . Then f_v^i will be larger than unity.

If a correlation factor larger than unity is associated with a jump, the jump must have a smaller than random probability of being followed by a reverse jump. This is indeed the case for the jump a vacancy makes in exchanging with a slow-diffusing atom. Since the slow-diffusing atom has only a

small probability of immediately reexchanging with the vacancy, this vacancy has a greater than average amount of time available during which it can exchange with some other atom. Nevertheless, according to Eq. (36), f_v^i never becomes greater than f_0^{-1} . For fast-diffusing atoms with w_i greater than Wf_v , the partial vacancy correlation factor f_v^i is less than unity.

The vacancy correlation factor f_v is the weighted average of the partial correlation factors f_v^i , as shown in Eq. (10), the average being weighted according to the number of exchanges vacancies make with each species. Since the f_v^i corresponding to fast-diffusing atoms, with which vacancies frequently exchange, are weighted more heavily in the average than are the f_v^i from the slow-diffusing atoms, one might expect that f_v would be less than unity. Detailed calculations show that this indeed is the case in a random alloy.

From Eqs. (10), (14), (36), and (40), we have

$$f_v = 1 - (2/M_0) [\sum_i N_i w_i (D_i^* - \bar{D}^*) / \bar{D}^* \sum_i N_i w_i], \quad (58)$$

where the average diffusion coefficient \bar{D}^* is given by

$$\bar{D}^* = \sum_m N_m D_m^*. \quad (59)$$

Since w_i increases with D_i^* , the summations in Eq. (58) are positive. This equation thus yields an f_v value less than or equal to unity for any random alloy.

Equations (37) and (40) allow the w_i to be eliminated from the expression for f_v . In terms of the

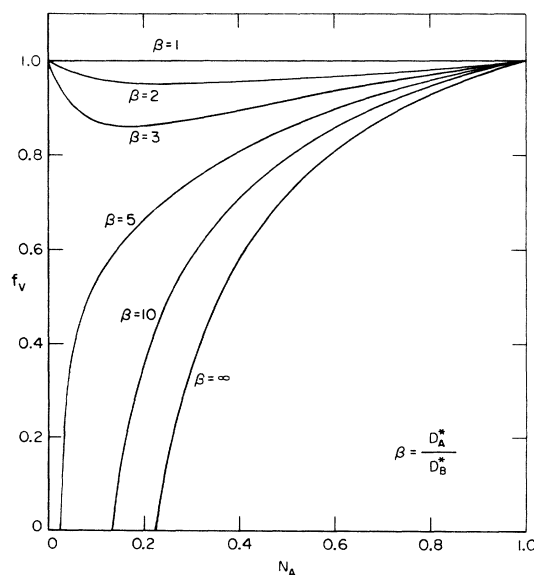


FIG. 6. Correlation factor f_v for diffusion of vacancies in random binary fcc alloy.

D_i^* and N_i alone,

$$f_v = 1 - (2/M_0) [\sum_i N_i D_i^* \psi_i (D_i^* - \bar{D}^*) / \bar{D}^* \sum_i N_i D_i^* \psi_i], \quad (60)$$

where

$$\psi_i = [M_0 \bar{D}^* - 2(D_i^* - \bar{D}^*)]^{-1}. \quad (61)$$

This becomes for a random binary alloy,

$$f_v = 1 - \frac{2}{M_0} \frac{(M_0 + 2) N_A N_B (D_A^* - D_B^*)^2}{(M_0 + 2)(\bar{D}^*)^2 - 2D_A^* D_B^*}. \quad (62)$$

Values of f_v for a binary alloy calculated from Eq. (62) are shown in Fig. 6. These values differ slightly from approximate values shown previously.^{4,5} In Ref. 5, an approximation was introduced by the assumption that H equaled H_0 . This approximation is important when f_v is small. In Ref. 4, an error was made in the numerical computation of the f_v values.

By definition, the atom correlation factor f_A for the faster-diffusing species in a random binary alloy

goes to zero at the boundary of the forbidden region. This is illustrated in Fig. 1. Also, Fig. 6 shows that the vacancy correlation factor in a random binary alloy goes to zero at the boundary of the forbidden region. This general result can be demonstrated from Eqs. (55) and (62).

At the boundary of the forbidden region, Eq. (55) yields

$$D_B^* = D_A^* (1 - f_0 N_B^{-1}). \quad (63)$$

Substituting this into Eq. (62) with f_0 equal to $M_0 / (M_0 + 2)$, as shown by Eq. (14), and \bar{D}^* equal to $N_A D_A^* + N_B D_B^*$ yields the result $f_v = 0$ for all values of N_A .

It would be interesting to compare experimental values of f_v with Eq. (60) or (62). In principle, the equation

$$D_v = \frac{1}{6} \lambda^2 W f_v z \quad (64)$$

would allow f_v to be determined experimentally in an alloy where D_v and W could be measured. No such measurements are available, however.

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Multiband Model for the Electronic Heat Capacity of Chromium

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The anomalous high-temperature values of the electronic heat capacity of Cr have been analyzed by a multiband model of the density of states with a nonstandard distribution of states about the Fermi level. This model was obtained from analysis of the anomalous high-temperature values of the conductivities without use of rigid-band arguments. The agreement of the model with the data not only explains their anomalous values but confirms that the anomalies in the conductivities are the result of band structure.

I. INTRODUCTION

It has been recently pointed out that the anomalous high-temperature Lorenz number of chromium

($L = k/\sigma T$, where k is the thermal conductivity, σ is the electrical conductivity, and T is the temperature) seems to depend upon the peculiar characteristics of the density of states of that metal.¹⁻³ A