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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 measureable 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

$$D_i^* = \tfrac{1}{6}\lambda^2 \nu_i \, , \tag{1}$$

where $\lambda$ is the jump distance and $\nu_i$ is the jump frequency for species $i$. When there is a correlated walk, this expression becomes

$$D_i^* = \tfrac{1}{6}\lambda^2 \nu_i f_i \, , \tag{2}$$

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]

$$f_i = H_i/(2w_i + H_i) , \tag{3}$$

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 $\alpha$ 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 $\alpha$ or to a site on the randomization plane before it returns to site $\alpha$. Jump paths where the vacancy returns to site $\alpha$ 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 $H_i$ depends linearly on the rate at which a vacancy diffuses away from site $\alpha$ 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

$$D_v = \tfrac{1}{6}\lambda^2 \nu_v f_v . \tag{4}$$

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

$$\nu_v^e = \nu_v f_v , \tag{5}$$

where $\nu_v^e$ 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 $\nu_v$ in Eq. (4) can be expressed as a sum over all species $i$,

$$\nu_v = z\textstyle\sum_i w_i N_i = \sum_i \nu_v^i , \tag{6}$$

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 $\nu_v^i$ is the total vacancy jump frequency from jumps with species $i$ and

$$\nu_v^i = z w_i N_i . \tag{7}$$

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

$$\nu_v^{ie} = \nu_v^i f_v^i = z w_i N_i f_v^i \, , \tag{8}$$

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

$$\nu_v^e = \textstyle\sum_i \nu_v^{ie} \, , \tag{9}$$

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

$$f_v = \textstyle\sum_i w_i N_i f_v^i / \textstyle\sum_i w_i N_i \, . \tag{10}$$

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

$$W = \textstyle\sum_i N_i w_i \, , \tag{11}$$

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 measureable 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

$$f_0 = H_0/(2W + H_0) \, . \tag{12}$$

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 |

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

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

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

or

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

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

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

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 $N_A w_A f_v^A + N_B w_B f_v^B + \cdots$. 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

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

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

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

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

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

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

$$J_v = c_v\langle v_F\rangle_v = c_v \textstyle\sum_i \langle v_F\rangle_v^i \,. \tag{20}$$

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 $\nu^e$. In cubic crystals if there is a single random jump frequency[2]

$$\langle v_F\rangle = DF/kT = \tfrac{1}{6}\,\lambda^2\nu^e F/kT\ , \tag{21}$$

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

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

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

$$c_v\langle v_F\rangle_v^i = \tfrac{1}{6}\,\lambda^2 zw_i c_v(kT)^{-1} f_v^i N_i F_v^i\,. \tag{23}$$

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

$$\nu_i = zw_i N_v\,, \tag{24}$$

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

$$c_i = N_i C\ , \tag{25}$$

$$c_v = N_v C\ , \tag{26}$$

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

$$J_v = \textstyle\sum_i (c_i D_i^*/kT)(f_v^i/f_i)\,F_v^i\,. \tag{27}$$

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,

$$F_v^i = -\frac{\partial\mu_i}{\partial x}\,. \tag{28}$$

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

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

where

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

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

$$J_j = -\sum_i L_{ji}\frac{\partial\mu_i}{\partial x}\,. \tag{31}$$

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

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

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

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

$$L_{vi} = -\textstyle\sum_j L_{ji}\,. \tag{34}$$

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

$$L_{vi} = \frac{c_i D_i^*}{kT}\left(1 + \frac{2}{M_0}\right) = \frac{c_i D_i^*}{kTf_0}\ , \tag{35}$$

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

$$f_i = f_0 f_v^i\,. \tag{36}$$

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

$$D_i^* = \tfrac{1}{6}\lambda^2 N_v z w_i f_i \ . \tag{37}$$

Here $D_i^*$ 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

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

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

$$f_i = [\,-2w_i f_i + (M_0 + 2)\textstyle\sum_m N_m w_m f_m]/ (M_0 + 2)\sum_m N_m w_m f_m \ . \tag{39}$$

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

$$f_i = [\,-2D_i^* + (M_0 + 2)\textstyle\sum_m N_m D_m^*]/(M_0 + 2)\sum_m N_m D_m^* \ . \tag{40}$$

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

Equation (40) shows that, when $D_i^*$ is zero, $f_i$ equals unity. Since $D_i^*$ cannot be negative, a nonzero $D_i^*$ 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 $D_i^*$ 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

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

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

Similarly, we have

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

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.

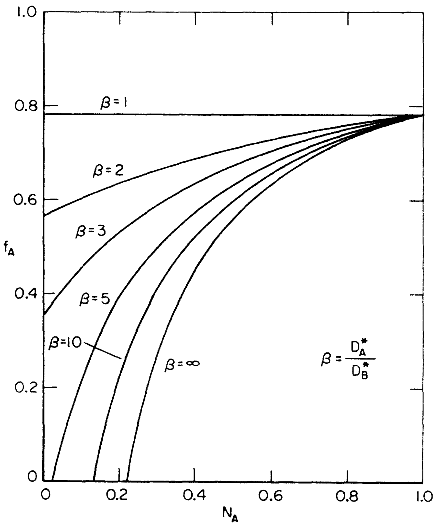

FIG. 1. Correlation factor $f_A$ of faster-diffusing atom species $A$ in random binary fcc $A$-$B$ alloy with diffusion by vacancy mechanism. Similar curves for other crystal structures can be obtained from Eq. (42) by using the appropriate $M_0$ values quoted in Table I.

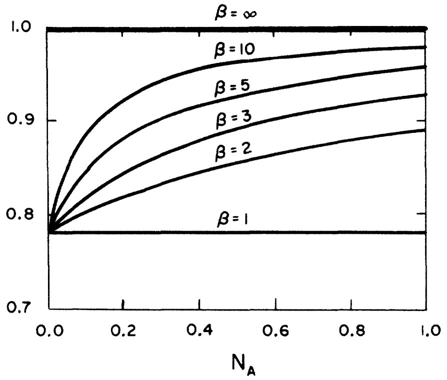

FIG. 2. Correlation factor $f_B$ of slower-diffusing atom species $B$ in random binary fcc alloy with diffusion by vacancy mechanism. Here $\beta = D_A^*/D_B^*$. Similar curves for other crystal structures can be obtained from Eq. (43) by using the appropriate $M_0$ values quoted in Table I.

## 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

$$D_i^*/D_k^* = w_i f_i / w_k f_k \,. \tag{44}$$

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

$$w_i/w_k = (D_i^*/D_k^*)[-2D_k^* + (M_0+2)\textstyle\sum_m N_m D_m^*]/ \\ [-2D_i^* + (M_0+2)\textstyle\sum_m N_m D_m^*] \tag{45}$$

or

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

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

$$1 - f_0 = 2/(M_0 + 2) \,. \tag{47}$$

For example, Eq. (45) reduces to

$$w_i/w_k = (D_i^*/D_k^*)[\textstyle\sum_m N_m D_m^* - (1 - f_0) D_k^*]/ \\ [\textstyle\sum_m N_m D_m^* - (1 - f_0) D_i^*] \,. \tag{48}$$

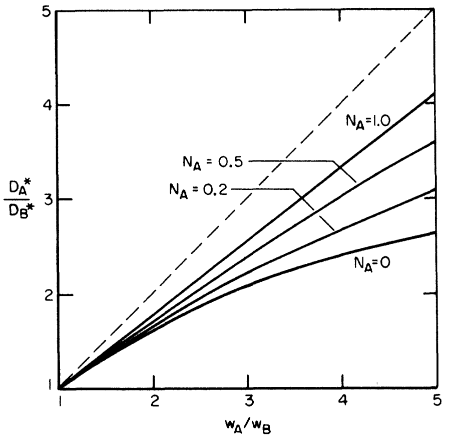

FIG. 3. Relation in fcc structure between jump frequency ratio $w_A/w_B$ and diffusion-coefficient ratio $D_A^*/D_B^*$ in random binary $A$-$B$ alloy with diffusion by vacancy mechanism. Note that for $D_A^*$ greater than $D_B^*$ all curves lie below the dashed line, which indicates the locus where $w_A/w_B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

In a binary alloy, this becomes

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

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 $f_0$.

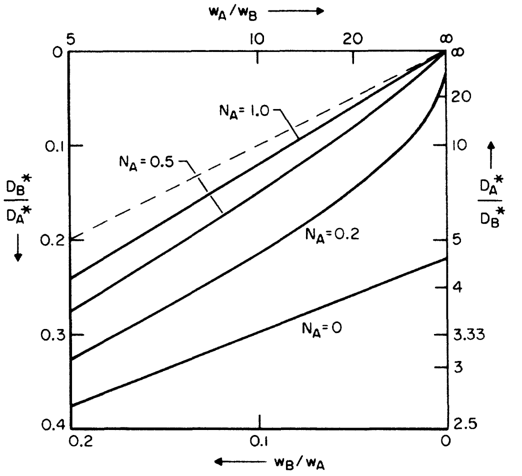

FIG. 4. Relation in fcc structure between jump frequency ratio $w_A/w_B$ and diffusion-coefficient ratio $D_A^*/D_B^*$ in random binary $A$-$B$ alloy with diffusion by vacancy mechanism. The dashed line indicates the locus where $w_A/w_B = D_A^*/D_B^*$. Relations for smaller values of $w_A/w_B$ are given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

$$-2D_i^* + (M_0 + 2)\textstyle\sum_m N_m D_m^* \geqq 0 \qquad (50)$$

or

$$D_i^* \leqq \tfrac{1}{2}(M_0 + 2)\textstyle\sum_m N_m D_m^* \,. \qquad (51)$$

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

$$D_i^*[1 - \tfrac{1}{2}(M_0 + 2)N_i] \leqq \tfrac{1}{2}(M_0 + 2)\sum_{m \neq i} N_m D_m^* \,, \qquad (52)$$

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 $N_i \geqq 2/(M_0 + 2) = 1 - f_0$, there is no restriction on $D_i^*$. However, if

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

it must be true that

$$D_i^* \leqq (1 - f_0 - N_i)^{-1} \sum_{m \neq i} N_m D_m^* \,. \qquad (54)$$

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

$$D_B^*/D_A^* \geqq 1 - f_0/N_B \,. \qquad (55)$$

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

$$N_B \geqq f_0 \,. \qquad (56)$$

An equation giving the boundary of the region of allowed values

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

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

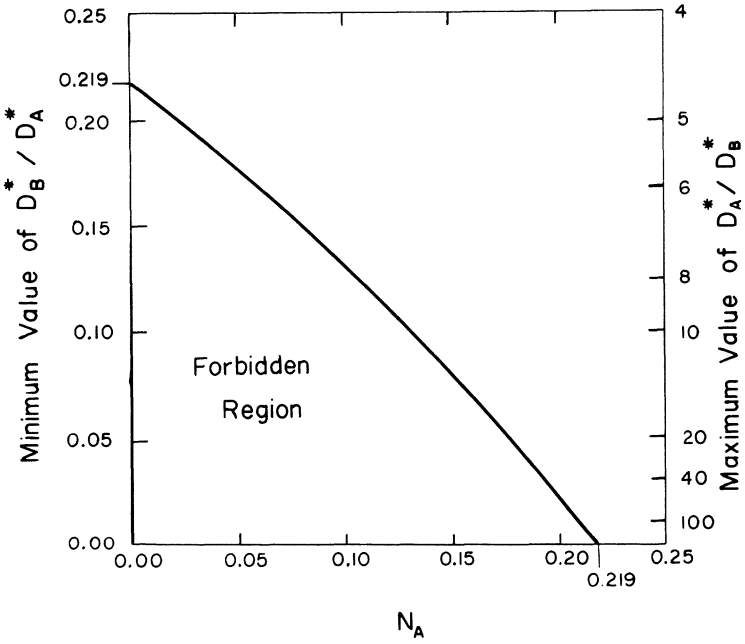

FIG. 5. Forbidden region for diffusion by vacancy mechanism in random binary fcc alloy. Values of $D_A^*/D_B^*$ in the forbidden region are not allowed in the random-alloy model.

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

Heumann and Reerink[9] 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 $D^*_{Cr}/D^*_{Ni} \simeq 2$. As discussed in Ref. 8, $E$ should equal $f \Delta K$, where $f$ is the atom correlation factor of the diffusing isotopes and $\Delta K$ 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 $E \simeq 0.5$ thus leads to the estimated value $f_{Cr} \simeq 0.5$. 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 $f_{Cr} \simeq 0.6$ from Fig. 1 is in reasonable agreement with the measured value and its possible experimental error.

A similar interdiffusion experiment by Johnson[10] 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 $1.0 \pm 0.2$. Here the critical data were those in the range 2–13% Ni. Since $D^*_{Cu}/D^*_{Ni} \simeq 3$ in this range,[11] this measurement is consistent with the result ($f_{Ni} \simeq 0.9$) predicted by Fig. 2.

Tracer measurements made by Peterson and Rothman[12] of $Zn^{65}$ and $Zn^{69}$ diffusing in ordered (411 °C) and disordered (560 °C) $\beta$-phase CuZn (approximately 48% Zn) yielded $E$ values of 0.20 and 0.24, respectively. These alloys are bcc with[13] $D^*_{Zn}/D^*_{Cu} \simeq 2$. Thus, the predicted value of $f_{Zn}$ from Eq. (42) is $\simeq 0.6$, which is appreciably larger than 0.20 or 0.24. The discrepancy here may arise from a very small $\Delta K$ or from short-range-ordering phenomena which persist even in the "disordered" alloy.

Similar measurements[14] on the diffusion of $Cu^{64}$ and $Cu^{67}$ gave values of $E$ for copper diffusing in $\beta$-CuZn which were larger than these for zinc, as would be expected from the present equations. For the disordered $\beta$-CuZn, the ratio $E_{Zn}/E_{Cu}$ was very close to that predicted from Eqs. (42)–(43) for the ratio $f_{Zn}/f_{Cu}$, with $E_{Zn}/E_{Cu} = 0.738$ compared to $f_{Zn}/f_{Cu} = 0.732$. This is consistent with the supposition that $\Delta K$ is nearly the same for copper and zinc in these alloys. For ordered $\beta$-CuZn, the agreement between $E_{Zn}/E_{Cu}$ and the value of $f_{Zn}/f_{Cu}$ 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 $\alpha$-phase CuZn, Peterson and Rothman's measurements[14] of $E_{Zn}/E_{Cu}$ showed rather poor agreement with predicted $f_{Zn}/f_{Cu}$ 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 $\beta$-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 Lieberman[15] in disordered equiatomic FeCo also show good agreement with the present predictions if allowance is made for a $\Delta K$ 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, $E_{\mathrm{Fe}} = 0.66$ compared to $f_{\mathrm{Fe}} = 0.75$); and, at the one temperature (1060 °C) where both $E_{\mathrm{Co}}$ and $E_{\mathrm{Fe}}$ were measured, the ratio $E_{\mathrm{Fe}}/E_{\mathrm{Co}}$ agrees very well with the random-alloy ratio for $f_{\mathrm{Fe}}/f_{\mathrm{Co}}$ 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

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

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

$$\bar{D}^* = \textstyle\sum_m N_m D_m^* . \tag{59}$$

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

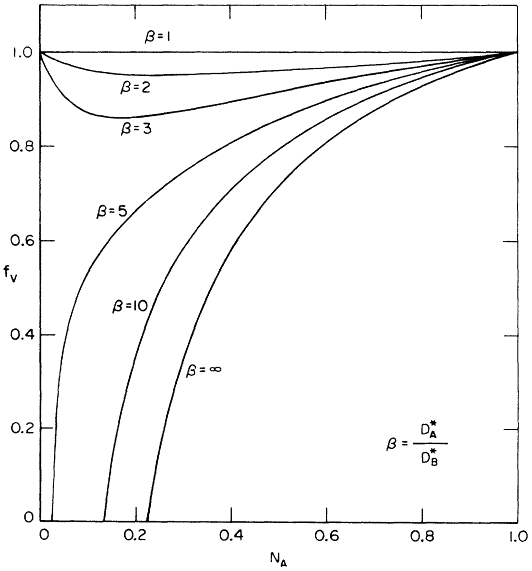

FIG. 6. Correlation factor $f_v$ for diffusion of vacancies in random binary fcc alloy.

$D_i^*$ and $N_i$ alone,

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

where

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

This becomes for a random binary alloy,

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

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

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

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

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

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, $\sigma$ 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