Analysis of Interdiffusion Data in Multicomponent Alloys to Extract Fundamental Diffusion Information

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This paper reviews new procedures based around the random alloy model that have been established recently for analyzing chemical diffusion data in binary and ternary alloy systems. The authors show how atom-vacancy exchange frequency ratios, individual tracer correlation factors, and vacancy-wind factors can be extracted from the chemical diffusion data. Examples are taken from intrinsic diffusion data in the Ag-Cd and Ag-Cd-Zn alloy systems and from interdiffusion data in the Fe-Ni-Cr and Cu-Fe-Ni alloy systems.

Keywords	chemical diffusivity, Darken's analysis, diffusion, diffusivity coefficient, interdiffusion, vacancy wind

1. Introduction

In 1947 a chemical diffusion experiment revealing a Kirkendall shift provided the conclusive evidence that vacancies are the principal vehicles for atomic transport in metals and alloys.[1] However, since that time, chemical diffusion data have rarely been analyzed to provide fundamental information about diffusion, by which the authors mean atom-vacancy exchange frequencies and correlations between jump directions of the atoms as embodied in correlation factors. Historically, such information has largely been furnished by *tracer* diffusion experiments by way of isotope effect measurements,[2] analysis of curvatures of Arrhenius plots,[3] pressure dependence,[4] analysis of enhancement factors for solvent diffusion in dilute alloys,[5] Haven Ratio measurements (in ionic conductors)[6] and so on. For a variety of reasons, relatively few laboratories worldwide continue to perform measurements of tracer diffusion coefficients using radioisotopes, though this trend has been offset to some extent by the widespread use of secondary ion mass spectroscopy (SIMS) measurements using stable isotopes. The amount of chemical diffusion data is very large; see, for example, the extensive compilations for binary alloys[7] and ternary alloys.[8] It is appropriate therefore to seek and develop new ways of extracting fundamental diffusion information from such data. Nonetheless, it needs to be recognized that the accuracy of chemical

diffusion data does not usually approach what is routinely possible in tracer diffusion experiments. In the interdiffusion experiment, vacancies are created and annihilated at sources and sinks, typically by dislocation climb. If these vacancy sources and sinks are not efficient or are not at sufficiently high concentrations, then vacancy supersaturation and undersaturation can readily occur. However, it is not easy to estimate the effects on interdiffusion of such possible nonequilibrium vacancy concentrations.[9] Furthermore, in contrast to standard tracer serial sectioning experiments, it is also not straightforward to estimate possible contributions to chemical diffusion from grain boundary diffusion processes.

This paper reviews some of the recent methods in the analysis of chemical diffusion data to extract fundamental diffusion information. Only interdiffusion forces are considered in the analyses. Section 2 introduces the random alloy model that will form the basis of the analysis of chemical diffusion in binary and ternary alloys. Section 2 also introduces the (random alloy) sum-rule relationship between the phenomenological transport coefficients. Section 3 introduces three diffusion kinetics formalisms that can be used with the random alloy model. Section 4 shows how this rule and these diffusion kinetics formalisms can be used to extract exchange frequency ratios and tracer correlation factors from intrinsic diffusion coefficients measured in binary and ternary alloy systems. Section 5 focuses on the analysis of interdiffusion coefficients in ternary systems and shows how exchange frequency ratios and tracer correlation factors quantities can be extracted. Section 6 shows how vacancy-wind factors can be extracted from interdiffusion coefficients in ternary systems.

2. The Random Alloy and the Sum Rule

In the random alloy model introduced first by Manning[10] the N atomic components and independent vacancies (at a vanishingly small concentration) are distributed randomly. The atom-vacancy exchange frequencies, notated as w_i can be conceptualized in one of two ways. On the one hand, one can consider them simply as explicit frequencies that depend *only* on the species of atom and *not* on the

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surroundings. For example w_A simply represents the basic vacancy-atom frequency of a given A atom at all compositions. On the other hand, one can also consider w_A as representing an *average* frequency at a given composition. Then w_A represents the average frequency of a given A atom as it migrates through the lattice sampling the various environments. Since the average environment must change with composition, then w_A can also be expected to change with composition.

A particularly useful and exact result of the random alloy model itself is the so-called "sum rule"[11] that relates the phenomenological coefficients of nonequilibrium thermodynamics L_{ij} to the vacancy-atom exchange frequencies. The sum rule reduces the number of independent phenomenological coefficients. For example, in the binary alloy there is only one independent phenomenological coefficient and not three. In the ternary alloy there are three independent phenomenological coefficients and not six. In the N component alloy the sum rule is written as:

$$\sum_{j=1}^{N} \frac{L_{ij}}{c_i} \frac{w_i}{w_j} = A w_i \qquad i = 1, \dots, N \tag{Eq 1}$$

where A is a constant.

The sum rule is not trivial. The general principle of its derivation can be described as follows. Consider a random alloy with the vacancy mechanism operating. Assume that an atom of species i has just made a jump. Accept this jump as the initial point in time and take a "snapshot" of the system. Then, for each quantity like L_{ij}, consider how the system changes from the initial configuration (after the jump of the i atom) during the jumping of the vacancies, that is, after the first jump, the second jump, and so on. At each moment in time choose a vacancy randomly from the current configuration (there is a specific probability for the system to get to this configuration starting with the initial one), then choose a *random direction* and find an atom of some type (or another vacancy). Accordingly, for each direction there is a defined probability that the vacancy makes an exchange with the atom there. If this is an atom of species j, then a contribution to the average cosine between the first jump of the i atom and the final jump of the j atom is equal to the probability for a system to get to the current configuration multiplied by the vacancy concentration and multiplied by the vacancy-atom j exchange frequency (and divided by the coordination number). Therefore, each contribution of this type for a different atomic species j differs from one another only by the corresponding exchange frequency. After all of the appropriate summations are done, find the sum-rule relation as shown in Eq 1. The sum rule is considered "instantaneous"—it refers to a particular composition, and it is therefore unnecessary to include molar volume changes.

In terms of the collective correlation factors, which are the correlated parts of the phenomenological coefficients, Eq 1 is rewritten as:

$$\sum_{j=1}^{N} \frac{f_{ij}^{(j)}}{w_i} w_j = 1 \qquad \text{all } j \tag{Eq 2}$$

where $f_{ij}^{(j)}$ are the collective correlation factors, sometimes called correlation functions. Some examples of the usefulness of the sum rule in chemical diffusion problems are provided in the next section.

3. Diffusion Kinetics Formalisms for Use with the Random Alloy

3.1 The Darken Theory

Although not originally intended as a diffusion kinetics formalism for the random alloy, it is convenient to treat the Darken theory[12] here along with the other formalisms. There are various manifestations of the Darken theory depending on the diffusion context. The common feature, however, is that all off-diagonal phenomenological coefficients are put equal to zero. The principal result of this is that the atoms follow uncorrelated random walks; that is, the tracer correlation factors are simply given by:

$$f_i \equiv 1 \tag{Eq 3}$$

Similarly, all vacancy-wind factors appearing in expressions between tracer diffusion coefficients and interdiffusion and intrinsic diffusion coefficients vanish. Using the Darken approach, a very simple relation exists between the *diagonal* phenomenological coefficients and the tracer diffusion coefficients:

$$L_{ii} = c_i D_i^* / kT \qquad L_{ij} = 0 \qquad \text{for } i \neq j \tag{Eq 4}$$

The Darken theory trivially follows the sum rule given previously.

3.2 The Manning Theory

In the Manning theory,[10] tracer correlation factors are given by:

$$f_i = \frac{H}{2\gamma_i + H} \tag{Eq 5}$$

with the function H being the positive root of the equation:

$$\sum_i \frac{\gamma_i c_i}{2\gamma_i + H} = \frac{1 - f_0}{2} \tag{Eq 6}$$

where f_0 is the geometric correlation factor defined by the crystal structure; for example, $f_0 = 0.78145$ for vacancy diffusion in the face-centered cubic (fcc) lattice. In Manning's approach, the phenomenological coefficients are directly related to the tracer diffusion coefficients by:

$$L_{ij} = \frac{c_i D_i^*}{kT} \left(1 + \frac{2 c_i D_i^*}{M_0 \sum_k c_k D_k^*} \right) \tag{Eq 7}$$

$$L_{ij} = \frac{2 c_i D_i^* c_j D_j^*}{kT \left(M_0 \sum_k c_k D_k^* \right)} \qquad \text{for } i \neq j$$
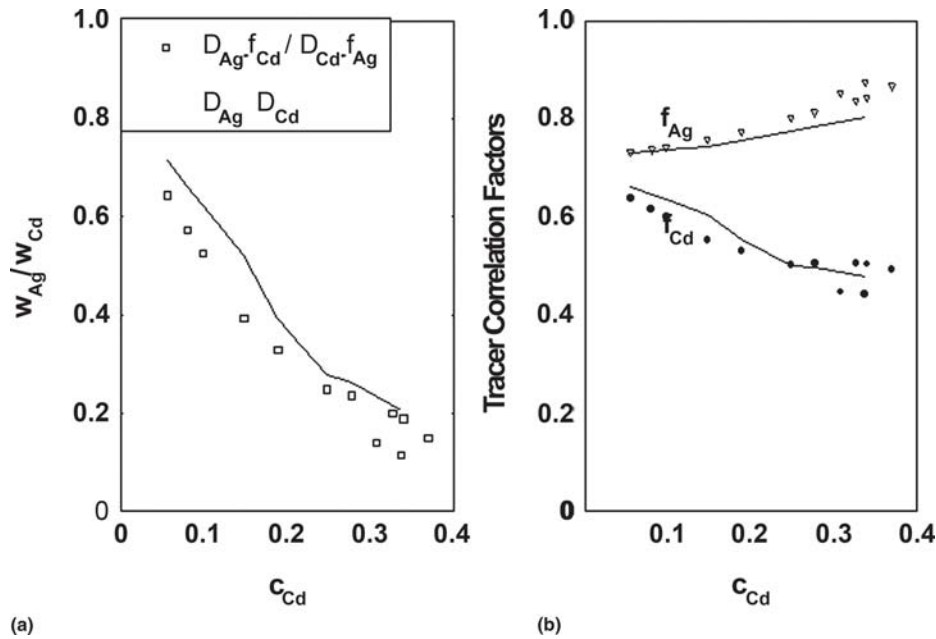
Fig 1 (a) The ratio w_{Ag}/w_{Cd} as a function of c_{Cd} at 873 K calculated using intrinsic diffusion coefficients[19] presented as a solid line and calculated from the tracer diffusion coefficients[20] using the Manning formalism and presented as symbols. (b) Corresponding tracer correlation factors, solid lines, calculated using ratio of the intrinsic diffusivities; symbols, calculated using experimental tracer data

where k and T have their usual meanings, and $M_0 = 2f_0/(1 - f_0)$. These relations are frequently referred to as the "Manning Relations." It is worth noting that the Manning Relations can also be obtained on the basis of two somewhat intuitive assumptions without recourse to the random alloy model.[13] These Relations have been shown to be good approximations, even for alloys showing order.[14]

3.3 The Moleko, Allnatt, and Allnatt (MAA) Theory

It has been shown by Belova and Murch[15,16] that the self-consistent Moleko, Allnatt, and Allnatt (MAA)[17] theory for diffusion kinetics in the random alloy provides the best agreement with results from Monte Carlo simulations. However, the MAA equations are a good deal more complicated in structure than those of Manning and somewhat more difficult to implement for analyzing experimental data. The expression for the tracer correlation factor f_i for the atomic species i is formally similar to that given above in the Manning approach:

$$f_i = \frac{H_i}{2\gamma_i + H_i} \qquad \text{(Eq 8)}$$

However, now the functions H_i are, in general, different for each species. The tracer correlation factors can be calculated using a system of equations; see, for example, Ref 16. Using the MAA theory, there are no closed-form relations between the phenomenological coefficients and the tracer diffusion coefficients. Nonetheless, it is still possible to use straightforward numerical methods to find all of the L_{ij} from a given set of tracer diffusion coefficients for all atomic species.[16]

4. Analysis of Intrinsic Diffusion Coefficients

4.1 Binary Alloy Systems

Intrinsic diffusivities are generally measured by way of marker shifts in the interdiffusion experiment. However, such measurements are rather tedious, especially in ternary alloys and, accordingly, the amount of intrinsic diffusion data is fairly limited compared with interdiffusion data.[7,8] For the random alloy, the sum rule provides a surprisingly simple relationship between the ratios of the intrinsic diffusion coefficients and the ratio of the atom-vacancy exchange frequencies at a given composition.[18] For the binary system:

$$w_A/w_B = D_A/D_B \qquad \text{(Eq 9)}$$

where D_A and D_B are the intrinsic diffusivities in the AB binary alloy and w_A and w_B are the atom-vacancy exchange frequencies. Note the absence of any off-diagonal phenomenological coefficients or correlation factors in Eq 9. Unfortunately, there are no simplifications for the corresponding tracer diffusion coefficients D_A^* and D_B^*; for the random alloy their ratio remains as:

$$D_A^*/D_B^* = w_A f_A/w_B f_B \qquad \text{(Eq 10)}$$

where f_A and f_B are the tracer correlation factors for A and B. As an example of the use of Eq 9 in Fig. 1(a), the results for the calculated ratio of the exchange frequencies w_{Ag}/w_{Cd} in the Ag-Cd system by way of the measured intrinsic diffusion coefficients[19] using Eq 9 are shown.
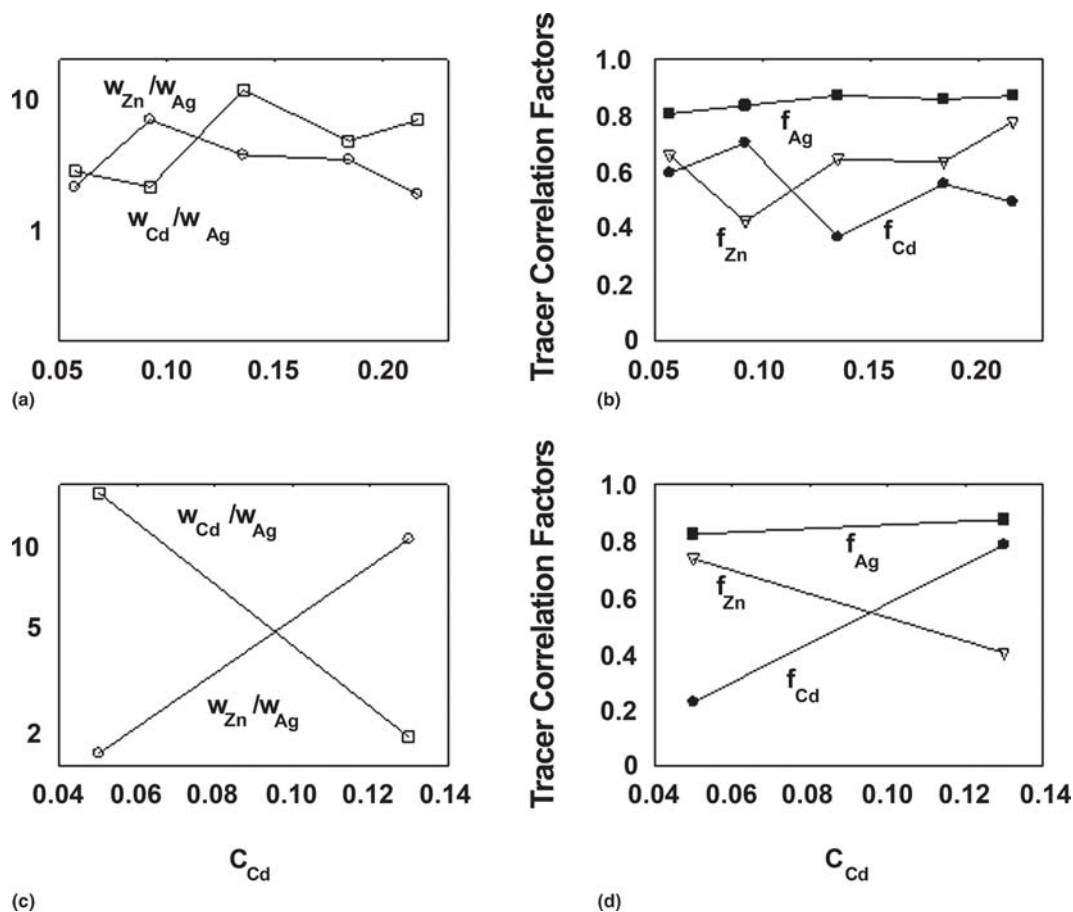
Fig. 2 The ratios of w_{Zn}/w_{Ag}, w_{Cd}/w_{Ag} and the corresponding tracer correlation factors (calculated by making use of the MAA formalism) in Ag-Cd-Zn alloys as a function of composition c_{Cd}. (a) and (b) $c_{Zn} = 0.112$; (c) and (d) $c_{Zn} = 0.181$

There has been a very long tradition in the field of diffusion research to determine tracer correlation factors because these factors give very direct information on the degree of correlation in the random walks of the atoms. Tracer correlation factors can be inferred by way of the diffusion isotope effect.[2] (In ionic conductors they can be inferred also from the Haven Ratio.[6]) They can also be calculated from the ratio of the tracer diffusion coefficients using the random alloy diffusion kinetics formalisms of Manning or MAA as given above. Importantly, they can also be determined directly using these theories if the ratio of the exchange frequencies is known. As an example, the results in Fig. 1(a) for w_{Ag}/w_{Cd} can be processed with the MAA formalism and the known geometric tracer correlation factor f_0 (= 0.7814 in this lattice) to give values for f_{Ag} and f_{Cd}. These are shown in Fig. 1(b). It is seen that Ag atoms have the higher tracer correlation factors and therefore have the least correlated motion and vice versa for Cd atoms. Figures 1(a) and (b) also present the analysis of the *tracer* diffusion data[20] by making use of Manning's random alloy formalism. It can be seen that there is quite reasonable agreement between the ratio of the exchange frequencies and also the correlation factors from these different diffusion experiments.

4.2 Ternary Alloy Systems

For the ternary alloy A-B-C the sum rule (Eq 1) gives that:

$$\frac{D_{BA}^{C}D_{CB}^{C} - D_{BB}^{C}D_{CA}^{C}}{D_{AA}^{C}D_{BB}^{C} - D_{AB}^{C}D_{BA}^{C}} = \frac{w_C}{w_A} \tag{Eq 11}$$

$$\frac{D_{AB}^{C}D_{CA}^{C} - D_{AA}^{C}D_{CB}^{C}}{D_{AA}^{C}D_{BB}^{C} - D_{AB}^{C}D_{BA}^{C}} = \frac{w_C}{w_B} \tag{Eq 12}$$

where D_{AA}^{C} and so forth are the ternary intrinsic diffusivities in the ternary alloy and C is, by convention the dependent concentration variable. Now one can make use of these equations in the analysis of intrinsic diffusion coefficients in a ternary alloy system. Figures 2(a) and (c) show results for the ratio of the exchange frequencies w_{Cd}/w_{Ag} and w_{Zn}/w_{Ag} (Eq 11 and 12) using intrinsic diffusion data in the Ag-Cd-Zn system at $T = 873$ K.[21] Again it is possible to gain access to the corresponding tracer correlation factors f_{Ag}, f_{Cd}, and f_{Zn}. For the ternary alloy system, either the diffusion kinetics formalisms of Manning and MAA can be used for this task. The results using the MAA formalism are shown

in Fig. 2(b) and (d). In general terms, as in the binary system discussed previously, it can be seen that the Ag atoms are the least correlated in their motion (highest correlation factors).

5. Analysis of Interdiffusion Coefficients in Ternary Systems

The processing of the four interdiffusivities $\tilde{D}_{AA}^{C}$, $\tilde{D}_{AB}^{C}$, $\tilde{D}_{BB}^{C}$ and $\tilde{D}_{BA}^{C}$ in a ternary alloy system to obtain ratios of exchange frequencies, and then tracer correlation factors, can become quite involved. First, as a zeroth approximation or Darken-type approximation one can simply neglect the off-diagonal phenomenological coefficients in the analysis. It is then straightforward to show that the ratios of the exchange frequencies can be expressed as (for example, Ref 22):

$$\frac{(1-c_A)((1-c_B)(m_{21}\tilde{D}_{AA}^{C}-m_{11}\tilde{D}_{AB}^{C})+c_A(m_{21}\tilde{D}_{BA}^{C}-m_{11}\tilde{D}_{BB}^{C}))}{c_A((m_{11}(1-c_B)+m_{12})\tilde{D}_{AB}^{C}-((1-c_B)m_{21}+m_{22})\tilde{D}_{AA}^{C}+c_A m_{11}\tilde{D}_{BB}^{C}-c_A m_{21}\tilde{D}_{BA}^{C})}=\frac{w_C}{w_A}$$

(Eq 13)

$$\frac{(1-c_B)(m_{21}\tilde{D}_{AA}^{C}-m_{11}\tilde{D}_{AB}^{C})+c_A(m_{21}\tilde{D}_{BA}^{C}-m_{11}\tilde{D}_{BB}^{C})}{c_B m_{11}\tilde{D}_{AB}^{C}-c_B m_{21}\tilde{D}_{AA}^{C}-c_A m_{11}\tilde{D}_{BB}^{C}+c_A m_{21}\tilde{D}_{BA}^{C}}=\frac{w_C}{w_B}$$

(Eq 14)

or

$$\frac{(1-c_A)(m_{12}\tilde{D}_{BB}^{C}-m_{22}\tilde{D}_{BA}^{C})+c_B(m_{12}\tilde{D}_{AB}^{C}-m_{22}\tilde{D}_{AA}^{C})}{c_B m_{12}\tilde{D}_{AB}^{C}-c_B m_{22}\tilde{D}_{AA}^{C}-c_A m_{12}\tilde{D}_{BB}^{C}+c_A m_{22}\tilde{D}_{BA}^{C}}=\frac{w_C}{w_A}$$

(Eq 15)

$$\frac{(1-c_B)((1-c_A)(m_{22}\tilde{D}_{BA}^{C}-m_{12}\tilde{D}_{BB}^{C})+c_B(m_{22}\tilde{D}_{AA}^{C}-m_{12}\tilde{D}_{AB}^{C}))}{c_B(-(m_{22}(1-c_A)+m_{21})\tilde{D}_{21}^{C}+((1-c_A)m_{12}+m_{11})\tilde{D}_{BB}^{C}+c_B m_{12}\tilde{D}_{AB}^{C}-c_B m_{22}\tilde{D}_{AA}^{C})}=\frac{w_C}{w_B}$$

(Eq 16)

where $\Delta_m = m_{11}m_{22}-m_{12}m_{21}$, $m_{ij}=c_j(kT)^{-1}\partial\mu_j/\partial c_i$ and μ_1 is the chemical potential of component A and μ_2 is the chemical potential of component B.

Manning,[23] among many others, has argued that the off-diagonal phenomenological coefficients should not be neglected in this way because they play an important role by carrying diffusion correlation information. In extreme cases, such as when there is vacancy binding to one or more atomic species or when one of the exchange frequencies is much smaller or much larger than the others, the off-diagonal coefficients may even predominate over the diagonal coefficients and can even change the direction of an atomic flux. It is sometimes remarked that from an experimental point of view, correlation information may be *implied* in the diagonal coefficients (when the off-diagonal coefficients are set equal to zero). In other words, by setting
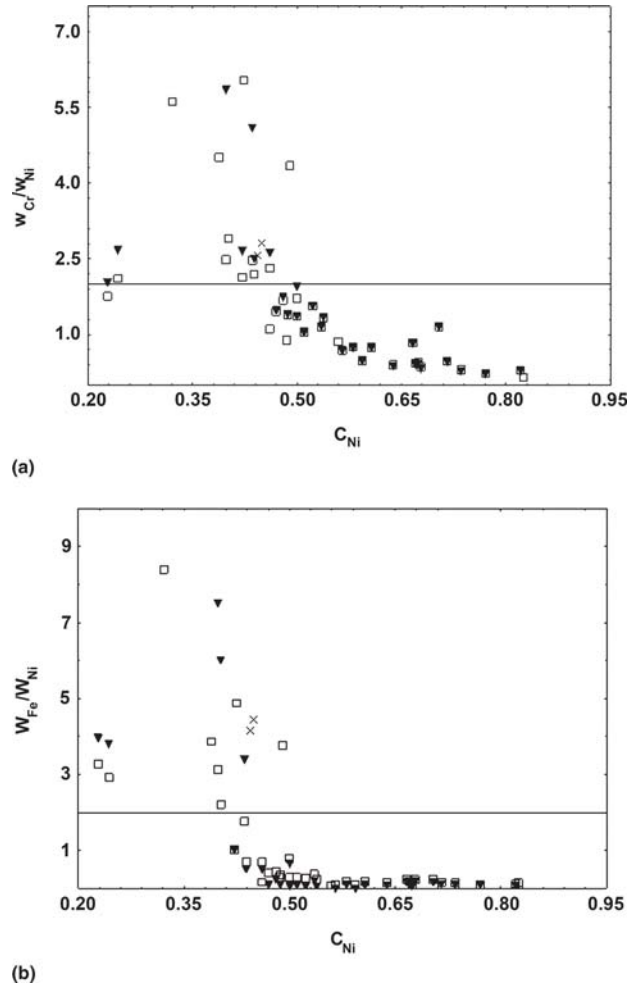

(a)

(b)

Fig. 3 Ratios (a) w_{Cr}/w_{Ni} and (b) w_{Fe}/w_{Ni} as functions of Ni composition (Cr and Fe compositions are not shown in these figures). Symbols × represent two points where all tracer diffusivities are available. Other symbols: □, results of analysis of the interdiffusion and thermodynamic data by making use of zero off-diagonal phenomenological coefficients approach; ▼, results of analysis of the interdiffusion and thermodynamic data by making use of MAA approach

the off-diagonal coefficients equal to zero, the diagonal coefficients are then forced to carry *all* of the experimental diffusion information. This is a questionable procedure because it can obscure valuable information and confounds the theoretical meaning of the phenomenological coefficients. However, for the purposes of obtaining ratios of exchange frequencies, Eq 13 to 16 will provide rough, order-of-magnitude estimates, but for greater accuracy it will be necessary to include the off-diagonal coefficients. Their inclusion then requires the use of the Manning or MAA diffusion kinetics formalisms and can be quite complicated to implement, involving the solution of a large set of nonlinear equations. Belova and Murch have provided details of the utilization of these formalisms in this context.[24]

As an example of the use of these formalisms to obtain the ratios of the exchange frequencies and also the tracer correlation factors, Fig. 3 gives results from the analysis[24]
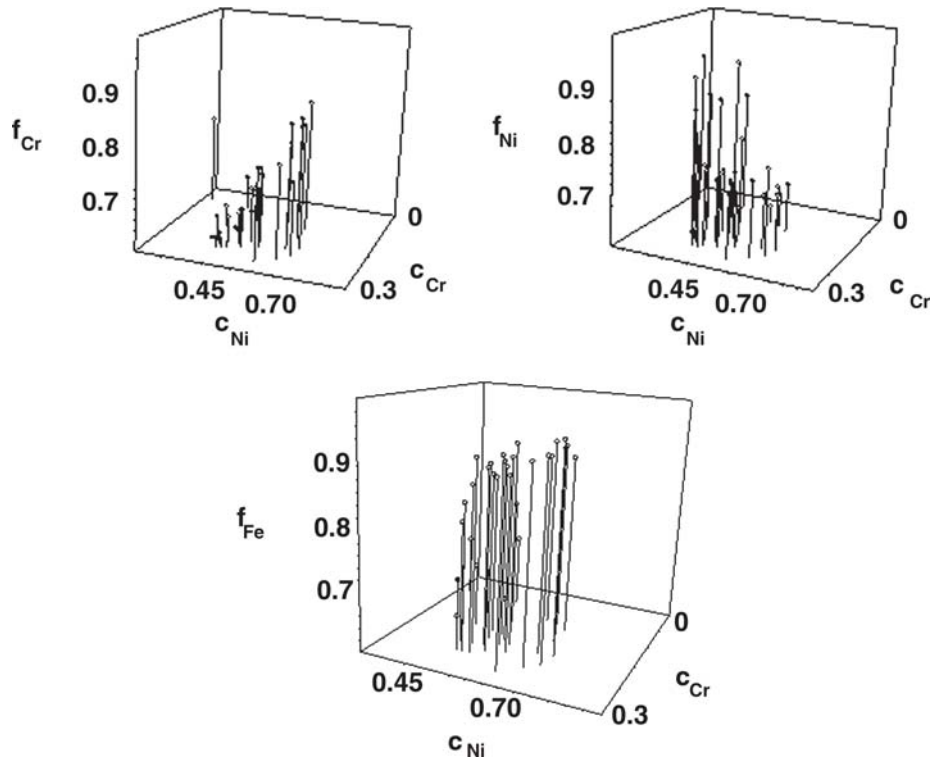
Fig. 4 Tracer correlation factors as functions of Ni and Cr compositions. Filled circles represent two points where all tracer diffusion coefficients are available; open circles, results of analysis of the interdiffusion and thermodynamic data by making use of the MAA approach.

of the extensive interdiffusion data provided by Duh and Dayananda[25] in the Fe-Ni-Cr system using the MAA formalism. The authors have also included in the analysis the thermodynamic activity data as estimated by Duh and Dayananda.[25] Figure 4 includes the corresponding results for the analysis of the tracer diffusion data (for two points only).[26] It can be seen that there is reasonable consistency between these two quite different types of diffusion measurements. With the exchange frequencies in hand, it is again possible to determine the tracer correlation factors in an analogous way to what was done in the binary system.

At high Ni compositions, the Fe atoms show the least degree of correlation (highest correlation factors), while Ni atoms show the greatest degree of correlation (lowest correlation factors). The behavior of the Cr atoms falls between these extremes. On the other hand, at low Ni compositions the Cr atoms are the most correlated and Ni atoms are the least correlated while the behavior of Fe atoms falls in between. This crossing over of the correlation behavior is a result of a change in the exchange frequencies with composition.

One of the possible sources of uncertainty in the analysis of the interdiffusion data in the ternary alloys from two diffusion couples measurements can be traced back to the fact that in principle the vacancy concentrations can be different in the two experiments even at the same atomic composition. Even a small difference in the vacancy concentrations can produce quite large effects in the resulting interdiffusion coefficients $\tilde{D}_{AA}^C$, $\tilde{D}_{AB}^C$, $\tilde{D}_{BB}^C$ and $\tilde{D}_{BA}^C$, and

later diffusion kinetics analysis. It is possible to eliminate this by simply checking the relation that can be derived from the four equations of the Matano method (they are written in the way according to Philibert[27]):

$$\tilde{D}_{AA}^C + \tilde{D}_{AB}^C \frac{dC_B}{dC_A} = \psi_1 \qquad \tilde{D}_{BB}^C + \tilde{D}_{BA}^C \frac{dC_A}{dC_B} = \psi_2 \qquad \text{(Eq 17)}$$

For one diffusion couple, and for the other diffusion couple:

$$\tilde{D}_{AA}^C + \tilde{D}_{AB}^C \frac{dC_B'}{dC_A'} = \psi_1' r \qquad \tilde{D}_{BB}^C + \tilde{D}_{BA}^C \frac{dC_A'}{dC_B'} = \psi_2' r \qquad \text{(Eq 18)}$$

where C_i and C_i' are the atomic concentrations (and therefore a possible change in volume should be taken into consideration), the functions ψ_i are the same functions as described in Ref 27 and $r = c_v^2/c_v^1-$ is the ratio of vacancy concentrations for the different diffusion couples (at the same atomic composition, this situation is quite possible if the vacancy concentration is very small compared with the atomic ones). Another relation that should be used is:

$$c_A c_B (\tilde{D}_{AA}^C - \tilde{D}_{BB}^C) + c_A (1 - c_A) \tilde{D}_{BA}^C - c_B (1 - c_B) \tilde{D}_{BA}^C = 0$$
$$\text{(Eq 19)}$$

After solving these five equations (Eq 17-19) with respect to $\tilde{D}_{AA}^C$, $\tilde{D}_{AB}^C$, $\tilde{D}_{BB}^C$ and $\tilde{D}_{BA}^C$ and r and putting the condition that $r = 1$, one arrives at the relation:

$$\left(c_B\psi_1\left(1 - c_B + \frac{dC_B'}{dC_A'}c_A \right) + \frac{dC_B}{dC_A}c_A\psi_2\left(\frac{dC_B'}{dC_A'}(1 - c_A) + c_B \right) \right)$$

$$\times \left(c_B\psi_1'\left(1 - c_B + \frac{dC_B}{dC_A}c_A \right) \right) \qquad \text{(Eq 20)}$$

$$+ \frac{dC_B'}{dC_A'}c_A\psi_2'\left(\frac{dC_B}{dC_A}(1 - c_A) + c_B \right) \Bigg)^{-1} = 1$$

This relation can be used to check if the vacancy concentration has remained the same (or relatively close in value) for the two diffusion couples (at the same atomic composition, at the point of interception of the two diffusion paths).

On the other hand, the "general" solution for the interdiffusivities $\tilde{D}_{AA}^C$, $\tilde{D}_{AB}^C$, $\tilde{D}_{BB}^C$ and $\tilde{D}_{BA}^C$ obtained as the solution to Eq 17 to 19 can be used even in the case when $r \neq 1$.

These considerations are applicable for a thermodynamically ideal system. In the general case, one has to start with the equations:

$$\begin{bmatrix} \tilde{D}_{AA}'^C & \tilde{D}_{AB}'^C \\ \tilde{D}_{BA}'^C & \tilde{D}_{BB}'^C \end{bmatrix}\begin{bmatrix} m_{11} & m_{21} \\ m_{12} & m_{22} \end{bmatrix}\begin{bmatrix} 1 \\ dC_B/dC_A \end{bmatrix} = \begin{bmatrix} \tilde{D}_{AA}'^C & \tilde{D}_{AB}'^C \\ \tilde{D}_{BA}'^C & \tilde{D}_{BB}'^C \end{bmatrix}\begin{bmatrix} b_1 \\ b_2 \end{bmatrix}$$

$$= \begin{bmatrix} \psi_1 \\ \psi_2 \end{bmatrix}$$

$$\qquad \qquad \text{(Eq 21)}$$

$$\begin{bmatrix} \tilde{D}_{AA}'^C & \tilde{D}_{AB}'^C \\ \tilde{D}_{BA}'^C & \tilde{D}_{BB}'^C \end{bmatrix}\begin{bmatrix} m_{11} & m_{21} \\ m_{12} & m_{22} \end{bmatrix}\begin{bmatrix} 1 \\ dC_B'/dC_A' \end{bmatrix} = \begin{bmatrix} \tilde{D}_{AA}'^C & \tilde{D}_{AB}'^C \\ \tilde{D}_{BA}'^C & \tilde{D}_{BB}'^C \end{bmatrix}\begin{bmatrix} b_1' \\ b_2' \end{bmatrix}$$

$$= \begin{bmatrix} \psi_1' \\ \psi_2' \end{bmatrix}$$

where Eq 19 holds for the functions $\tilde{D}_{ij}'^C$. It is straightforward now to repeat a similar type of analysis to the system of Eq 21.

6. Determination of Vacancy-Wind Factors in Interdiffusion (Ternary Systems)

This section discusses the determination of the vacancy-wind factors occurring in interdiffusion in ternary systems. These factors are very well known for binary systems, but only recently have the vacancy-wind factors themselves formally appeared.[28,29] For the fluxes of atoms J_A^0, J_B^0 and $J_C^0 (= -J_A^0 - J_B^0)$ relative to a fixed (usually to one end of the sample) frame of reference we have that:[28]

$$J_A^0 = -\tilde{D}_{AA}^C \nabla c_A - \tilde{D}_{AB}^C \nabla c_B$$
$$J_B^0 = -\tilde{D}_{BA}^C \nabla c_A - \tilde{D}_{BB}^C \nabla c_B \qquad \text{(Eq 22)}$$

where $\tilde{D}_{ij}^C$, $i,j = $ A,B are the interdiffusion coefficients (functions).

For the matrix of the interdiffusion coefficients:

$$\begin{bmatrix} \tilde{D}_{AA}^C & \tilde{D}_{AB}^C \\ \tilde{D}_{BA}^C & \tilde{D}_{BB}^C \end{bmatrix} = \begin{bmatrix} \tilde{D}_{AA}'^C & \tilde{D}_{AB}'^C \\ \tilde{D}_{BA}'^C & \tilde{D}_{BB}'^C \end{bmatrix}\begin{bmatrix} m_{11} & m_{21} \\ m_{12} & m_{22} \end{bmatrix} \qquad \text{(Eq 23)}$$

and

$$\tilde{D}_{AA}'^C = kT\left(\frac{L_{AA}}{c_A} - \frac{L_{AC}}{c_C} - L_A + \frac{c_A L_C}{c_C} \right)$$

$$\tilde{D}_{AB}'^C = kT\left(\frac{L_{AB}}{c_B} - \frac{L_{AC}}{c_C} - \frac{c_A L_B}{c_B} + \frac{c_A L_C}{c_C} \right)$$

$$\text{(Eq 24)}$$

$$\tilde{D}_{BA}'^C = kT\left(\frac{L_{AB}}{c_A} - \frac{L_{BC}}{c_C} - \frac{c_B L_A}{c_A} + \frac{c_B L_C}{c_C} \right)$$

$$\tilde{D}_{BB}'^C = kT\left(\frac{L_{BB}}{c_B} - \frac{L_{BC}}{c_C} - L_B + \frac{c_B L_C}{c_C} \right)$$

where $L_i = \sum_k L_{ik}$ and one assumes the reciprocity condition $L_{ij} = L_{ji}$. There is also a relation between the $\tilde{D}_{ij}'^{C[27]}$ that is analogous to Eq 19:

$$c_B(1 - c_B)\tilde{D}_{AB}'^C - c_A(1 - c_A)\tilde{D}_{BA}'^C - c_A c_B \tilde{D}_{AA}'^C + c_B c_A \tilde{D}_{BB}'^C = 0$$
$$\text{(Eq 25)}$$

The authors denote the approximation for the interdiffusion functions $D_{ij}'^C$ using the Darken approach by $\tilde{D}_{ij}^{Darken}$, $i,j = $ A,B. Since the vacancy-wind effect is always a result of off-diagonal phenomenological coefficients, there is no vacancy-wind effect implied by the Darken approach. Accordingly, one can combine the ratios of the interdiffusion functions and the Darken approximation into a matrix of vacancy-wind factors:

$$[S] = \begin{bmatrix} S_{AA} & S_{AB} \\ S_{BA} & S_{BB} \end{bmatrix}$$

For the vacancy-wind matrix elements S_{ij}:

$$S_{AA} = \frac{\tilde{D}_{AA}'^C}{(1 - c_A)D_A^* + c_A D_C^*} \qquad S_{AB} = \frac{\tilde{D}_{AB}'^C}{c_A(D_C^* - D_B^*)}$$

$$\text{(Eq 26)}$$

$$S_{BA} = \frac{\tilde{D}_{BA}'^C}{c_B(D_C^* - D_A^*)} \qquad S_{BB} = \frac{\tilde{D}_{BB}'^C}{(1 - c_B)D_B^* + c_B D_C^*}$$

(As an aside, it should be noted that the two diagonal elements S_{AA} and S_{BB} of the S matrix reduce to the well-known result[27] for the binary case when chosen as A-C or B-C, respectively.) The "vacancy-wind" type expression for the matrix of interdiffusion coefficients can be formally written as:

$$\begin{bmatrix} \tilde{D}_{AA}^{C} & \tilde{D}_{AB}^{C} \\ \tilde{D}_{BA}^{C} & \tilde{D}_{BB}^{C} \end{bmatrix} = \begin{bmatrix} S_{AA}\tilde{D}_{AA}^{Darken} & S_{AB}\tilde{D}_{AB}^{Darken} \\ S_{BA}\tilde{D}_{BA}^{Darken} & S_{BB}\tilde{D}_{BB}^{Darken} \end{bmatrix} \begin{bmatrix} m_{11} & m_{21} \\ m_{12} & m_{22} \end{bmatrix}$$
(Eq 27)

Equation 26 can be compared with the well-known expression for the binary case:[26]

$$\tilde{D} = S\tilde{D}^{Darken}\phi = S(c_B D_A^* + c_A D_B^*)\phi$$
(Eq 28)

where S is the vacancy-wind factor.

In their Monte Carlo study of the binary random alloy[30] the authors found, in agreement with the MAA approach, that S is not restricted by $1/f_0$ as predicted by the Manning. In fact, S can become very large at and around the percolation limit composition $c_A = f_0$ if $w_A/w_B \gg 1$.

As a first approximation for the analysis of the vacancy-wind factors in the ternary system, the Manning approach can be applied, keeping in mind that at compositions close to the percolation threshold the vacancy-wind factors could, in principle, behave differently from the Manning's theory prediction. If one applies the Manning approach to the off-diagonal vacancy-wind factors, one soon has that in terms of tracer diffusion coefficients:

$$S_{AA} = 1 + \frac{2c_A(c_B(D_A^* - D_B^*) + c_C(D_A^* - D_C^*))(D_A^* - D_C^*)}{M_0((1 - c_C)D_A^* + c_A D_C^*)(c_A D_A^* + c_B D_B^* + c_C D_C^*)}$$

$$S_{BB} = 1 + \frac{2c_B(c_A(D_B^* - D_A^*) + c_C(D_B^* - D_C^*))(D_B^* - D_C^*)}{M_0((1 - c_C)D_B^* + c_B D_C^*)(c_A D_A^* + c_B D_B^* + c_C D_C^*)}$$
(Eq 29)

$$S_{AB} = 1 + \frac{2}{M_0}\left(1 - \frac{D_A^*}{c_A D_A^* + c_B D_B^* + c_C D_C^*}\right)$$

$$S_{BA} = 1 + \frac{2}{M_0}\left(1 - \frac{D_B^*}{c_A D_A^* + c_B D_B^* + c_C D_C^*}\right)$$

In terms of tracer correlation factors and atom-vacancy exchange frequencies, one has very simple relations for the off-diagonal vacancy-wind factors:

$$S_{BA} = \frac{f_B}{f_0} \qquad S_{AB} = \frac{f_A}{f_0}$$

And for the diagonal terms:

$$S_{AA} = \frac{(f_A/f_0)f_C c_A(w_A - w_C) - w_A}{f_C c_A(w_A - w_C) - w_A}$$
(Eq 30)

$$S_{BB} = \frac{(f_B/f_0)f_C c_B(w_B - w_C) - w_B}{f_C c_B(w_B - w_C) - w_B}$$

One can see now, that according to the Manning's approach, the off-diagonal vacancy-wind factors must have an upper bound of $1/f_0$, but the lower bound is zero. The diagonal vacancy-wind factors are bounded by $1/f_0$ and unity.

Table 1 Results of calculations of the vacancy-wind factor matrix (S_{ij}) based on a Manning-type analysis of the interdiffusion data in the Cu-Fe-Ni alloy system

c_{Fe}	c_{Ni}	c_{Cu}	S_{CuCu}	S_{FeFe}	S_{FeCu}	S_{CuFe}
0.1496	0.5116	0.3388	1.05	1.00	1.00	0.83
0.1594	0.5325	0.3081	1.02	1.00	0.95	0.88
0.2012	0.6058	0.1930	1.01	1.01	0.88	0.93
0.5417	0.3874	0.0709	1.01	1.00	0.99	0.71
0.5423	0.3407	0.1140	1.02	1.15	0.86	0.89
0.5353	0.3026	0.1621	1.01	1.04	0.93	0.93
0.6930	0.2676	0.0394	1.00	1.16	0.91	0.95

Table 2 Results of calculations of the vacancy-wind factor matrix (S_{ij}) based on a Manning-type analysis of the measured tracer diffusion data in the Cu-Ni-Fe alloy system

c_{Fe}	c_{Ni}	c_{Cu}	S_{CuCu}	S_{FeFe}	S_{CuFe}	S_{FeCu}
0.127	0.686	0.187	1.09	1.01	0.52	0.91
0.265	0.503	0.232	1.12	0.99	0.52	1.06
0.108	0.464	0.428	1.19	0.99	0.71	1.12
0.298	0.375	0.327	1.06	1.02	0.83	0.93
0.105	0.802	0.093	1.01	1.04	0.82	0.53

For the binary random alloy A-B one has the reduction for the vacancy-wind factor S:

$$S = \frac{(f_A/f_0)f_B c_C(w_A - w_B) - w_A}{f_B c_A(w_A - w_B) - w_A} = \frac{(f_B f_0)f_A c_B(w_B - w_A) - w_B}{f_A c_B(w_B - w_A) - w_B}$$
(Eq 31)

One can apply these expressions to the ternary alloy Cu-Fe-Ni (A-B-C).[28] With information being available for the activities a_{Cu}, a_{Fe}, a_{Ni} of the constituent atomic species,[31] the tracer diffusion coefficients can be calculated for the composition points from the available interdiffusion coefficients.

To calculate the phenomenological coefficients, the Darken and Manning approaches can be used. There are six variants of the system of four equations with three unknown parameters (these are the three tracer diffusion coefficients). To solve these systems a strategy can be taken: out of three equations for the interdiffusion coefficients, keep three in the these combinations (a) the equation for $\tilde{D}_{CuCu}^{Ni}$, the equation for $\tilde{D}_{FeFe}^{Ni}$, and the equation for $\tilde{D}_{CuCu}^{Ni}$; (b) the equation for $\tilde{D}_{CuCu}^{Ni}$, equation for $\tilde{D}_{FeFe}^{Ni}$, and the equation for $\tilde{D}_{FeCu}^{Ni}$; (c) the equation for $\tilde{D}_{CuCu}^{Ni}$, the equation for $\tilde{D}_{FeFe}^{Ni}$, and the sum of the equations for $\tilde{D}_{CuFe}^{Ni}$ and $\tilde{D}_{FeCu}^{Ni}$. These three systems are then solved for each theoretical method (where possible) and the solutions are then averaged.

From the analysis presented in Tables 1 and 2, one sees that all diagonal vacancy-wind factors S_{ii} are relatively close to unity, but the off-diagonal vacancy-wind factors can deviate quite substantially from unity. This again seems to confirm that the Darken approximation works reasonably well only for the diagonal vacancy-wind factors. In Ref 31, it was found that in Cu-Fe-Ni alloys the use of the Darken

approximation in numerical calculations of the interdiffusion profiles gives good agreement with the corresponding experimental data. This together with the previous conclusion suggests that the terms containing diagonal vacancy-wind factors are the major contributors to the system of the flux equations relative to a fixed end, and the off-diagonal vacancy-wind factors are included in the terms that only play a minor role in the whole analysis for these alloys.

This paper concludes with a few remarks about the accuracy of the vacancy-wind factors as provided by the Manning analysis. In Table 2 the Manning analysis was applied to the available tracer diffusion data. In an exact (random alloy) analysis the diagonal terms could be slightly higher (if they are already higher than 1.2 from Manning). On the other hand, for the off-diagonal factors the following is a guide: if the value obtained by the Manning approach is 0.6 and lower then the exact value could be much lower and can even change the sign. For the results presented in Table 1 the situation is more complicated because the analysis of the interdiffusion data is itself generally more complicated and involves thermodynamic data as well as interdiffusion data. Nonetheless, the general guide is very similar to the tracer diffusivities analysis: diagonal terms could be slightly higher (if they are already higher than 1.2 from Manning) and the off-diagonal factors could be significantly lower if they are 0.6 and lower from Manning.

7. Conclusions

This paper reviews a number of new procedures based around the random alloy model that was established recently for analyzing chemical diffusion data in binary and ternary alloy systems. The authors showed how atom-vacancy exchange frequency ratios, individual tracer correlation factors, and vacancy-wind factors can be extracted from the chemical diffusion data. Examples were taken from intrinsic diffusion data in the Ag-Cd and Ag-Cd-Zn alloy systems and from interdiffusion data in the Fe-Ni-Cr and Cu-Fe-Ni alloy systems.

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