

# Assessing Concentration Dependence of FCC Metal Alloy Diffusion Coefficients Using Kinetic Monte Carlo

B. Swoboda, A. Van der Ven, and D. Morgan

(Submitted October 30, 2009)

Intrinsic diffusion coefficients have been calculated for a solid solution binary fcc metal alloy with vacancies using grand canonical and kinetic Monte Carlo (MC) methods for a variety of model Hamiltonians. Model Hamiltonians include a kinetically and thermodynamically ideal case, solute-vacancy attraction and repulsion, and solute-solute attraction and repulsion. These model Hamiltonians are chosen to have constant average activation energies in order to focus on contributions from other thermodynamic and kinetic factors. The thermodynamic factor calculated using MC is compared to a mean-field regular solution model. It is shown that the mean-field model accurately predicts the thermodynamic factors for each model alloy Hamiltonian except for the alloys with a solute-solute interaction and concentration that are in the spinodal region (as predicted by the regular solution model). The MC determined concentration-dependent intrinsic diffusion coefficients are compared to values determined from the dilute five-frequency model and Darken and Manning analytical approximations. The results indicate that for a solid solution with known average barriers and vacancy concentration, Darken and Manning approximation-based analytic expressions and mean-field theory can be used to predict concentration-dependent diffusion coefficients within a factor of approximately three, provided the system is outside of the spinodal region. The good accuracy of this approximate approach follows from the fact that the thermodynamic factor is the main contribution to the concentration dependence of the diffusion constants, and that this thermodynamic factor is well described by mean-field theory.

**Keywords** diffusion constant, diffusion modeling, metallic alloys, Monte Carlo simulations, thermodynamic modeling

## 1. Introduction

Diffusion of atoms, driven by heat, radiation, or other factors, often results in changes of the mechanical, chemical, and microstructural properties of a material. In order to understand and predict these changes, it is important to be able to predict the fluxes with which atoms migrate through the solid.

A general challenge in modeling diffusion is relating diffusion constants to atomic scale processes and energetics. Such relationships can be used to learn about materials from measured diffusion coefficients, or in reverse, predict diffusion coefficients from measured or calculated atomic scale energetics. In this work, we will consider only vacancy-mediated diffusion through nearest-neighbor hops, as is known to occur in most metals (Ref 1) However, even for this well-studied mechanism, a general analytical relationship between atomic energetics and diffusion constants for concentrated alloys only exists for thermodynamically ideal alloys with hop frequencies that are independent

of the local environment (Ref 3, 24, 25). For realistic alloys, which exhibit short and long range order and in which the migration barriers depend on the local environment, diffusion constants must be solved numerically (Ref 2, 9, 13). When analytical expressions are obtained, they require severe approximations and often quite complex expressions (Ref 3) However, in dilute alloys it is possible to make approximations that allow diffusion constants to be written as quite accurate and convenient analytical expressions of atomic energies. As ab initio methods become more widely accessible, there is increasing interest in applying these dilute alloy analytical diffusion models, as they can be used to quickly obtain diffusion coefficients from the ab initio energetics. However, it is often desirable to extend the dilute model results to more concentrated systems, if only approximately. The focus of this paper is to explore the magnitude and source of errors associated with approximating concentrated alloy diffusion coefficients with dilute alloy diffusion coefficient values. Specifically, the changes in diffusion coefficients with concentration will be examined for Hamiltonians representing a range of alloy types. In addition, two approximations that allow diffusion coefficients in concentrated alloys to be estimated from dilute diffusion coefficient values (the Darken and Manning approximations) will be assessed. The approach will be to compare exact (except for numerical error) intrinsic diffusion coefficients calculated with kinetic and thermodynamic Monte Carlo (MC) methods to approximate analytical predictions. Note that the intrinsic diffusion coefficient (and other types of diffusion coefficients) will be defined below.

**B. Swoboda** and **D. Morgan**, University of Wisconsin-Madison, 1509 University Ave., Madison, WI 53706; **A. Van der Ven**, University of Michigan, 2300 Hayward St., Ann Arbor, MI 48109. Contact e-mails: ddmorgan@wisc.edu, bswoboda@wisc.edu, and avdv@umich.edu.

This work will focus on the dilute alloy model of Lidiard and LeClaire (Ref 4-6) (often called the “five-frequency” model). The five-frequency model, and its similar multifrequency variants, has proven to be a very accurate model for dilute alloys and has been widely used. However, the five-frequency model requires two key assumptions. The first assumption is that the interactions between solute and vacancy are only nearest-neighbor. This constraint can be extended (Ref 7, 8) but it will not be the focus of this study and we will restrict ourselves to nearest-neighbor Hamiltonians. The second assumption, at least in the simplest form of the model, is that two solutes never interact with each other (it is additionally assumed that vacancies are dilute and do not interact with each other). This assumption effectively limits the rigorous application of dilute diffusion models to solute concentrations of 1-2%. It should be noted that the assumption of noninteracting solutes can be relaxed through adding progressively higher order interaction terms into the model (Ref 6) However, as the five-frequency formalism is extended to account for solute pair and triplet interactions, the number of unique jumps that must be accounted for more than doubles. To increase solute concentration to an appreciable value would require the specification of a very large number of hop frequencies. In this work, we focus on only the case where no solute-solute interaction is included. Given the approximation of no solute-solute interaction, it is not clear how quickly the approximations of the five-frequency model break down with increasing solute concentration.

The mechanisms by which increasing solute concentration can alter diffusion constants from dilute solute values in a solid solution A-B alloy include (here V represents a vacancy and B the solute):

1. Changes in hopping barriers due to increasing concentration of B atoms.
2. Changes in vacancy formation energies and, consequently, changes in vacancy concentration.
3. Changes in effective B-V binding due to B-B-V interactions.
4. Changes in hopping paths due to increasingly long percolating networks of B-type chains.
5. Changes in the thermodynamic factors due to B-B interactions.

In a complete model, the above contributions must all be taken into account; however, such a complete model is very time consuming to construct and requires extensive ab initio parameterization (Ref 9, 10) It is therefore useful to see, for a simple solid solution, how significant the above factors might be in typical alloys, and to what extent their effects can be ignored. Factor (1) is not considered, as it will clearly lead to exponential changes in diffusion constants and therefore cannot be approximated as small unless the changes in the barriers are small. Second, factor (2) is not considered explicitly, and all diffusion coefficients are normalized by the vacancy concentration. The exclusion of factors (1) and (2) are not meant to imply that they are small. They can both clearly have large effects in ways that are easy to understand. Any quantitative model of

concentrated alloys needs to consider their possible contribution. Therefore, we focus on the additional factors (3-5) in order to understand the importance of these more subtle contributions.

To explore the effects of factors (3-5) several ratios of MC to approximate intrinsic diffusion coefficients will be calculated. Specifically, we will examine the ratio of the MC determined coefficients at solute concentration  $c_B$  to:

1. The five-frequency model determined dilute intrinsic diffusion coefficient.
2. The intrinsic diffusion coefficient at concentration  $x_B$  determined by applying Darken and Manning approximations to MC determined tracer diffusion coefficients at concentration  $x_B$ .
3. The intrinsic diffusion coefficient at concentration  $x_B$  determined by applying Darken and Manning approximations to the five-frequency model determined dilute intrinsic diffusion coefficient.

The purpose of test (1) is to determine the extent by which the intrinsic diffusion coefficient varies from the dilute five-frequency value as solute concentration is increased. The Darken and Manning approximations allow one to obtain intrinsic diffusion coefficients at arbitrary composition from tracer diffusion coefficients. Tests (2) and (3) apply these approaches, but in two different ways. For test (2), the tracer diffusion coefficients are determined exactly (except for numerical error) from MC, which means that test (2) is essentially just a test of the accuracy of the Darken and Manning approximations. Test (3) uses the dilute tracer diffusion coefficient for calculating intrinsic diffusion coefficients at all  $c_B$ , and therefore compounds errors from the changes in composition and from the Darken or Manning approximations. However, this test (3) assesses the accuracy of the typical way that intrinsic diffusion coefficients in concentrated alloys will be obtained from dilute diffusion models.

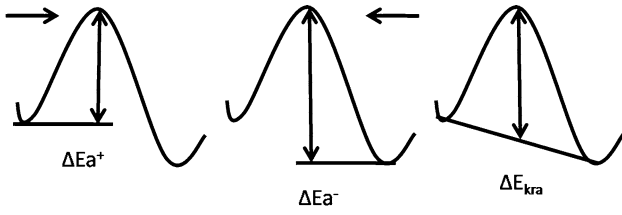
## 2. System Model

The system we have chosen to investigate is an fcc lattice consisting of A solvent atoms, B solute atoms, and a vanishingly small number of V vacancies. We allow only first nearest-neighbor interactions and only first nearest-neighbor atom-vacancy exchange.

Previous studies of a similar system have been performed by Allnatt and Allnatt (Ref, 11, 12), but their model effectively alters the hopping barriers quite significantly with concentration effects. As mentioned above, this effect will exponentially change the diffusion coefficients and makes it difficult to establish the role of factors (3-5) above. Therefore, we have constructed a different model for the atomic scale energetics from that used by Allnatt and Allnatt.

In our model, we attempt to eliminate large changes in the activation barrier with concentration in order to study the

## Section I: Basic and Applied Research



**Fig. 1** Kinetically resolved activation barrier

subtle changes certain interactions have on diffusion. The activation energy effects are minimized by using a fixed kinetically resolved activation barrier,  $\Delta E_{KRA}$  (Ref 13),  $\Delta E_{KRA}$  is defined as:

$$\Delta E_{KRA} = E_{act} - \frac{1}{2}(E_{init} + E_{fin}). \quad (\text{Eq 1})$$

The value of  $\Delta E_{KRA}$  is schematically represented in Fig. 1 and is independent of hop direction.

By holding  $\Delta E_{KRA}$  fixed, we effectively modify the energy of the activated state according to the initial and final states of the hop. This allows the activated state energy to change based on the hop endpoint energies without knowledge of activated state interactions. Fixed  $\Delta E_{KRA}$  is a reasonable initial approximation for hopping, as the activated state energy is likely to be closely correlated with the initial and final state energies. A similar assumption to having a fixed  $\Delta E_{KRA}$  underlies the Brønsted-Evans-Polanyi (BEP)-type formalism used in reaction kinetics and the Butler-Volmer rate equations used in electrochemical kinetics (Ref 14)

Depending on the interactions in the model and the local environment surrounding the vacancy and hopping atom, the initial and final states will vary. We determine the activation barrier by simply solving Eq 1 to get:

$$E_{barrier} = \Delta E_{KRA} - \frac{1}{2}E_{init} + \frac{1}{2}E_{fin} \quad (\text{Eq 2})$$

It is evident from Eq 2 that the activation barriers will depend to some extent on the local configurations of the hop's initial and final states.

A range of different Hamiltonians on a face-centered-cubic (fcc) lattice have been tested in order to investigate factors (3-5). The Hamiltonians can be written using cluster expansion formalism where we include only nearest-neighbor solute and vacancy interactions and use an occupation basis (Ref 2, 10):

$$E(\vec{p}) = \sum_{(i,j)} J_{BB} p_{i,B} p_{j,B} + J_{BV} p_{i,B} p_{j,V} \quad (\text{Eq 3})$$

Here the summation is over unique sets of nearest-neighbor pairs. The variable  $p_{i,I}$  is 1 if the species  $I$  occupies site  $i$  and 0 otherwise. The solute-vacancy nearest-neighbor interactions are captured in the term  $J_{BV}$ , and solute-solute nearest-neighbor interactions are contained in  $J_{BB}$ . Note that no coupling with species A (the solvent) are included as this is taken as the reference state.

In all Hamiltonians, the  $\Delta E_{KRA}$  is set to 1 eV, a typical values for fcc metals. First, a kinetically and thermodynamically ideal simulation was performed as a standard for comparison. In this case, the solute and solvent have the same activation barriers and there are no solute-vacancy or solute-solute interactions.

Factor (3) is investigated by adding a solute-vacancy nearest-neighbor interaction for both an attractive ( $J_{BV} = -30$  meV) and repulsive ( $J_{BV} = +30$  meV) interaction. Similarly, factors (4) and (5) are investigated by implementing an attractive ( $J_{BB} = -25$  meV) and repulsive ( $J_{BB} = +25$  meV) interaction. The values of  $-25$  meV was determined so that the simulations temperature of 800 K was above the transition temperature for phase separation driven by  $J_{BB}$  (the value of  $J_{BB} = \pm 25$  meV drives ordering at a significantly lower temperature than the corresponding phase separating case due to frustration on the fcc lattice). The transition temperature for phase separation from the fcc Ising model is (Ref 15, 16):

$$\frac{kT_c}{(zJ_{BB}/4)} = 0.84045 \quad (\text{Eq 4})$$

Here,  $T_c$  is the transition temperature and  $z$  is the number of nearest neighbors (12 for fcc). Simulations were performed at 800 K, which yields a maximum  $J_{BB}$  interaction of approximately 27 meV if we wish to remain in the solid solution phase (stronger interactions would put our simulation within a miscibility gap for at least some temperatures). It was our intent not only to choose an interaction energy that would be above the critical temperature, but also near it for maximum effect of short-range-order. While the results presented here are given in terms of absolute energies and temperatures to aid in intuition, they can be cast in a unit less form by simply dividing by  $kT$ . For  $T = 800$  K (500 K), this yields  $\Delta E_{KRA}/kT = 14.5$  (23.2),  $J_{BV}/kT = \pm 0.435$  ( $\pm 0.696$ ),  $J_{BB}/kT = \pm 0.363$  ( $\pm 0.580$ ).

### 3. Diffusion Theory

In this section, we define all the terms necessary to calculate concentration-dependent intrinsic diffusion coefficients from kinetic and grand canonical MC. We will also discuss the Darken and Manning approximations. These approximations provide a useful comparison when examining concentration-dependent values and will be compared to the exact (except for numerical error) kMC results.

In the absence of external forces, the fluxes in a binary crystalline solid can be related to gradients in chemical potentials according to (Ref 1):

$$J_A = -L_{AA} \nabla(\mu_A - \mu_V) - L_{AB} \nabla(\mu_B - \mu_V) \quad (\text{Eq 5})$$

$$J_B = -L_{BA} \nabla(\mu_A - \mu_V) - L_{BB} \nabla(\mu_B - \mu_V), \quad (\text{Eq 6})$$

where the  $L$ 's are phenomenological coefficients and the  $\mu$ 's are chemical potentials. Most solids at intermediate to high temperature contain a sufficiently high density of extended

defects (grain boundaries and dislocations) to regulate an equilibrium vacancy concentration such that  $\mu_V = 0$  and  $d\mu_V = 0$  throughout the solid. Using the Gibbs-Duhem relation:

$$x_A d\mu_A + x_B d\mu_B = 0, \quad (\text{Eq 7})$$

where  $x_i$  is the mole fraction of species  $i$ , it is then possible to rewrite the flux expressions (5)-(6) in terms of concentration gradients according to (Ref 1, 17):

$$J_A = -D_A \nabla C_A \quad (\text{Eq 8})$$

$$J_B = -D_B \nabla C_B, \quad (\text{Eq 9})$$

where the intrinsic diffusion coefficients take the form:

$$D_A = \left( \frac{\tilde{L}_{AA}}{x_A} - \frac{\tilde{L}_{AB}}{x_B} \right) \frac{x_A}{kT} \left( \frac{d\mu_A}{dx_A} \right) = \left( \frac{\tilde{L}_{AA}}{x_A} - \frac{\tilde{L}_{AB}}{x_B} \right) \theta_A \quad (\text{Eq 10})$$

$$D_B = \left( \frac{\tilde{L}_{BB}}{x_B} - \frac{\tilde{L}_{BA}}{x_A} \right) \frac{x_B}{kT} \left( \frac{d\mu_B}{dx_B} \right) = \left( \frac{\tilde{L}_{BB}}{x_B} - \frac{\tilde{L}_{BA}}{x_A} \right) \theta_B \quad (\text{Eq 11})$$

and can be viewed as a product of a kinetic factor with a thermodynamic factor  $\theta_i$  defined as:

$$\theta_i = \frac{x_i}{kT} \left( \frac{d\mu_i}{dx_i} \right) \quad (\text{Eq 12})$$

The derivative of the chemical potential with respect to mole fraction occurs under the constraint that  $\mu_V = 0$  and  $d\mu_V = 0$ . The modified phenomenological coefficients,  $\tilde{L}_{ij}$ , appearing in the expressions for the intrinsic diffusion coefficients are defined in terms of the phenomenological coefficients  $L_{ij}$  of Eq 5 and 6 according to (Ref 17):

$$\tilde{L}_{ij} = \Omega kT L_{ij} \quad (\text{Eq 13})$$

The phenomenological coefficients  $L_{ij}$  are related to fluctuations in atomic positions at equilibrium according to the following Kubo-Green expression (Ref 17, 18):

$$L_{ij} = \frac{\left\langle \left( \sum_{\zeta} \Delta \vec{R}_{\zeta}^i(t) \right) \left( \sum_{\xi} \Delta \vec{R}_{\xi}^j(t) \right) \right\rangle}{2dtM\Omega kT}, \quad (\text{Eq 14})$$

where  $\Omega$  is the volume per substitutional site. The  $\Delta \vec{R}_{\zeta}^i(t)$  are vectors linking the end points of the trajectory of atom  $\zeta$  of specie  $i$  after time  $t$ ,  $d$  is the dimension of the lattice,  $M$  is the number of lattice sites, and  $T$  is the temperature.

The thermodynamic factors can be written in terms of second derivatives of the free energy of the solid per substitutional site,  $g$ , and take the form (Ref 17):

$$\theta_A = \frac{x_A}{kT} \left( \frac{d\mu_A}{dx_A} \right)_{\mu_V=0} = \frac{x_A x_B}{kT} \left( \frac{\frac{\partial^2 g}{\partial x_A^2} \frac{\partial^2 g}{\partial x_B^2} - \left( \frac{\partial^2 g}{\partial x_A \partial x_B} \right)^2}{x_A \frac{\partial^2 g}{\partial x_A \partial x_B} + x_B \frac{\partial^2 g}{\partial x_A \partial x_B}} \right) \quad (\text{Eq 15})$$

$$\theta_B = \frac{x_B}{kT} \left( \frac{d\mu_B}{dx_B} \right)_{\mu_V=0} = \frac{x_A x_B}{kT} \left( \frac{\frac{\partial^2 g}{\partial x_A^2} \frac{\partial^2 g}{\partial x_B^2} - \left( \frac{\partial^2 g}{\partial x_A \partial x_B} \right)^2}{x_A \frac{\partial^2 g}{\partial x_A \partial x_B} + x_B \frac{\partial^2 g}{\partial x_A \partial x_B}} \right) \quad (\text{Eq 16})$$

For a regular solution,  $g$  can be written as (Ref 19):

$$g(x_A, x_B) = x_A x_B W_{AB} + x_B x_V W_{BV} + x_V x_A W_{VA} + kT [x_A \ln x_A + x_B \ln x_B + x_V \ln x_V] \quad (\text{Eq 17})$$

Here,  $x_V = 1 - x_A - x_B$  due to conservation of lattice sites. The  $W$ 's can be expressed in terms of the  $J$ 's in Eq 3 by noting that Eq 17 is obtained from a cluster expansion Hamiltonian by a mean-field averaging that ignores all but single-site correlations. With that approximation and invoking the relation  $x_1 = \langle p_1 \rangle$  for any given site (where the brackets denote a thermal average), it can be shown that  $W_{AB} = -6J_{BB}$  and  $W_{BV} = 6J_{BV} - 6J_{BB}$ . Additional terms zeroth or first order in  $x_B$  or  $x_V$  are necessary to make the mean-field average of the Hamiltonians in Eq 17 and the mean-field average of Eq 3 equivalent, but these terms play no role in the kinetics and will not be discussed further here.

The derivatives of the chemical potentials appearing in the thermodynamic factors can be written using terms from the regular solution model:

$$\left( \frac{d\mu_A}{dx_A} \right) = x_B \left( \frac{\left( \frac{1-x_B}{x_A x_V} \right) \left( \frac{-2W_{BV}}{kT} + \frac{1-x_A}{x_B x_V} \right) - \left( \frac{W_{AB}-W_{BV}}{kT} + \frac{1}{x_V} \right)^2}{x_A \left( \frac{W_{AB}-W_{BV}}{kT} + \frac{1}{x_V} \right) + x_B \left( \frac{-2W_{BV}}{kT} + \frac{1-x_A}{x_B x_V} \right)} \right) \quad (\text{Eq 18})$$

$$\left( \frac{d\mu_B}{dx_B} \right) = x_A \left( \frac{\left( \frac{1-x_B}{x_A x_V} \right) \left( \frac{-2W_{BV}}{kT} + \frac{1-x_A}{x_B x_V} \right) - \left( \frac{W_{AB}-W_{BV}}{kT} + \frac{1}{x_V} \right)^2}{x_A \left( \frac{1-x_B}{x_A x_V} \right) + x_B \left( \frac{W_{AB}-W_{BV}}{kT} + \frac{1}{x_V} \right)} \right) \quad (\text{Eq 19})$$

The second derivatives of the free energy can also be calculated using grand canonical MC by expressing the free energy in terms of the variances in the number of A and B atoms in the system (Ref 17).

The intrinsic diffusion Eq 10 and 11 contain thermodynamic and kinetic quantities. The thermodynamic contributions are captured in the thermodynamic factor as defined in Eq 12, while the kinetic contributions are captured in the phenomenological coefficients. We will use this division into thermodynamic and kinetic terms to determine which contributions are dominating the changes in the diffusion coefficients in the test cases discussed in this work.

We have now defined all the quantities necessary to determine concentration-dependent intrinsic diffusion coefficients. It is useful to compare these quantities with approximations that relate the concentration-dependent values to dilute theory values determined using the five-frequency model framework.

Darken and Manning approximations allow one to use tracer diffusion coefficients to determine intrinsic diffusion

## Section I: Basic and Applied Research

coefficients and phenomenological coefficients, respectively. In dilute alloys, the tracer diffusion coefficients can be analytically determined. The self-diffusion coefficient is a tracer diffusion coefficient for pure solvent and is written (Ref 6):

$$D_A^*(0) = a^2 v_A x_V f_0 \exp\left(\frac{-E_A}{kT}\right). \quad (\text{Eq 20})$$

Here  $a$  is the lattice parameter,  $f_0$  is the correlation factor, and  $E_A$  is the activation energy. The correlation factor accounts for the solvent hop paths deviating from random walk behavior. For a completely random walker, the correlation factor is unity. The correlation factor is 0.7815 for fcc crystals (Ref 6). The solute tracer diffusion coefficient can be determined by:

$$D_B^*(0) = a^2 v_B x_V f_B \exp\left(\frac{-E_B - E_{\text{bind}}}{kT}\right) \quad (\text{Eq 21})$$

The  $E_{\text{bind}}$  term represents the vacancy-solute binding energy and  $E_B$  is the activation energy for species B. The solute correlation factor,  $f_B$ , is defined as (Ref 6):

$$f_B = \frac{2w_1 + w_3 F\left(\frac{w_4}{w_0}\right)}{2w_1 + 2w_2 + w_3 F\left(\frac{w_4}{w_0}\right)} \quad (\text{Eq 22})$$

The  $w$  terms are hop frequencies and are defined within the five-frequency model and  $F$  is a known function (Ref 6).

At non-dilute concentrations, the tracer diffusion coefficients can be calculated in kinetic Monte Carlo simulations using the well-known expression (Ref 20):

$$D_i^* = \frac{\langle (\Delta \vec{R}^i)^2 \rangle}{2dt} \quad (\text{Eq 23})$$

Here  $\Delta \vec{R}^i$  is the vector linking the displacement of atom  $i$  after time  $t$ . The Darken approximation can be used to relate the tracer diffusion coefficient to the intrinsic diffusion coefficient by neglecting cross terms that correlate the trajectories of different types of diffusing particles (Ref 17, 21):

$$D_i^{\text{Darken}} = D_i^* \frac{x_i}{kT} \left( \frac{d\mu_i}{dx_i} \right) \quad (\text{Eq 24})$$

The Manning relations can be used to relate the tracer diffusion coefficients to the phenomenological coefficients in a concentrated alloy and can be written as (Ref 3):

$$L_{ii} = \left( \frac{c_i D_i^*}{kT} \right) \left( 1 + \frac{(1-f_0)}{f_0} \frac{c_i D_i^*}{\sum_m c_m D_m^*} \right) \quad (\text{Eq 25})$$

$$L_{ij} = L_{ji} = \frac{(1-f_0)}{f_0} \frac{c_i c_j D_i^* D_j^*}{kT \sum_m c_m D_m^*} \quad (\text{Eq 26})$$

Here,  $c_i$  is the concentration per unit volume of species  $i$ . Equation 24, and Eq 25 and 26 (combined with Eq 10-11) allow intrinsic diffusion coefficients to be obtained from tracer diffusion coefficients based on the Darken ( $D_i^{\text{Darken}}$ )

and Manning ( $D_i^{\text{Manning}}$ ) approximations, respectively. The true intrinsic diffusion coefficients will be compared to these approximate values in tests (2) and (3) described above.

## 4. Results

Intrinsic diffusion coefficients are determined by both thermodynamic and kinetic factors (Eq 10 and 11), and we will assess the behavior of each with concentration separately. Grand canonical MC was performed to determine the thermodynamic contributions and kinetic MC was used to determine the kinetic coefficients. Simulations were performed on a 512 atom fcc structure at a temperature of 800 K. Simulations were also performed at 500 K for all cases except those with solute-solute interactions, as this temperature is below the miscibility gap and far into the mean-field spinodal region for these cases.

### 4.1 Thermodynamic Factors

The thermodynamic factors defined in Eq 12 were determined using grand canonical MC by evaluating Eq 15 and 16 (Ref 17) and Eq 18 and 19 for the regular solution model. The results are plotted versus increasing solute concentration in Fig. 2 and 3. The approximate

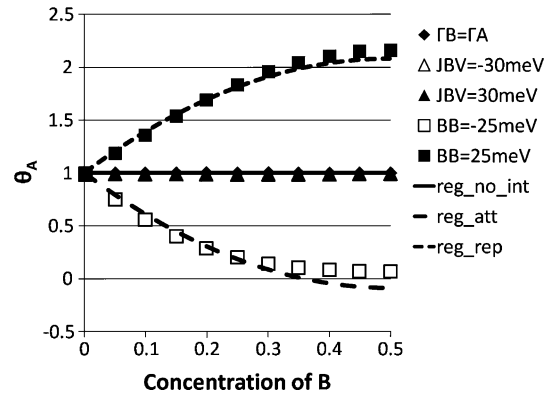


Fig. 2 Solvent thermodynamic factors at  $T = 800$  K

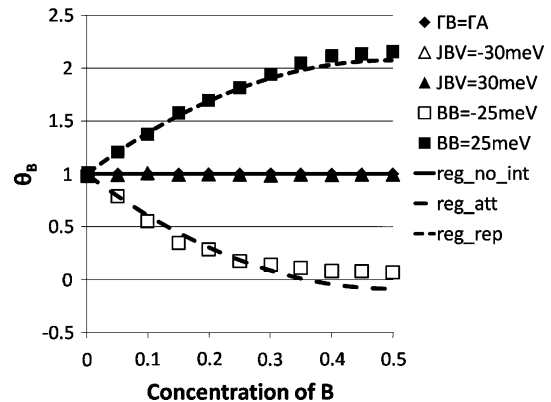


Fig. 3 Solute thermodynamic factors at  $T = 800$  K

regular solution value obtained from Eq 12, 18, and 19 are also plotted as continuous lines.

The regular solution model successfully approximates the behavior of the thermodynamic factors for most cases. The vacancy interactions have essentially no impact on the thermodynamics as the vacancy content is very low and the thermodynamic factors for the two  $J_{BV}$  cases are therefore equal to one. However, the regular solution model for the solute-solute cases deviates from the MC values between 30% and 40% solute concentration. This discrepancy is due to choosing a temperature that is near the critical temperature for the interaction energy and is an artifact of the mean-field approximation. The mean-field approximation implicit in the regular solution model has a critical temperature set by  $k_B T_c / z J_{BB} = 1$  (Ref 16). For the  $J_{BB} / kT = \pm 0.363$  value used here the mean-field result is below the critical temperature, causing the predicted thermodynamic factor predicted with Monte Carlo to deviate for the solute-solute cases. The discrepancy is most pronounced in the spinodal region, which occurs when  $x_B > 0.36$ .

The regular solution model works well for the interacting vacancy models because the vacancy concentration is extremely small. In fact, the value of one for the thermodynamic factor shows that the system behaves as an ideal solution, which is to be expected. We have also calculated analogous data to that shown in Fig. 2 and 3 at 500 K (excluding the cases where  $J_{BB} \neq 0$  as they are far in the spinodal region) and the system continues to behave as an ideal solution (data not shown).

#### 4.2 Test (1) Results

Test (1) assesses the change in intrinsic diffusion coefficients with solute concentration by calculating the ratio of the MC determined coefficients at solute concentration  $x_B$  to the five-frequency model determined dilute intrinsic diffusion coefficient. As described in Section 3, the kinetics contributions of the system are determined using kMC and Eq 14, and the thermodynamic factors were determined as in Section 4.1 (grand canonical MC and Eq 12, 18, and 19). The thermodynamic and kinetic quantities are combined according to Eq 10 and 11 to calculate  $D_i$ . We are interested in the deviation of the  $D_i$ 's at higher solute concentrations from their dilute values. To show these deviations a ratio is taken of the values at higher concentration to the dilute values. The dilute tracer diffusion coefficients ( $D_i^*$  (dilute)) are determined using five-frequency formalism and Eq 20-22 (note that this gives the same result as calculating them directly from MC to within numerical error). The results are presented in Fig. 4-7.

Examining the plots of  $D_i$  ratios we find that the ideal case shows that  $D_i$  is essentially constant as solute concentration increases, which is expected, as it has been previously shown that  $D_i$  is not concentration dependent in noninteracting systems (Ref 22, 23)

At 800 K, the largest deviations from the solvent dilute values occur for the solute-solute ( $J_{BB}$ ) interaction cases. In both the attractive and repulsive cases, the deviation follows the trends observed in the thermodynamic factors, increasing for repulsive interactions and decreasing when the

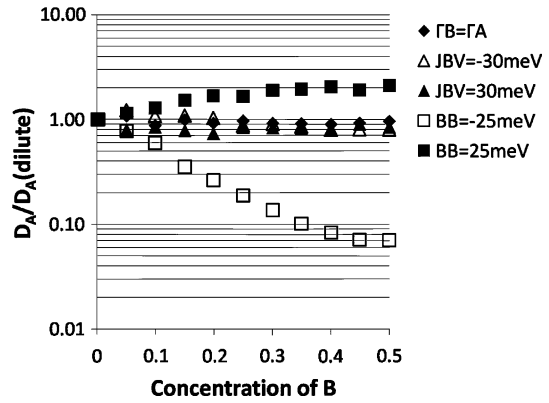


Fig. 4  $D_A$  and dilute  $D_A$  ratios at  $T = 800$  K

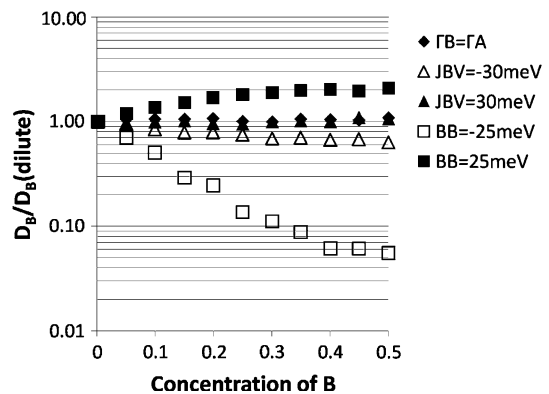


Fig. 5  $D_B$  and dilute  $D_B$  ratios at  $T = 800$  K

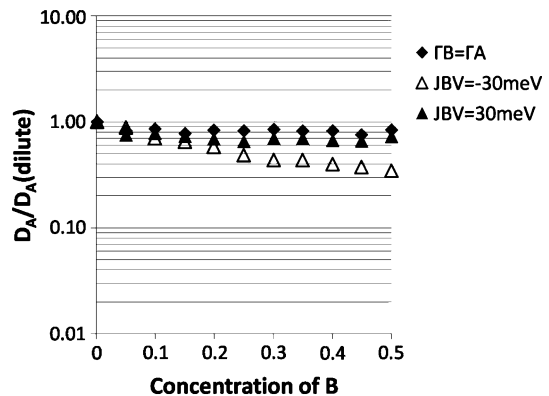


Fig. 6  $D_A$  and dilute  $D_A$  ratios at  $T = 500$  K

interactions are attractive.  $D_B$  also deviates from the dilute values for the solute-solute cases. It will be demonstrated in tests (2) and (3) below that the deviations induced by solute-solute coupling from dilute values for  $D_A$  and  $D_B$  are in fact largely due to the changes in the thermodynamic factor.

Little conclusion can be drawn from the  $J_{BV} = 30$  meV case, other than the increasing solute concentration only slightly changes the solvent and solute diffusion coefficients. For the  $J_{BV} = -30$  meV case, both  $D_A$  and  $D_B$

## Section I: Basic and Applied Research

decrease as solute concentration is increased. This is most likely due to the vacancy preferentially exchanging with the solute. As the solute concentration increases, the size of solute clusters increases making it more difficult for the vacancy to hop away from the clusters and retarding diffusion for both species. As with all the analysis at 500 K in this paper, the solute-solute interaction cases ( $J_{BB} \neq 0$ ) are excluded as the system is far into the mean-field spinodal region at  $T = 500$  K).

### 4.3 Test (2) Results

Test (2) assesses the accuracy of the Darken and Manning approximations for predicting intrinsic diffusion constants from tracer diffusion constants. We can relate the  $D_i^*$ 's to the  $D_i$ 's using the Darken and Manning approximations stated in Eq 24-26. Tests (2) involves ratios of  $D_i$ 's. In all cases, whether using the exact MC, Darken, or Manning expressions,  $D_i$  is proportional to the thermodynamic factor. Assuming these thermodynamic factors are calculated in the same manner they will cancel, and this test therefore assesses only kinetic properties. Note that this cancellation of the thermodynamic contribution occurs for test (3) as well.

In the calculations presented here, kMC and Eq 23 were used to calculate  $D_i^*$ , which results in a concentration-dependent tracer diffusion coefficient.  $D_i$ 's were determined by the same mechanism as Section 4.2. The results are analyzed as the ratio of the exact (except for numerical error) concentration-dependent  $D_i$ 's and the approximate value determined using  $D_i^{\text{Darken}}$  or  $D_i^{\text{Manning}}$  from MC calculated  $D_i^*$ 's. It is found that up to  $x_B = 0.5$  there are almost no clear trends or statistically significant deviations from a ratio of one (data not shown). In general, numerical noise creates fluctuations of up to about factors of two in the ratios. The results suggest that the Darken and Manning approximations are very accurate for the Hamiltonians and temperature conditions considered here. The Manning approximation considers cross-correlation terms that are not accounted for in the Darken approximation. These results indicate that the kinetic effects of the cross-correlation terms the Manning approximation captures are small in the cases and composition range we tested. Previous tests of the Manning

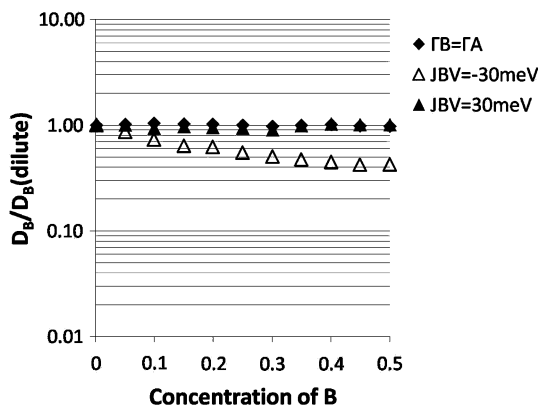


Fig. 7  $D_B$  and dilute  $D_B$  ratios at  $T = 500$  K

approximation by Allnatt and Allnatt (Ref 11) were performed and indicated that the accuracy of the approximation for  $D(ci)$  decreases as  $ci$  goes to 1. Our results do not show a similar trend because the cross terms (the phenomenological coefficients  $L_{AB}$ ) that arise from our Hamiltonian are orders of magnitude lower than the on-diagonal terms. The differences between our present results and those of Ref 11 are presumably due to our use of a different type of Hamiltonian. Specifically, while their use a fixed activated state energy we are using a fixed kinetically resolved activation barrier.

### 4.4 Test (3) Results

Test (3) helps determine if diffusion coefficients calculated using dilute theories are acceptable to use at increased solute concentrations. To determine this, we calculated the dilute  $D_i^*$ 's as in test (1), using the five-frequency formalism and Eq 20-22. These dilute values were then fixed as the  $D_i^*$ 's for all concentrations and used with the Darken and Manning approximations to obtain approximate concentration-dependent diffusion coefficients. Then, ratios of the exact (except for numerical error) MC calculated concentration-dependent  $D_i$ 's and the dilute  $D_i^*$  derived  $D_i^{\text{Darken}}$  and  $D_i^{\text{Manning}}$  values were taken. Note that, as discussed for test (2), the thermodynamic factors cancel from the ratios being presented. The results are plotted in Fig. 8-15.

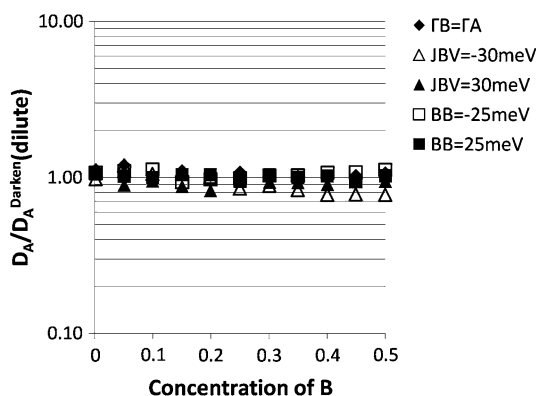


Fig. 8  $D_A$  and dilute  $D_A^{\text{Darken}}$  ratios at  $T = 800$  K

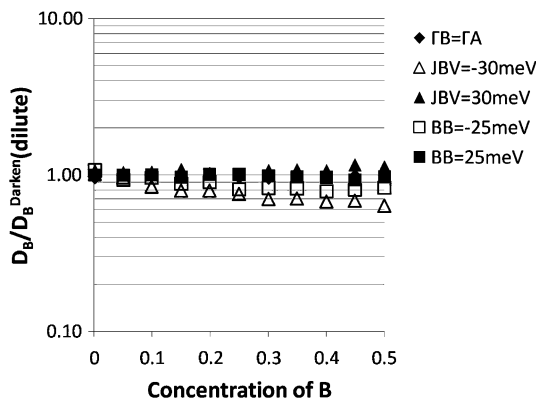


Fig. 9  $D_B$  and dilute  $D_B^{\text{Darken}}$  ratios at  $T = 800$  K

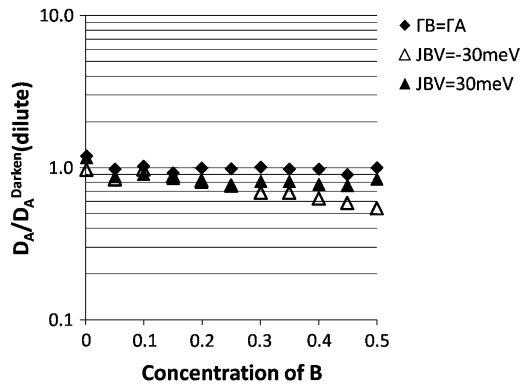


Fig. 10  $D_A$  and dilute  $D_A^{\text{Darken}}$  ratios at  $T = 500$  K

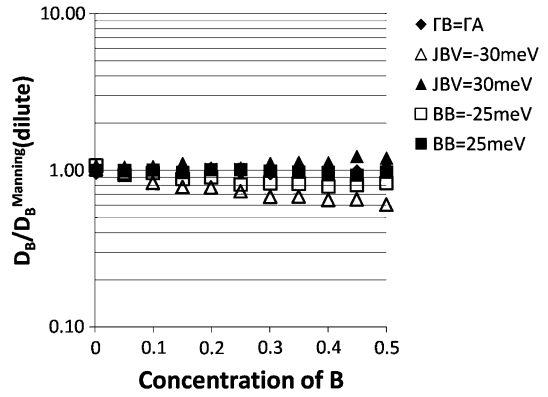


Fig. 13  $D_B$  and dilute  $D_B^{\text{Manning}}$  ratios at  $T = 800$  K

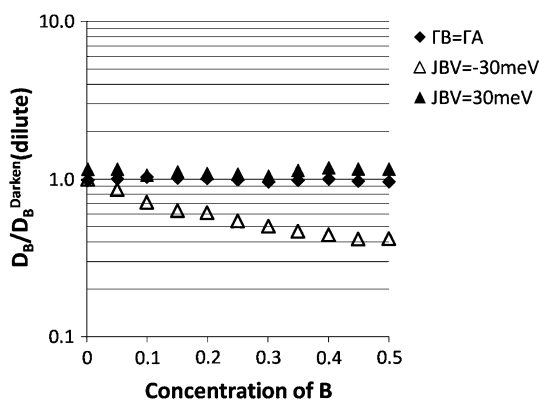


Fig. 11  $D_B$  and dilute  $D_B^{\text{Darken}}$  ratios at  $T = 500$  K

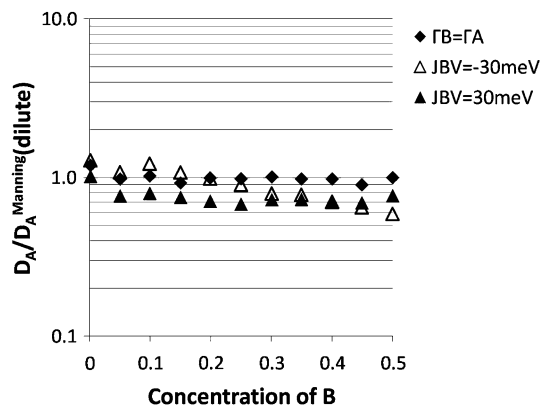


Fig. 14  $D_A$  and dilute  $D_A^{\text{Manning}}$  ratios at  $T = 500$  K

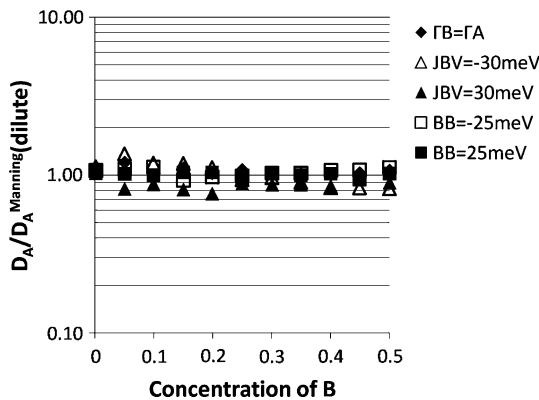


Fig. 12  $D_A$  and dilute  $D_A^{\text{Manning}}$  ratios at  $T = 800$  K

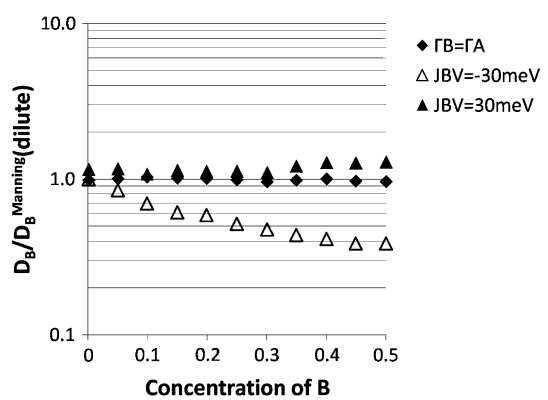


Fig. 15  $D_B$  and dilute  $D_B^{\text{Manning}}$  ratios at  $T = 500$  K

In the solute diffusion coefficient, for the solute-vacancy binding case ( $J_{BV} = -30$  meV), there is a kinetic effect that is not captured by the dilute diffusion coefficient. This effect, which can be seen in Fig. 9, 11, 13, and 15, causes the true solute diffusion coefficient to be somewhat less than predicted by either Darken or Manning approximations. The effect is enhanced at lower temperatures, as can be seen by comparing Fig. 11 to 9 and 15 to 13.

### 5. Conclusion

In this paper, a variety of model alloys have been investigated using grand canonical MC and kinetic MC. These include a kinetically and thermodynamically ideal case, cases for attractive and repulsive vacancy-solute interactions, and cases for attractive and repulsive solute-solute interactions.



## Section I: Basic and Applied Research

First, we determined that the regular solution model expressed in Eq 17 accurately determines the thermodynamic factors for each model alloy except for the alloys with a solute-solute interaction inside the spinodal region (as predicted by the regular solution model).

Test (1) compared concentration-dependent  $D_i$ 's as determined by MC and kMC to dilute  $D_i$ 's determined using the five-frequency model. As expected, the kinetically ideal case remains constant (except for numerical noise) with increasing solute concentration. Increasing solute concentration only slightly changes the  $D_i$ 's in the alloys having B-V interactions. However, both  $D_A$  and  $D_B$  deviate from their dilute values as concentration is increased in the alloys with solute-solute interactions. This deviation follows the trends noted in the thermodynamic factors and is due primarily to changes in the thermodynamics rather than kinetics. The fact that the thermodynamic factor is the dominant contribution to changes for the solute-solute interaction cases is demonstrated more rigorously in test (3). This test shows that, for solute-solute interaction cases, when the thermodynamic factor contributions are properly accounted for the correct  $D_A$  and  $D_B$  can be obtained from dilute values.

Test (2) compared the kMC and MC determined intrinsic diffusion coefficients,  $D_i$ 's, and the Darken,  $D_i^{\text{Darken}}$ , and Manning,  $D_i^{\text{Manning}}$ , values calculated using kMC determined concentration-dependent tracer diffusion coefficients,  $D_i^*$ 's (Eq 24 for Darken and Eq 25-26 along with Eq 10-11 for Manning). These approximations take into account thermodynamic changes as the solute concentration is increased. Both approaches approximate the kinetic contributions ( $L_{ij}$ ), but  $D_i^{\text{Darken}}$  does not contain cross-correlation terms that are incorporated in  $D_i^{\text{Manning}}$ . The results of test (2) show that  $D_i^{\text{Darken}}$  and  $D_i^{\text{Manning}}$  are very accurate for the conditions and temperatures examined and generally reproduce the exact simulations within numerical errors. The comparable accuracy of the Darken and Manning approximations indicates that the cross-correlation terms omitted by the Darken approximation are small.

Test (3) compared the kMC and MC determined  $D_i$ 's with the concentration-dependent  $D_i^{\text{Darken}}$  and  $D_i^{\text{Manning}}$  calculated by applying the Darken and Manning approximations using dilute tracer diffusion coefficients  $D_i^*$ 's determined with the dilute five-frequency formalism. It is this test that most directly assesses what one might do to predict  $D_i$ 's at arbitrary concentration from dilute  $D_i^*$ 's. The test (3) results show that the true  $D_i$ 's and approximate  $D_i^{\text{Darken}}$  and  $D_i^{\text{Manning}}$  are the same within the error bars of the simulation except for the alloys having a solute-vacancy binding energy of  $J_{\text{BV}} = -30$  meV, where the true  $D_B$  decreases faster than the approximate values with solute concentration.

In test (1), the deviation from the dilute  $D_i$  value for the alloys with solute-solute interactions (i.e., nonzero  $J_{\text{BB}}$ ) arises primarily from the concentration dependence of the thermodynamic factor, which is captured in the Darken and Manning approximations in tests (2) and (3). This can be seen by comparing results from tests (1)-(3).

For the model alloys having a solute-vacancy interaction (i.e., nonzero  $J_{\text{BV}}$ ) the intrinsic diffusion coefficients at

nondilute solute compositions exhibit only slight deviations from their dilute values. However, there are kinetic effects that are not fully captured by the dilute theory diffusion coefficient. In test (3), this results in larger deviations as concentration is increased between the numerical diffusion coefficient,  $D_i$ , and  $D_i^{\text{Darken}}$  and  $D_i^{\text{Manning}}$ .

Overall, our results indicate that using concentration-dependent tracer diffusion coefficients (test (2)), correct thermodynamic factors, and the Darken or Manning approximation will give an error of at most approximately factors of two (about our numerical error) for systems with interactions of the same types and order as those investigated. However, while using these approximations with dilute theory tracer diffusion coefficients (test (3)) will capture the thermodynamics of the system, it will not accurately track the kinetic effects and larger errors (up to a factor of three for our cases) will occur. While the errors seen in our model alloys having either solute-solute or solute-vacancy interactions are small compared to the accuracy of the simulations, larger errors can be expected for more strongly interacting systems. The largest error occurs when simply using dilute diffusion coefficients to describe nondilute alloys. In this situation neither the change in thermodynamic effects nor the change in kinetic effects is accounted for.

These results suggest that for a solid solution with known average barriers and vacancy concentration, Darken and Manning approximation-based analytic expressions and mean-field theory can be used to give concentration-dependent diffusion coefficients within a factor of approximately three, provided the system is outside of the spinodal region. This is due to the fact that the thermodynamic factor is the main contribution to the concentration dependence of diffusion constants from the factors (3)-(5) discussed in Section 1, and that this thermodynamic factor is well described by mean-field theory. If we assume our Hamiltonians are representative of more general alloys then, if correct average hopping and vacancy energetics can be obtained as a function of concentration, an accurate solid solution diffusion constant can be determined from analytical expression [Darken, Manning, or possibly other approaches (Ref 1, 24)].

### Acknowledgment

We gratefully acknowledge financial support from the DOE Nuclear Engineering Research Initiative Program (NERI), award number DE-FC07-06ID14747.

### References

1. R.E. Howard and A.B. Lidiard, *Matter Transport in Solids, Rep. Prog. Phys.*, 1964, **27**, p 161-240
2. A. Van der Ven, J.C. Thomas, Q. Xu, B. Swoboda, and D. Morgan, Nondilute Diffusion from First Principles: Li Diffusion in  $\text{Li}_x\text{TiS}_2$ , *Phys. Rev. B: Condens. Matter Mater. Phys.*, 2008, **78**, p 104306
3. J.R. Manning, Correlation Factors for Diffusion in Nondilute Alloys, *Phys. Rev. B*, 1971, **4**(4), p 1111-1121

4. A.B. Lidiard, Impurity Diffusion in Crystals (Mainly Ionic Crystals with the Sodium Chloride Structure), *Philos. Mag.*, 1955, **46**, p 1218-1237
5. A.D. LeClaire and A.B. Lidiard, Correlation Effects in Diffusion in Crystals, *Philos. Mag.*, 1956, **1**(6), p 518-527 (8th series)
6. A.D. LeClaire, Solute Diffusion in Dilute Alloys, *J. Nucl. Mater.*, 1978, **69-70**(1-2), p 70-96
7. V. Barbe and M. Nastar, Phenomenological Coefficients in a Concentrated Alloy for the Dumbbell Mechanism, *Philos. Mag.*, 2006, **86**(23), p 3503-3535
8. V. Barbe and M. Nastar, Phenomenological Coefficients in a Dilute BCC Alloy for the Dumbbell Mechanism, *Philos. Mag.*, 2007, **87**(11), p 1649-1669
9. A. Van der Ven and G. Ceder, First Principles Calculation of the Interdiffusion Coefficient in Binary Alloys, *Phys. Rev. Lett.*, 2005, **94**, p 045901
10. A. Van der Ven and G. Ceder, Vacancies in Ordered and Disordered Binary Alloys Treated with the Cluster Expansion, *Phys. Rev. B: Condens. Matter: Mater. Phys.*, 2005, **71**, p 054102-1-054102-2
11. A.R. Allnatt and E.L. Allnatt, Computer Simulation Study of the Manning Relations and Related Approximations in a Strictly Regular Solution Model, *Phil. Mag. A*, 1991, **64**(2), p 341-353
12. A.R. Allnatt and E.L. Allnatt, Comparison of Computer Simulated and Theoretical Tracer Diffusion Coefficients for a Strictly Regular Solution Model of a Concentrated Alloy, *Phil. Mag. A*, 1992, **66**(1), p 165-171
13. A. Van der Ven, G. Ceder, M. Asta, and P.D. Tapesch, First-Principles Theory of Ionic Diffusion with Nondilute Carriers, *Phys. Rev. B: Condens. Matter: Mater. Phys.*, 2001, **64**(18), 184307-1-184307-17
14. G.K. Boreskov, *Heterogeneous Catalysis*, Nova Science Publishers Inc., New York, 2003
15. J.M. Yeomans, *Statistical Mechanics of Phase Transitions*. Clarendon Press/Oxford University Press, Oxford, New York, 1992
16. J.M. Sanchez and D.d. Fontaine, The FCC Ising Model in the Cluster Variation Approximation, *Phys. Rev. B*, 1978, **17**(7), p 2926-2936
17. A. Van der Ven, H.C. Yu, G. Ceder, and K. Thornton, Vacancy Mediated Substitutional Diffusion in Binary Crystalline Solids, *Progr. Mater. Sci.*, 2010, **55**(2), p 61-105
18. A.R. Allnatt, Einstein and linear response formulae for the phenomenological coefficients for isothermal matter transport in solids, *J. Phys. C: Solid State*, 1982, **15**, p 5605-5613
19. Y. Kakuda, E. Uchida, and N. Imai, A New Model of the Excess Gibbs Energy of Mixing for a Regular Solution, *Proc. Jpn. Acad. Ser. B*, 1994, **70**(10), p 163-168
20. A.R. Allnatt and A.B. Lidiard, *Atomic Transport in Solids*, Cambridge University Press, Cambridge, 1993
21. L.S. Darken, Diffusion, Mobility and their Interrelation Through Free Energy in Binary Metallic Systems, *Trans. AIME*, 1948, **175**, p 184-201
22. G.E. Murch, Chemical Diffusion in Highly Defective Solids, *Phil. Mag. A*, 1980, **41**(2), p 157-163
23. R. Kutner, Chemical Diffusion in the Lattice Gas of Non-Interacting Particles, *Phys. Lett. A*, 1981, **81**(4), p 239-240
24. L.K. Moleko, A.R. Allnatt, and E.L. Allnatt, A Self-Consistent Theory of Matter Transport in a Random Lattice Gas and Some Simulation Results, *Phil. Mag. A*, 1989, **59**(1), p 141-160
25. I.V. Belova and G.E. Murch, Collective Diffusion in the Binary Random Alloy, *Phil. Mag. A*, 2000, **80**(3), p 599-607