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Theory of the enhancement factors of solute diffusion in dilute BCC solid solutions

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The enhancement factors for the solute diffusion in dilute b.c.c. alloys are discussed on the lines of two approaches. One of them is based on the Taylor's expansion series of activation energy and pre-exponential factor on concentration. The convergency of these series is studied. The second approach is formulated in the framework of the statistical theory. The comparative analyses of these two ways for the explanation of the enhancement of diffusion is carried out. The concentration dependencies of jump frequencies are investigated for V–Zr dilute solid solution as an example. It is shown that these dependencies are connected with the changes of the migration energy $E_m(c)$ as well as with the changes of the frequencies of vibrations. Different mechanisms that are possible for the explanation of the enhancement of $D(c)$ are discussed.

1. Introduction

The investigation of diffusion in dilute b.c.c. alloys is of great importance because of several circumstances. There is a group of b.c.c. metals that show the deviation of the temperature dependence of self-diffusion from the Arrhenius law. These are so-called "anomalous" b.c.c. metals. The statistical theory, taking into consideration different types of atom jumps for solute diffusion in b.c.c. alloys is not formulated so far. It has to be more complicated because the difference in the distances between the first and the second nearest neighbours in the b.c.c. lattice is about 15% while in f.c.c. lattice it is about 40%. This means that more types of jumps have to be involved.

The purpose of this paper is to study the solute diffusion in dilute substitutional b.c.c. alloys. For many binary substitutional alloys it is well known that the diffusion occurs via vacancies. Therefore the diffusion coefficient is influenced by the vacancies concentration. When changing the concentration of an alloy is done it results in the changing of the activation energies for vacancies as well as in the deviations of the pre-exponential factor for the diffusion process. Thus the diffusion highly depends on the concentration of an alloy. It is also a well-established experimental fact that alloying of a pure metal by an additional element produces changes in diffusion coefficient of solvent and of solute atoms [1]. For a successful description of this dependence several empirical approximations are widely used. In one of these approximations the exponential dependence of diffusion coefficient on the concentration, c, of the solute in a solid solution is used

$$D_2(c) = D_2(0)\exp(Bc) \qquad (1)$$

Here $D_2(c)$ is the diffusion coefficient of solute in dilute alloy, $D_2(0)$ is the diffusion coefficient of solute in the pure solvent, B is a temperature dependent constant [2]. Another approximation is represented by

$$D_2(c) = D_2(0)(1 + B_1c + B_2c^2 + \ldots) \qquad (2)$$

with temperature dependent parameters B_1, B_2, ... Both of these equations are representing some empirical regularity that gives an opportunity to describe the concentration dependence of $D_2(c)$. Equation 2 seems to be more natural because it may be assumed that it is given in the form of Taylor's series on the small parameter that is concentration of the solute

$$D_2(c) = D_2(0) + \left.\frac{\partial D_2(c)}{\partial c}\right|_{c=0} c + \frac{1}{2}\left.\frac{\partial^2 D_2(c)}{\partial c^2}\right|_{c=0} c^2 + \ldots$$

At the same time, Equation 1 includes less empirical parameters and sometimes may be reduced to Equation 2 by expansion in Taylor's series, thus giving a simple possibility to evaluate the constants B_1,B_2, ... in the following form

$$B_1 = B,$$
$$B_2 = \frac{1}{2}B_1^2, \ldots \qquad (3)$$

Such an approach was discussed recently for the diffusion of solvent atoms in dilute f.c.c. solid solutions [3]. It is obvious that using Equation 2 gives more accurate results in the fitting procedure, and the precision in this case is higher, because fitting is done with larger number of adjustable parameters. In any case the physical meaning of these parameters is not eliminated enough, although some attempts were done in the case of self-diffusion in dilute solid solutions (see, for example, [4, 5]).

0022–2461

In order to eliminate the concentration dependence of diffusion coefficient one can start with the Arrhenius law, representing the temperature dependence of D

$$D = D_0 \exp\left(-\frac{Q}{kT}\right) \qquad (4)$$

where Q is the activation energy, D_0 is the pre-exponential factor, T is the temperature and k is the Boltzman constant. It may be assumed that for dilute alloys this temperature dependence is just the same, but includes the concentration dependence both in activation energy and pre-exponential factor. If only the concentration dependence of Q is taken into consideration it is possible to use Equation 1 thus justifying also Equation 3. Nevertheless the possible dependence of D_0 on concentration means that several additional dependences have to be taken into account. They are: (a) the concentration dependence of the lattice parameter in an alloy and (b) the changes of the effective frequency of vibrations when the concentration of the solute is varied. Then it is easy to understand that the coefficients $B_1, B_2, \ldots$ from Equation 2 have to include this additional information and it is impossible to use a simple Equation 3, as in [3]. Indirectly the importance of taking into consideration these circumstances follows also from the results of fitting of Q and the pre-exponential factor to experimental data, provided in [6, 7].

In Tables I and II the results of our fitting of Equation 1 and Equation 2 to experimental data for different alloys are represented. It is seen that the constants B_1 and B_2 from Equation 2 for these alloys do not satisfy Equation 3 and B from Equation 1 is not equal to B_1 from Equation 2. This is an expected result in consequence with the predictions of Le Claire [8].

TABLE I Enhancement factor B for some b.c.c. systems (results of fitting of Equation 1)

System	Temperature, °K	B
V–Zr	1628	12.42
	1788	14.28
V–Co	1438	23.85
	1521	46.70
Zr–V	1245	− 16.88
	1435	− 30.27
βZr–Fe	1173	− 17.18

The experimental data for fitting were taken from [6] V–Zr, [7] Zr–V, [14] V–Co, [15] βZr–Fe.

TABLE II Enhancement factors B_1 and B_2 for some b.c.c. systems (approximation of Equation 2)

System	Temperature, °K	B_1	B_2
V–Zr	1788	14.8	163.1
V–Co	1438	14.55	886.67
Zr–V	1435	− 25.52	92.62
βZr–Fe	1173	− 34.62	707.87

The experimental data for fitting were taken from [6] V–Zr, [7] Zr–V, [14] V–Co, [15] βZr–Fe.

TABLE III Enhancement factor B for some b.c.c. systems (linear approximation of Equation 2)

System	Temperature, °K	B
V–Zr	1628	13.85
	1788	18.76
V–Co	1438	28.91
	1521	46.70
Zr–V	1245	− 14.76
	1435	− 23.97
βZr–Fe	1173	− 12.74

The experimental data for fitting were taken from [6] V–Zr, [7] Zr–V, [14] V–Co, [15] βZr–Fe.

If one is restricted only by the linear concentration term from Equation 2 then the coefficient B, as seen from Table III, is also not equal to B from Equation 1. In this table we show the results of our fitting of $D_2(c) = D_2(0)(1 + Bc)$ to the same experimental data as in Tables I and II. On the other hand the use of Equation 2 as a start point for the description of the diffusion behaviour gives a possibility of constructing the statistical theory of diffusion. Such a theory was worked out previously in [9, 10], where only the linear term in the concentration for diffusion coefficient was assumed. This was done for the solvent diffusion in dilute b.c.c. solid solutions. Nevertheless as shown in Table II the convergence of the expansion series that take only the linear term in concentration into consideration is not obvious. Assuming that the range of the dilute solution is limited by approximately 2 at% in solute concentration it is easy to estimate that for some alloys the ratio $B_1 c/B_2 c^2$ is not small enough to neglect the second (and sometimes higher) terms in the expansion series. The results of Table II allow the provision of the analyses of convergency and the estimation of the value of concentration when these series are converged. So, for example, for V–Zr alloy this limiting value of concentration, when only the terms up to c^2 were taken, is $\sim$ 1 at% and for V–Co it is equal to 0.2 at%. Thus the possibility of restricting by the terms of order c^2 for higher concentrations have to be checked in each case especially. Up to these values of concentrations one can use the linear fitting and evaluate the single parameter B. For this case the microscopic statistical theory that describes the changes in the jump frequencies and the changes in the interaction energies was carried out in [5, 9, 10].

The aim of this paper is twofold. On the one hand we are showing how to take into account the concentration dependencies of the activation energy, lattice parameter and effective frequencies of vibrations of atoms. The solving of this problem gives a way for arriving at simple relations between the values of parameters B_1, B_2 and the changes of thermodynamic characteristics of the dilute solid solution. Thus, measuring the concentration dependencies of these values one can predict also the $D_2(c)$ dependence. On the other hand the statistical theory gives the necessary understanding of the diffusion process, evaluates the ratios of the jump frequencies and allows the estimation of the conditions for the formation of clusters of solute atoms.

2. Thermodynamic approach to the evaluation of enhancement parameters

Let us assume following, for example [6, 7, 12], that the temperature dependence of diffusion coefficient of solute diffusion in dilute solid solution may be represented in the Arrhenius form

$$D_2 = D_{20}\exp\left(-\frac{Q}{kT}\right) \tag{5}$$

It is natural to assume the concentration dependence $D_{20} = D_{20}(c)$ and $Q = Q(c)$. Because of the small concentration of the solute we can produce the Taylor's series

$$D_{20}(c) = D_{20}(0) + \left.\frac{\partial D_{20}(c)}{\partial c}\right|_{c=0} c + \frac{1}{2}\left.\frac{\partial^2 D_{20}(c)}{\partial c^2}\right|_{c=0} c^2 + \cdots \tag{6}$$

$$Q(c) = Q(0) + \left.\frac{\partial Q(c)}{\partial c}\right|_{c=0} c + \frac{1}{2}\left.\frac{\partial^2 Q(c)}{\partial c^2}\right|_{c=0} c^2 + \cdots \tag{7}$$

where $D_{20}(0)$ and $Q(0)$ are the pre-exponential factor and the activation energy for the diffusion of the solute into the pure solvent. Restricting ourselves to the terms of the second order in concentration and substituting Equations 6 and 7 into Equation 5 we get

$$D_2(c) = D_2(0)\left(1 + \frac{1}{D_{20}(0)}\left.\frac{\partial D_{20}(c)}{\partial c}\right|_{c=0} c + \frac{1}{2}\frac{1}{D_{20}(0)}\left.\frac{\partial^2 D_{20}(c)}{\partial c^2}\right|_{c=0} c^2\right) \times \exp\left(-\left.\frac{\partial Q(c)}{\partial c}\right|_{c=0}\frac{c}{kT}\right) \times \exp\left(-\frac{1}{2}\left.\frac{\partial^2 Q(c)}{\partial c^2}\right|_{c=0}\frac{c^2}{kT}\right) \tag{8}$$

The last two exponents may be also expanded into concentration series up to the same order in concentration. The result of this procedure can be given in a form

$$D_2(c) = D_{20}(0)\exp\left(-\frac{Q(0)}{kT}\right)(1 + \alpha c + \beta c^2)\left(1 - \gamma c + \frac{1}{2}\gamma^2 c^2\right)(1 - \delta c^2) \tag{9}$$

where

$$\alpha = \frac{1}{D_{20}(0)}\left.\frac{\partial D_{20}(c)}{\partial c}\right|_{c=0}$$

$$\beta = \frac{1}{2}\frac{1}{D_{20}(0)}\left.\frac{\partial^2 D_{20}(c)}{\partial c^2}\right|_{c=0}$$

$$\gamma = \frac{1}{kT}\left.\frac{\partial Q(c)}{\partial c}\right|_{c=0};$$

$$\delta = \frac{1}{2}\frac{1}{kT}\left.\frac{\partial^2 Q(c)}{\partial c^2}\right|_{c=0} \tag{10}$$

Combining the terms that are linear and square in concentration and comparing the result with Equation 2 one gets immediately

$$B_1 = \alpha - \gamma \tag{11}$$

$$B_2 = \frac{1}{2}\gamma^2 - \alpha\gamma - \delta + \beta \tag{12}$$

(The terms of the order c^3 and higher were neglected.)

Now it is easy to understand that some physical conditions have to be satisfied if one wishes to use Equations 1–3. If $D_{20}(c)$ is a constant value ($D_{20}(c) = D_{20}(0)$ and the activation energy is a linear function of concentration, Equation 3 follows from Equations 11 and 12. In this case it is possible to get a positive or negative value for B_1, but B_2 is always positive. When the above mentioned conditions are not satisfied, B_2 may be negative also. These conditions obviously restrict the range of application of Equation 3, so, Equation 1 is useful when no changes of pre-exponential factor in diffusion coefficient with concentration are observed and $Q(c) = Q(0) + cQ^{(1)}$, where $Q^{(1)}$ is a constant. When $D_{20}(c)$ and $Q(c)$ are both linear functions in concentration then

$$B_2 = \frac{1}{2}B_1^2 - \frac{1}{2}\alpha^2 \tag{13}$$

and Equation 2 with $B_2 \neq \frac{1}{2}B_1^2$ seems to be more adequate to describe the diffusion. When $D_{20}(c)$ and $Q(c)$ are nonlinear functions, the more general Equation 12 has to be used.

On the other hand, it is clear that the results of fitting of $D_2(c)$ by means of Equation 2 give the necessary information about the behaviour of concentration dependencies $D_{20}(c)$ and $Q(c)$. Actually, if $B_2 = \frac{1}{2}B_1^2$ then D_{20} is a constant and $Q(c)$ is a linear function. In this case Equation 1 describes $D_2(c)$ with the same accuracy as Equation 2. All these results do not depend on the type of the lattice and are applicable both to the b.c.c. and f.c.c. systems and for solute as well as for solvent diffusion in the dilute solid solution.

3. Microscopic definition of enhancement parameters

We shall produce the evaluation of enhancement of solute diffusion following the method suggested by Le Claire [9] for calculations of enhancement factor for solvent diffusion in the dilute substitutional alloys. Nevertheless some initial points have to be noted. The first point of the calculations is the choice of the relevant group of atoms in the lattice, where the changes in the diffusion process in dilute solution in comparison with pure solvent have to be taken into consideration. We shall assume that: (1) this group is defined by the number of lattice sites from which the tracer atom or the vacancy may jump to the first or second coordination shell of the reference solute (RS) atom; (2) the solute atoms are forming the absolutely disordered homogeneous solid solution; (3) the solute atoms in the solution are noninteracting, because they are far enough from each other, and each solute tracer atom may be influenced only by one solute atom; (4) the changes in the energies of formation of vacancies are considered only for vacancies forming on the first or second coordination shell of the solute atom.

These assumptions restrict the choice of group of atoms by the fifth coordination shell of the solute atom in the b.c.c. lattice. This atom is situated in the "0" position (Fig. 1). So in the b.c.c. lattice our group includes 59 lattice sites, that are the zero position and the common number of sites in the five nearest coordination shells of this position. This corresponds to the concentration of solutes that is approximately 1.7 at%. When the concentration of solutes in an alloy is higher, one has to take into account the fact that the atoms of the fifth coordination shell are influenced by two solute atoms. This will change the group of atoms that have to be taken for modelling the jumps in diffusion. We shall define here the diffusion coefficient in the following form:

$$D_2 = \frac{1}{8}\Gamma_2 a^2 f_2, \qquad (14)$$

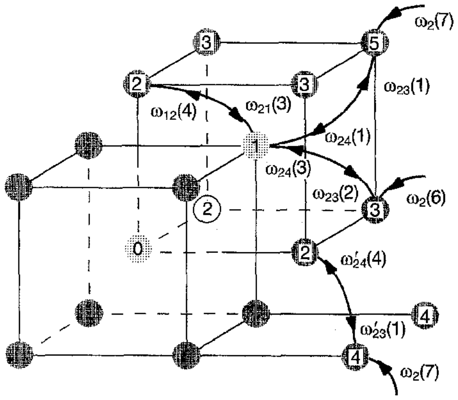
where Γ_2 is the average number of jumps of the diffusing solute atoms, f_2 is the correlation factor for solute diffusion, which is assumed to be concentration independent [8], a is the lattice parameter that is also assumed to be constant.

In a pure solvent Γ_2 is defined by the concentration of vacancies, and takes into consideration the changes in the bonding energies. Following Le Claire [9]

$$\Gamma_2 = 8\omega_2 \exp\left(-\frac{g + \Delta g_1}{kT}\right) \qquad (15)$$

where ω_2 is the jump frequency for solute (impurity)–vacancy jumps (see Fig. 1) in pure solvent; g is the free energy of vacancy formation in a pure solvent; Δg_1 is the additional free energy to form a vacancy on a first nearest-neighbour site. Thus the diffusion coefficient is

$$D_2 = f_2 a^2 \omega_2 \exp\left(-\frac{g + \Delta g_1}{kT}\right) \qquad (16)$$



the numbers in parentheses indicate the number of possible jumps with their respective frequencies

Figure 1 Schematic illustration of the cluster in b.c.c. structure. ○, vacancy; ◍, solute atom; ●, solvent atom. The numbers in parentheses indicate the number of possible jumps with their respective frequencies.

In dilute solid solution the jump frequency of a tracer near the RS will differ from ω_2. Moreover the presence of some concentration of solutes in the solution changes the vacancy concentration. These two effects determine the enhancement (dehancement) of the solute diffusion.

In b.c.c. structure where the difference in the first and second nearest neighbours' distances is small (less than 15%) one has to consider the bonding solute – solute and solute – vacancy on both shells. (In the case of f.c.c. structure it seems to be possible to neglect the influence of the RS on the atoms that are on the second shell.) All the jump frequencies of a tracer, that are not bringing it to the first or second neighbour position of the solute in the solution are assumed to be equal to ω_2.

Let us define the binding energies $(-\Delta g_i;\ i = 1, 2)$ between solute and vacancy on the i-th coordination shell. The binding energies solute–solute will be $(-\Delta g_{pi};\ i = 1, 2)$ respectively.

The conditions on the jump frequencies that follow from the principle of detailed balancing (as shown for f.c.c. structure in [9]) are

$$\omega_{12}\exp\left(\frac{\Delta g_1}{kT}\right)\exp\left(\frac{\Delta g_{p2}}{kT}\right) = \omega_{21}\exp\left(\frac{\Delta g_2}{kT}\right)\exp\left(\frac{\Delta g_{p1}}{kT}\right) \qquad \text{(a)}$$

$$\omega_{23}\exp\left(\frac{\Delta g_1}{kT}\right) = \omega_{24}\exp\left(\frac{\Delta g_{p1}}{kT}\right) \qquad \text{(b)}$$

$$\omega'_{23}\exp\left(\frac{\Delta g_2}{kT}\right) = \omega'_{24}\exp\left(\frac{\Delta g_{p2}}{kT}\right) \qquad \text{(c)}\,(17)$$

In these relations ω_{ij} are jump frequencies, and are shown in Fig. 1. The jump frequencies ω_{12} and ω_{21} change the binding energy of solute–solute and solute–vacancy pairs. These changes are connected with the fact that the solute from the nearest position jumps to the second nearest neighbour position (ω_{12}), while ω_{21} is connected with the reverse jump; ω_{23} and ω'_{23} are dissociative and break the solute–solute pairs; ω_{24} and ω'_{24} are associative and create the solute–solute pairs. The statistical analyses given in the Appendix allows us to obtain the values B_1 and B_2 from Equation 2 as functions of these jump frequencies. These functions are given by Equations A.17 and A.18.

We would like to emphasize here that Equation A.18 is not the same that the evaluation of B_2 from Equation 2. Actually, the coefficients in Equation 2, starting from B_2, are taking into consideration all possible solute clusters in the dilute solution, while expression A.18 shows the contribution of single solutes only. Nevertheless, if by using Equation A.17 one estimates the ratio of frequencies and substitutes them into Equation A.18 it is possible to compare the obtained value of coefficient B_2, with the results of the fitting of Equation 2 to experimental data. If the difference between the values of the coefficient obtained by these two methods is small enough (not more than the error of experimental data), then the above technique describes the diffusion process in a proper way. If this does not happen, the solute atom clusters are contributing to the diffusion process.

4. Discussion

Making use of the approach derived in Section 2 and on the basis of fitting of Equation 6 to the experimental data it is possible to evaluate the concentration dependence of the vibrational frequency $\nu(c)$. Assuming, as in Section 3, that the correlation factor is a constant and independent of concentration

$$D_{20}(c) = a^2(c)\nu(c)f_2 \qquad (18)$$

For a dilute solid solution the concentration dependence of the lattice parameter is well represented by Vegard's law. Using, as in Section 2, the Taylor's series for $a(c)$ and $\nu(c)$ and restricting by the linear in concentration terms in $a(c)$ and by square in c terms in $\nu(c)$ the following expressions for the derivatives from Equation 6 may be obtained

$$\left.\frac{\partial D_{20}(c)}{\partial c}\right|_{c=0} = f_2\left(a_A^2\left.\frac{\partial\nu(c)}{\partial c}\right|_{c=0} + 2\nu(0)a_A\left.\frac{\partial a(c)}{\partial c}\right|_{c=0}\right) \qquad (19)$$

$$\left.\frac{1}{2}\frac{\partial^2 D_{20}(c)}{\partial c^2}\right|_{c=0} = f_2\left(\frac{a_A^2}{2}\left.\frac{\partial^2\nu(c)}{\partial c^2}\right|_{c=0} + 2a_A\left.\frac{\partial a(c)}{\partial c}\right|_{c=0}\left.\frac{\partial\nu(c)}{\partial c}\right|_{c=0} + \nu(0)\left(\left.\frac{\partial a(c)}{\partial c}\right|_{c=0}\right)^2\right) \qquad (20)$$

Noting that $a(c) = ca_B + (1-c)a_A$, the value $\left.\frac{\partial a(c)}{\partial c}\right|_{c=0} = a_B - a_A$, where A and B are solvent and solute atoms respectively. Now the values $\left.\frac{\partial\nu(c)}{\partial c}\right|_{c=0}$ and $\left.\frac{\partial\nu(c)}{\partial c^2}\right|_{c=0}$ may be obtained. As an example we carried out the fitting of $D_{20}(c)$ (Equation 6) to the experimental data for V–Zr alloy [6] with a small concentration of Zr (from 0 to 2 at%). For this alloy $\nu(0) = 1.29\times 10^{17}\ \text{sec}^{-1}$, $\left.\frac{\partial\nu(c)}{\partial c}\right|_{c=0} = 1.01\times 10^{19}\ \text{sec}^{-1}$ and $\left.\frac{\partial^2\nu(c)}{\partial c^2}\right|_{c=0} = 2\times 10^{20}\ \text{sec}^{-1}$. These results may be used for estimation of the convergency of Taylor's series for concentration dependence of frequency of vibrations. It is easy to see that these series are converged only for very small concentrations, and the contribution of the linear term is of the same order, that is the frequency $\nu(0)$ for the concentration ~ 1 at%, while the square term is one order smaller for this concentration. So, in this case we can restrict ourselves to linear terms in concentration series for frequency $\nu(c)$. That does not mean that the same conclusion may be reached for other dilute solutions. Obtained values may be useful for the estimation of the changes of the vacancy migration energy with concentration. For this purpose we shall introduce several simplifying assumptions for the model described in Section 3. The value of B_1 for the V–Zr alloy, for example, is positive (see Table II) and $D(c) > D(0)$. This is true even if B_2 is negative, because $|B_1c| > |B_2c^2|$. Let us assume now that

$$\Delta g_2 = \Delta g_{p1} = \Delta g_{p2} = 0 \qquad (21)$$

Then from Equation 17a–c

$$\omega_{12}\exp\left(\frac{\Delta g_1}{kT}\right) = \omega_{21} \qquad \text{(a)}$$

$$\omega_{23}\exp\left(\frac{\Delta g_1}{kT}\right) = \omega_{24} \qquad \text{(b)}$$

$$\omega'_{23} = \omega'_{24} \qquad \text{(c)(22)}$$

Let us calculate Δg_1 for an alloy in the following way. The value Δg_1 is the difference between the energy of vacancy formation for solvent self-diffusion and the energy of vacancy formation for the solute diffusion in pure solvent. For Zr diffusion in pure V $\Delta g_1 = 0.205$ eV. This result was obtained using $g = 2.1$ eV from [13] and the assumption that the energy of vacancy formation for Zr diffusion in pure V is equal to $0.6\,Q(0)$. Taking into account Equation 21 it is possible to obtain $\omega_{23} = \omega_{12}$ from Equation 22a, b. This follows immediately from the conclusion that these frequencies are influenced only by the vacancy–solute binding and the probability of jumps to the second shell from the first one is just the same as to the third or to the fifth shell. We can also obtain $\omega'_{23} = \omega_2$ because it was already assumed that $\Delta g_2 = 0$ and the atom on the second shell for this jump is independent of the reference solute. Then, using Equations 20, 21, A.11–A.15 one can rewrite Equation A.17 in this form

$$B_1 = 7\frac{\omega_{23}}{\omega_2} + 7\frac{\omega_{23}}{\omega_2} - 14 \qquad (23)$$

Recalling now that

$$\omega = \nu\exp\left(-\frac{E_m}{kT}\right) \qquad (24)$$

we can get the equation for concentration dependence of vacancy migration energy.

$$\frac{\omega_{23}}{\omega_2} = \frac{\nu(c)}{\nu(0)}\exp\left(\frac{E_m(0) - E_m(c)}{kT}\right) \qquad (25)$$

where

$$E_m(c) = E_m(0) + \left.\frac{\partial E_m(c)}{\partial c}\right|_{c=0} c. \qquad (26)$$

Using the equation

$$\nu(c) = \nu(0) + \left.\frac{\partial\nu(c)}{\partial c}\right|_{c=0} c + \left.\frac{1}{2}\frac{\partial^2\nu(c)}{\partial c^2}\right|_{c=0} c^2 \qquad (27)$$

with the above obtained values of the first and second derivatives of $\nu(c)$ on concentration for V–Zr alloy with $B_1 = 14.8$ (Table II), $c = 1$ at%, $T = 1788$ K the following parameters were calculated: $\left.\frac{\partial E_m(c)}{\partial c}\right|_{c=0} = -0.9$ eV, $\omega_{23}/\omega_2 = 2.06$. The migration energy $E_m(0) \sim 0.4\,Q(0)$ and is equal to 1.54 eV. Thus using Equation 26, $E_m(0.01) = 1.53$ eV.

5. Conclusions

The obtained values for the concentration dependencies of parameters of diffusion allow us to conclude that the increase (or decrease) of the diffusion coefficient with the increase of the solute concentration in the dilute alloy is dependent on a lot of factors, especially on the concentration dependencies of the energies of formation and migration of vacancies as well as on the concentration dependencies of the lattice parameter and of the frequencies of vibrations. In each case an additional analysis is needed in the way proposed above as an example. Thus, in the case of V–Zr alloy it is shown that although the number of vacancies decreases ($E_v(c) > E_v(0)$) the value $D(c) > D(0)$. This occurs because the frequency of vibrations grows significantly with the concentration of the solute. Although in the V–Zr alloy $E_m(c) < E_m(0)$ this difference is small enough and does not influence the $D(c)$ dependence. In any case, one has to check the $E_m(c)$ dependence because sometimes this may be important, for example, in a case when these changes may compensate the concentration dependence of $E_v(c)$.

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Appendix

Let us calculate the total number of solute jumps made per unit time, adding the contribution from vacancies at each of five different types of site. Let N_i be the number of solute atoms and p_1 and p_2 the fractions of these that have vacancies associated with them at first- and second-neighbour sites. Here we are assuming that the additional free energy to form a vacancy near two solute atoms $\Delta g_{1m} = \Delta g_1 + \Delta g_m$, where $1, m$ are the numbers of coordination shells. If p_1 and $p_2 \ll 1$ [5] then

$$p_1 = 8\exp\left(-\frac{g + \Delta g_1 + \Delta g_1}{kT}\right) \qquad \text{(A1)}$$

$$p_2 = 6\exp\left(-\frac{g + \Delta g_1 + \Delta g_2}{kT}\right) \qquad \text{(A2)}$$

The number of solute jumps per unit time effected by these associated vacancies is then

$$N_i p_1\left(3\omega_{21}\exp\left(-\frac{\Delta g_{p2}}{kT}\right) + 4\omega_{24}\right) \qquad \text{(A3)}$$

$$N_i p_2\left(4\omega_{12}\exp\left(-\frac{\Delta g_{p1}}{kT}\right) + 4\omega'_{24}\right) \qquad \text{(A4)}$$

Here we are taking into consideration that the jumps with the frequencies ω_{12} and ω_{21} are influenced by the RS atom at the start and at the final position. On the contrary, all other jumps are influenced by RS on one of the possible atom positions (starting one or final one). Let N_s be the total number of crystal sites, so that $c = \frac{N_i}{N_s}$, $z1$ and $z2$ is the number of lattice sites at the first and second shells. A number $N_s - (z1 + z2 + 1)N_i = N_s(1 - 15c)$ of solvent sites are outside the second-neighbour shells of solute atoms and contain a total number, n_v, of randomly distributed free vacancies. There are 12 third-nearest neighbours to each solute, so the number of vacancies on third coordination shells is $c = \frac{N_i}{N_s}$. The number of solute jumps effected by these per unit time is

$$\frac{n_v 12 N_i}{N_s(1 - 15c)}\left(2\omega_{23}\exp\left(-\frac{\Delta g_{p1}}{kT}\right) + 6\omega_2\right) \qquad \text{(A5)}$$

Similarly, the number of solute jumps effected by the vacancies of the fourth and fifth coordination shells may be obtained as

$$\frac{n_v 24 N_i}{N_s(1 - 15c)}\left(\omega'_{23}\exp\left(-\frac{\Delta g_{p2}}{kT}\right) + 7\omega_2\right) \qquad \text{(A6)}$$

$$\frac{n_v 8 N_i}{N_s(1 - 15c)}\left(\omega_{23}\exp\left(-\frac{\Delta g_{p1}}{kT}\right) + 7\omega_2\right) \qquad \text{(A7)}$$

The remaining free vacancies beyond fifth neighbour

$$n_v - \frac{n_v 44 N_i}{N_s(1 - 15c)}$$

thus giving the total contribution of

$$\left(n_v - \frac{n_v 44 N_i}{N_s(1 - 15c)}\right)8\omega_2 \qquad \text{(A8)}$$

solute jumps. We now add the contribution of A3 to A8 and divide by the number of solvent atoms, $N_s(1 - c)$, to give the jump rate per solute atom

$$\Gamma_2(c) = \frac{1}{N_s(1 - c)}\left\{\begin{aligned} &8N_i\exp\left(-\frac{g + \Delta g_1 + \Delta g_1}{kT}\right)\left(3\omega_{21}\exp\left(-\frac{\Delta g_{p2}}{kT}\right) + 4\omega_{24}\right) + \\ &6N_i\exp\left(-\frac{g + \Delta g_1 + \Delta g_2}{kT}\right)\left(4\omega_{12}\exp\left(-\frac{\Delta g_{p1}}{kT}\right) + 4\omega'_{24}\right) + \\ &\frac{n_v 12 N_i}{N_s(1 - 15c)}\left(2\omega_{23}\exp\left(-\frac{\Delta g_{p1}}{kT}\right) + 6\omega_2\right) + \frac{n_v 24 N_i}{N_s(1 - 15c)}\left(\omega'_{23}\exp\left(-\frac{\Delta g_{p2}}{kT}\right) + 7\omega_2\right) + \\ &\frac{n_v 8 N_i}{N_s(1 - 15c)}\left(\omega_{23}\exp\left(-\frac{\Delta g_{p1}}{kT}\right) + 7\omega_2\right) + \left(n_v - \frac{n_v 44 N_i}{N_s(1 - 15c)}\right)8\omega_2 \end{aligned}\right\} \qquad \text{(A9)}$$

In the following step we used an equation similar to that of Lidiard [5],

$$n_v = \exp\left(-\frac{g + \Delta g_1}{kT}\right) N_s(1 - 14c) \qquad \text{(A10)}$$

but took into account the energy of vacancy formation near the solute atom. Using the definitions

$$\phi = \left(3\omega_{21}\exp\left(-\frac{\Delta g_{p2}}{kT}\right) + 4\omega_{24}\right)\exp\left(-\frac{\Delta g_1}{kT}\right) \qquad \text{(A11)}$$

$$\eta = \left(3\omega_{12}\exp\left(-\frac{\Delta g_{p1}}{kT}\right) + 3\omega'_{24}\right)\exp\left(-\frac{\Delta g_2}{kT}\right) \qquad \text{(A12)}$$

$$\chi = \omega_{23}\exp\left(-\frac{\Delta g_{p1}}{kT}\right) + 3\omega_2 \qquad \text{(A13)}$$

$$\lambda = \omega'_{23}\exp\left(-\frac{\Delta g_{p2}}{kT}\right) + 7\omega_2 \qquad \text{(A14)}$$

$$\varepsilon = \omega_{23}\exp\left(-\frac{\Delta g_{p1}}{kT}\right) + 7\omega_2 \qquad \text{(A15)}$$

and producing the Taylor's series on concentration (neglecting all terms of power greater than 2) it is possible to rewrite Equation A9 in a compact form

$$\Gamma_2(c) = \Gamma_2(1 + B_1 c + B_2 c^2) \qquad \text{(A16)}$$

$$B_1 = \frac{1}{\omega_2}(\phi + \eta + 3\chi + 3\lambda + \varepsilon) - 57 \qquad \text{(A17)}$$

$$B_2 = \frac{1}{\omega_2}(\phi + \eta + 6\chi + 6\lambda + 2\varepsilon) - 101 \qquad \text{(A18)}$$

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