

Calculation of impurity-vacancy and impurity-impurity interactions from enhancement of solvent and solute diffusion

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The enhancement of solvent as well as solute diffusion is discussed for substitutional alloys with impurities of positive excess charge as a function of composition and temperature. The enhancement factors of solvent diffusion up to third order in the impurity concentration and the corresponding enhancement factors of solute diffusion up to second order are calculated in terms of the complex model of Dorn and Mitchell and its application to diffusion introduced by Hehenkamp *et al.* The binding free enthalpies of the different vacancy-impurity complexes and the impurity-impurity interaction energies are calculated from these quantities, without resorting to further assumptions as in former treatments. This formalism is applied to AgSn and AgSb alloys. Employing a modified rigid-band model of Friedel, together with measurements of the nuclear Knight shift, we find the complex model to be applicable far beyond the range of infinite dilution. As for noble metals, it applies quantitatively up to solute concentrations of about 5 at. % and, at least qualitatively, for alloys with even higher concentrations.

I. INTRODUCTION

In very dilute substitutional alloys only free vacancies and vacancies associated with just one impurity atom are likely to form. Neglecting contributions of divacancies, which are only important possibly close to the melting point, Lomer¹ calculated the equilibrium concentration of vacancies N_v as a function of the molar fraction N_B of solute component B and temperature T :

$$N_v(N_B) = N_v(0) \left[1 - ZN_B + ZN_B \exp \left\{ \frac{g_{b_1}}{kT} \right\} \right] \quad (1)$$

Here $(-g_{b_1})$ is the binding free enthalpy of a vacancy-solute-atom pair, Z the coordination number, and $N_v(0)$ the molar fraction of vacancies in the pure metal A at temperature T . In this case solvent diffusion is enhanced in a linear way by alloying impurity atoms which attract vacancies. The solvent diffusion coefficient $D_{A^*}^{AB}(N_B)$ in the alloy is given by²

$$D_{A^*}^{AB}(N_B) = D_{A^*}^A (1 + b_1 N_B), \quad (2)$$

where $D_{A^*}^A$ is the tracer diffusion coefficient of the A atoms in the pure solvent and b_1 the linear enhancement factor.

The five-frequency model^{2,3} applies very well to the explanation of Eq. (2). It yields a detailed picture of the different vacancy jumps in terms of the three jump-frequency ratios w_2/w_1 , w_3/w_1 , and w_4/w_0 with w_i defined in the usual way. The binding free enthalpy of a vacancy-impurity pair is closely linked to the ratio w_4/w_3 :⁴

$$\frac{w_4}{w_3} = \exp \left[- \frac{g_{b_1}}{kT} \right]. \quad (3)$$

In order to get values of w_4/w_3 from the jump-frequency ratios w_2/w_1 , w_3/w_1 , and w_4/w_0 an additional assumption is necessary. Dirkes and Heumann⁵ assumed that the mean jump frequency of a vacancy at nearest-neighbor sites of the impurity is approximately the same as the one in the pure solvent, i.e.,

$$4w_1 + 7w_3 + w_2 \simeq 12w_0. \quad (4)$$

In more concentrated alloys vacancies can be associated with more than one solute atom in the first neighbor shell.⁶ According to Dorn and Mitchell⁶ the equilibrium concentration of such complexes N_{v_i} with i solute and $Z-i$ solvent atoms around a vacancy is given by

$$N_{v_i} = N_v(0) \binom{Z}{i} N_A^{Z-i} N_B^i \exp \left[\frac{g_{b_i}}{kT} \right], \quad (5)$$

where N_A is the molar fraction of solvent component A and $(-g_{b_i})$ is the binding free enthalpy of a given complex, which here is assumed to be independent of the configuration of the B atoms. The formation of complexes with more than one impurity atom leads to a nonlinear enhancement of solvent diffusion upon alloying,⁷⁻⁹ as one can see in the case of AgSb alloys in Fig. 1. In several systems a linear dependence between normalized vacancy concentration $N_v^N \equiv N_v(N_B)/N_v(0)$ and normalized solvent diffusion coefficient $D_{A^*N}^{AB} \equiv D_{A^*}^{AB}(N_B)/D_{A^*}^A(0)$ has been observed experimentally,⁷⁻⁹ which can be expressed by the following empirical equation⁸

$$D_{A^*N}^{AB}(N_B) = 1 + A [N_v^N(N_B) - 1]. \quad (6)$$

Here A is independent of concentration, within experimental errors, for a given temperature over a wide range of alloying. Equation (6) indicates that the nonlinear enhancement of solvent diffusion upon alloying is essentially due to a corresponding nonlinear increase in the va-

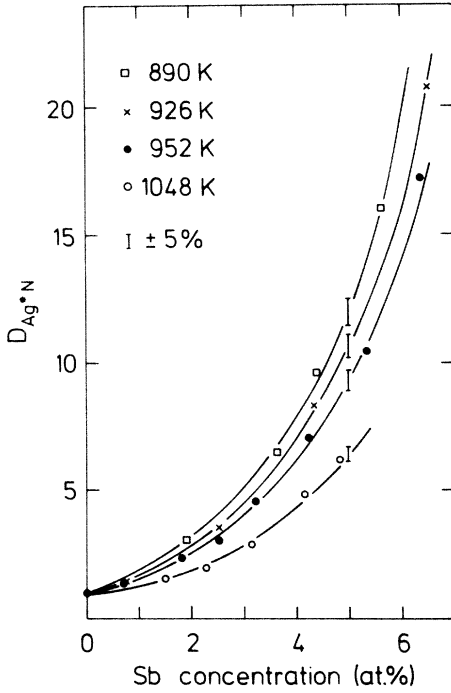


FIG. 1. Normalized solvent Ag(110^m)-tracer diffusion coefficient D_{A^*N} vs Sb concentration in AgSb alloys with absolute temperature as parameter according to Schmidt (Ref. 7).

cancy concentration. In order to get A and the binding free enthalpy ($-g_{b_1}$) from Eq. (6) an additional assumption concerning the impurity-impurity interaction has to be used.¹⁰

Hehenkamp *et al.*^{7,8} also gave a more general expression of the normalized solvent diffusion coefficient in the framework of the complex model of Dorn and Mitchell by introducing average effective jump frequencies per A atom $\langle w_{\text{eff}}^A \rangle_i$ in the i th complex:

$$D_{A^*N}(N_B, T) = N_A^{Z-1} + \sum_{i=1}^{Z-1} \frac{\langle w_{\text{eff}}^A \rangle_i}{f_0 w_0} (z_{i-1}) \times N_A^{Z-1-i} N_B^i \exp \left[\frac{g_{b_i}}{kT} \right]. \quad (7)$$

Here f_0 is the correlation factor of solvent diffusion in pure solvent and $f_0 w_0$ the corresponding effective jump frequency. It is the purpose of this paper to discuss the enhancement of solvent diffusion in terms of Eq. (7) and to calculate the binding free enthalpies ($-g_{b_i}$).

We will show in this paper that knowledge of the enhancement of solute diffusion in addition to solvent diffusion provides useful further information in order to completely eliminate the additional assumptions necessary above.

II. SOLVENT DIFFUSION

In order to describe the nonlinear enhancement of solvent diffusion upon alloying one expands Eq. (7):

$$D_{A^*N} = 1 + b_1 N_B + b_2 N_B^2 + b_3 N_B^3 + \dots \quad (8)$$

b_2 and b_3 are the second- and third-order enhancement factors, respectively. Higher-order enhancement factors are not needed in the following treatment. From Eqs. (7) and (8) one obtains

$$b_1 = 11(W_1 B_1 - 1), \quad (9)$$

$$b_2 = 55(W_2 B_2 - 2W_1 B_1 + 1), \quad (10)$$

$$b_3 = 165(W_3 B_3 - 3W_2 B_2 + 3W_1 B_1 - 1), \quad (11)$$

where B_i and W_i are defined by

$$B_i \equiv \exp \left[\frac{g_{b_i}}{kT} \right], \quad W_i \equiv \frac{\langle w_{\text{eff}}^A \rangle_i}{f_0 w_0}, \quad i = 1, 2, 3. \quad (12)$$

Hehenkamp, Schmidt, and Schlett⁷ have shown that a linear dependence between D_{A^*N} and N_v^N leading to Eq. (6) implies that the effective jump frequency of the A atoms at a free vacancy $f_0 w_0$ decreases drastically in the average to that of $\langle w_{\text{eff}}^A \rangle_1$ in the first complex due to the attraction between vacancy and impurity, whereas the addition of a second and third impurity has a much smaller influence on $\langle w_{\text{eff}}^A \rangle_2$ and $\langle w_{\text{eff}}^A \rangle_3$, respectively. Therefore validity of Eq. (6) involves

$$W_1 \simeq W_2 \simeq W_3. \quad (13)$$

In our calculations we take into account possible deviations of the average effective jump frequency per A atom in the $(i+1)$ th complex as against the i th complex, replacing Eq. (13) by

$$\frac{W_{i+1}}{W_i} = 1 - \frac{i+1}{i} \hat{\gamma}, \quad i = 1, 2, \quad (14)$$

Eq. (14) gives with $\gamma = 2\hat{\gamma}$

$$W_2 = W_1(1 - \gamma), \quad (15)$$

$$W_3 = W_2(1 - \frac{3}{4}\gamma). \quad (16)$$

Substituting Eqs. (15) and (16) into Eqs. (9), (10), and (11) yields

$$W_1 B_1 = \tilde{b}_1, \quad (17)$$

$$(1 - \gamma) B_2 / B_1 = \tilde{b}_2 / \tilde{b}_1, \quad (18)$$

$$(1 - \frac{3}{4}\gamma) B_3 / B_2 = \tilde{b}_3 / \tilde{b}_2. \quad (19)$$

Here the \tilde{b}_i are only dependent on the enhancement factors b_i according to

$$\tilde{b}_1 = \frac{b_1}{11} + 1, \quad (20)$$

$$\tilde{b}_2 = \frac{b_2}{55} + 2\tilde{b}_1 - 1, \quad (21)$$

$$\tilde{b}_3 = \frac{b_3}{165} + 3\tilde{b}_3 - 3\tilde{b}_2 + 1. \quad (22)$$

If we define

$$G_{21} \equiv kT \ln(\tilde{b}_2 / \tilde{b}_1), \quad G_{32} \equiv kT \ln(\tilde{b}_3 / \tilde{b}_2), \quad (23)$$

Eqs. (18) and (19) can be written as

$$G_{21} = g_{b_2} - g_{b_1} + kT \ln(1 - \gamma), \quad (24)$$

$$G_{32} = g_{b_3} - g_{b_2} + kT \ln(1 - \frac{3}{4}\gamma). \quad (25)$$

In order to solve Eqs. (17), (24), and (25) knowledge of b_1 , b_2 , and b_3 is not sufficient. In case further information is not available, it would be a good approximation to use Eq. (13) instead of Eq. (14), thus putting $\gamma = 0$.

To avoid such assumptions for the value of γ we include solute diffusion in our treatment additionally in order to determine γ directly.

III. SOLUTE DIFFUSION

Solute diffusion can be described in terms of the complex model of Dorn and Mitchell by introducing average effective jump frequencies per B atom $\langle w_{\text{eff}}^B \rangle_i$ in the i th complex, which include correlation effects.

In infinitely diluted alloys ($i=1$) one has $\langle w_{\text{eff}}^B \rangle_1 = f_2 w_2$, where w_2 is the jump frequency of the solute atom, as defined in the five-frequency model, and f_2 is the corresponding impurity correlation factor.

Taking into account the contributions of the impurity atoms in the different complexes to the average jump rate of the B atoms in a similar way as in the case of solvent diffusion,^{7,8,11} one arrives at the following equation for the solute diffusion coefficient normalized to its value $D_{B^*}^A(0)$ in pure metal A :

$$D_{B^*N} = N_A^{Z-1} + \sum_{i=2}^Z \frac{i}{Z} \frac{\langle w_{\text{eff}}^B \rangle_i}{f_2 w_2} (N_A^Z)^{Z-i} N_B^{i-1} \times \exp \left[\frac{g_{b_i} - g_{b_1}}{kT} \right]. \quad (26)$$

It should be pointed out that the formation of complexes with i B atoms leads to an enhancement of solvent diffusion of i th order, whereas solute diffusion is only enhanced in $(i-1)$ th order.

Expanding Eq. (26) up to second order in N_B yields

$$D_{B^*N} = 1 + a_1 N_B + a_2 N_B^2 + \dots, \quad (27)$$

$$a_1 = 11(V_2 B_2 / B_1 - 1), \quad (28)$$

$$a_2 = 55(V_3 B_3 / B_1 - 2V_2 B_2 / B_1 + 1), \quad (29)$$

where B_i is given by Eq. (12) and V_i is defined by

$$V_i \equiv \langle w_{\text{eff}}^B \rangle_i / (f_2 w_2), \quad i = 2, 3. \quad (30)$$

If one associates an additional B atom to a complex containing already one B atom at the vacancy, the attractive interaction of the vacancy is then distributed among both B atoms. Thus one should expect the average effective jump frequency per B atom to decrease to about half the value in a complex with one impurity atom alone. This would imply $V_i \approx 1/i$ for $i=2,3$. In order to be more precise a more general approach is being used here, introducing an additional parameter P , which has to be determined:

$$V_i = \frac{1}{iP}, \quad i = 2, 3. \quad (31)$$

Substituting Eq. (31) into Eqs. (28) and (29), one obtains

$$g_{b_3} - g_{b_2} = kT \ln \bar{a}, \quad (32)$$

$$P = \frac{\exp[(g_{b_2} - g_{b_1})/kT]}{2(a_1/11 + 1)}. \quad (33)$$

Here \bar{a} , which is defined by

$$\bar{a} = \frac{3}{2} \frac{a_2/55 - 1}{a_1/11 + 1} + 3, \quad (34)$$

depends on the enhancement factors a_1 and a_2 of solute diffusion only.

Equation (32) yields the difference in the binding free enthalpies between vacancy-impurity complexes containing three and two B atoms, respectively, which is a direct measure of the binding free enthalpy of a third impurity to a complex with two B atoms.

Knowledge of $g_{b_3} - g_{b_2}$ enables one to calculate γ from Eq. (25):

$$\gamma = \frac{4}{3} \left[1 - \exp \left[\frac{G_{32} - (g_{b_3} - g_{b_2})}{kT} \right] \right]. \quad (35)$$

Equation (24) can also be written as

$$g_{b_2} - g_{b_1} = G_{21} - kT \ln(1 - \gamma). \quad (36)$$

Thus, by substituting γ into Eq. (36), one obtains $-(g_{b_2} - g_{b_1})$, i.e., the binding free enthalpy of a second impurity to a vacancy-impurity pair.

Provided that the binding free enthalpy ($-g_{b_1}$) of a vacancy-impurity pair is known, knowledge of $(g_{b_2} - g_{b_1})$ and $(g_{b_3} - g_{b_2})$ allows one to determine g_{b_2} and g_{b_3} immediately. On the other hand g_{b_1} can be estimated from $(g_{b_2} - g_{b_1})$ and $(g_{b_3} - g_{b_2})$.

Neglecting any energetic interference of bound impurity atoms between themselves, the binding free enthalpy of a second B atom to a vacancy-impurity pair $-(g_{b_2} - g_{b_1})$ can be taken as equal to $(-g_{b_1})$. To a good approximation, the difference between $(-g_{b_1})$ and $-(g_{b_2} - g_{b_1})$ should be given by the difference between $-(g_{b_2} - g_{b_1})$ and the binding free enthalpy of a third impurity to a complex with two B atoms. Thus one arrives at the equation

$$g_{b_1} = (g_{b_2} - g_{b_1}) + [(g_{b_2} - g_{b_1}) - (g_{b_3} - g_{b_2})]. \quad (37)$$

Recently Bércecs and Kovács¹² gave the following expression for the binding free enthalpy ($-g_{b_i}$) of a vacancy-impurity complex containing i B atoms

$$g_{b_i} = i g_{b_1} + \langle n_i^{BB} \rangle \Delta. \quad (38)$$

In the case of fcc alloys these authors took into account nearest-neighbor interactions of the impurity atoms at the vacancy, introducing $\langle n_i^{BB} \rangle$, the average number of impurity-impurity nearest-neighbor bonds, and the corresponding interaction energy $(-\Delta)$.

$(-\Delta)$ is the difference in energy between complexes containing two impurity atoms at first-neighbor positions and at more distant ones of the Z nearest neighbors around a given vacancy, respectively.

The authors point out, that Eq. (38), which implies a statistical distribution of the impurities at the vacancy, is only applicable in the case

$$|\Delta/kT| < 1. \quad (39)$$

By means of Eq. (38) g_{b_1} and Δ can be calculated from $(g_{b_2}-g_{b_1})$ and $(g_{b_3}-g_{b_2})$. For fcc metals Bércecs and Kovács found $\langle n_2^{BB} \rangle = 0.364$ and $\langle n_3^{BB} \rangle = 1.09$. Thus one obtains

$$\Delta = 2.76[(g_{b_3}-g_{b_2})-(g_{b_2}-g_{b_1})], \quad (40)$$

$$g_{b_1} = (g_{b_2}-g_{b_1}) - 0.364\Delta. \quad (41)$$

Substituting Eq. (40) into Eq. (41), one again arrives at Eq. (37).

W_1 and P may be calculated from Eqs. (17) and (33), respectively, after having determined g_{b_1} and $(g_{b_2}-g_{b_1})$.

IV. APPLICATION TO SILVER-ANTIMONY AND SILVER-TIN ALLOYS

The enhancement of solute diffusion was measured by Schmidt^{7,13} and Nortrup¹⁴ in silver-antimony and silver-tin alloys, respectively. Schmidt also measured solvent diffusion. The diffusion coefficients for different temperatures are given in Table I. Data on solvent diffusion in AgSn alloys are published by Hehenkamp and Faupel⁸ over a large range of temperature and concentration. Recently these data were amended by Köhler, Neuhaus, and Herzig,¹⁵ who measured the enhancement of solvent diffusion in a concentration range of less than 1 at. % tin.

To avoid effects from a possible concentration dependence of the binding free enthalpies g_{b_i} , only points up to impurity concentrations of 5 at. % have been taken into account in the present investigation (see below).

In the case of solute diffusion, polynomials of second order were fitted to the experimental points. The diffusion coefficient in pure solvent was always taken from the fitted value for $N_B=0$. A commercial fitting program, which also yielded standard errors of the polynomial coefficients has been used.

From the enhancement factors a_1 and a_2 values of $(g_{b_3}-g_{b_2})$ have been calculated employing Eqs. (32) and (34). The results are given in Table II. One can see that $(g_{b_3}-g_{b_2})$ is not very sensitive to variations of a_1 and a_2 . Despite the large standard errors, especially in the case of a_1 , the corresponding errors in $(g_{b_3}-g_{b_2})$ are relatively small.

Within the error margins no significant temperature dependence could be observed in the temperature range covered by these experiments. We therefore calculated a weighted mean value of $(g_{b_3}-g_{b_2})$ for both systems:

$$g_{b_3}-g_{b_2} = (0.154 \pm 0.009) \text{ eV for AgSb,}$$

$$g_{b_3}-g_{b_2} = (0.155 \pm 0.014) \text{ eV for AgSn.}$$

In the case of AgSn two points with impurity concentrations as high as 5.7 at. % ($T=1106$ K) and 5.6 at. % ($T=978$ K) have been taken into account in this calculation. Omitting these points does not change the value of $(g_{b_3}-g_{b_2})$ given above within the error margins stated.

As we have already pointed out, second-order enhancement of solute diffusion corresponds to an enhancement of third order in the case of solvent diffusion. Polynomials of third order were fitted to the solvent diffusion data in AgSb alloys presented in Table I. Table III gives the enhancement factors b_1 , b_2 , and b_3 together with the values of G_{21} and G_{32} calculated from Eqs. (24) and (25). Due to the small number of data points, the values given for $T=926$ and 1048 K can only be regarded as rough estimates. Nevertheless they are in good agreement with those given for $T=952$ K and corresponding values calculated for AgSn.

Within present accuracy no deviations between G_{32} (Table III) and $g_{b_3}-g_{b_2}$ can be observed in the case of AgSb. Thus we obtain from Eq. (25)

$$\gamma = 0.$$

As mentioned above, this implies an almost linear dependence between D_{A^*N} and N_v^N in agreement with former observations.⁷ With $\gamma=0$ Eq. (24) yields

$$G_{21} = g_{b_2} - g_{b_1} = (0.18 \pm 0.08) \text{ eV for AgSb,}$$

where G_{21} has been taken from Table III.

In AgSn solvent diffusion is less enhanced than in AgSb alloys.⁸ Some of the diffusion coefficients given by Faupel⁸ have been measured at tin concentrations, which exceed the 5 at. % limit introduced below. Thus for a given temperature only few data points were available.

On the other hand the normalized diffusion coefficients are only slightly dependent on temperature. Therefore, within experimental accuracy, it was possible to combine the normalized data given for 1108 and 1145 K as well as those for 946 and 989 K in the concentration range $N_{Sn} < 0.045$.⁸ For this purpose values of the solvent diffusion coefficients for $N_{Sn}=0$ from a polynomial fit for each temperature have been taken in order to normalize the data.

The results are presented in Table III. The enhancement factors given for 946 and 989 K were taken from a third-order fit. The standard error in b_3 was too large to take this value into account. For 1108 and 1145 K the data result from a second-order fit, corresponding to a stronger dissociation of the complexes (see below). The values of G_{21} agree well with the one calculated from the diffusion coefficients given by Köhler, Neuhaus, and Herzig¹⁵ for 1046 and 1058 K, which is also listed in Table III.

Köhler *et al.* measured solvent diffusion in AgSn alloys below 1 at. % tin and obtained $b_1=20.2$ from a linear fit, neglecting, however, any contributions of higher-order impurity complexes. Taking these higher orders, which are

TABLE I. Measured diffusion coefficients as a function of temperature and concentration in AgSb and AgSn alloys taken from Refs. 7, 13, and 14.

Temperature (K)	Solute diffusion coefficient in AgSb D_{Sb}^{AgSn} (10^{10} cm ² /s)		D_{Sb}^{AgSn} 124	Solute diffusion coefficient in AgSn D_{Sn}^{AgSn} (10^{10} cm ² /s)		D_{Sn}^{AgSn} 113	Solvent diffusion coefficient in AgSb D_{Ag}^{AgSb} (10^{10} cm ² /s)		Temperature (K)
	N_{Sb}	N_{Sb}		N_{Sn}	N_{Sb}				
870	0	0.425	0.425	0	0	1.13	0	0	926
	0.0129	0.476	0.476	0.0100	0	1.17	0.00740	0.00740	0.165
	0.0203	0.523	0.523	0.0201	0.0100	1.27	0.0252	0.0252	0.231
	0.0320	0.745	0.745	0.0365	0.0201	1.58	0.0432	0.0432	0.573
	0.0416	0.913	0.913	0.0579	0.0365	2.37	0.0655	0.0655	1.33
	0.0488	1.032	1.032	0.0790	0.0579	3.40			3.32
	0.0677	1.627	1.627	0.102	0.0790	5.59			0.321
901	0	0.88	0.88	0	0	4.10	0.00700	0.00700	0.419
	0.0159	1.11	1.11	0.0168	0	4.44	0.0180	0.0180	0.774
	0.0244	1.22	1.22	0.0331	0.0168	5.30	0.0252	0.0252	0.950
	0.0326	1.42	1.42	0.0428	0.0331	6.35	0.0323	0.0323	1.42
	0.0417	1.68	1.68	0.0533	0.0428	7.10	0.0425	0.0425	2.18
	0.0497	1.94	1.94	0.0560	0.0533	7.52	0.0533	0.0533	3.24
	0.0712	3.17	3.17	0.0802	0.0560	10.94	0.0637	0.0637	5.32
939	0	2.19	2.19	0	0	18.60			2.83
	0.0146	2.56	2.56	0.00490	0	15.8	0	0	4.62
	0.0233	2.85	2.85	0.0152	0.00490	16.5	0.015	0.015	5.54
	0.0343	3.34	3.34	0.0318	0.0152	18.0	0.0232	0.0232	8.46
	0.0484	4.77	4.77	0.0626	0.0318	21.6	0.0318	0.0318	14.04
	0.0688	7.64	7.64	0.0725	0.0626	37.9	0.0413	0.0413	17.86
						44.9	0.0484	0.0484	
952	0	2.80	2.80	0	0	41.1			
	0.0070	2.97	2.97	0.00750	0	42.8			
	0.0180	3.45	3.45	0.0176	0.00750	48.6			
	0.0252	3.75	3.75	0.0267	0.0176	51.8			
	0.0323	4.42	4.42	0.0409	0.0267	61.6			
	0.0422	5.77	5.77	0.0498	0.0409	75.5			
	0.0533	7.22	7.22	0.0571	0.0498	81.0			
970	0	4.28	4.28	0	0				
	0.0143	4.99	4.99	0.00750	0				
	0.0233	6.04	6.04	0.0176	0.00750				
	0.0332	6.56	6.56	0.0267	0.0176				
	0.0416	8.28	8.28	0.0409	0.0267				
	0.0493	9.12	9.12	0.0498	0.0409				
	0.0686	14.40	14.40	0.0571	0.0498				
992	0	10.94	10.94	0	0				
	0.0070	16.92	16.92	0.00750	0				
	0.0180	18.60	18.60	0.0176	0.00750				
	0.0252	21.6	21.6	0.0267	0.0176				
	0.0323	37.9	37.9	0.0409	0.0267				
	0.0422	44.9	44.9	0.0498	0.0409				
	0.0533			0.0571	0.0498				
1048	0	1048	1048	0	0				
	0.0070	1048	1048	0.00750	0				
	0.0180	1048	1048	0.0176	0.00750				
	0.0252	1048	1048	0.0267	0.0176				
	0.0323	1048	1048	0.0409	0.0267				
	0.0422	1048	1048	0.0498	0.0409				
	0.0533	1048	1048	0.0571	0.0498				

TABLE II. Enhancement factors a_1 and a_2 of solute diffusion and calculated values of the difference in the binding free enthalpies of a second- and third-order complex ($g_{b_3}-g_{b_2}$) for AgSb and AgSn alloys at different temperatures.

System	T (K)	a_1	a_2	$g_{b_3}-g_{b_2}$ (eV)
AgSb	870	6±5	523±108	0.18±0.03
	901	9±2	299±33	0.15±0.01
	939	6±6	424±115	0.18±0.04
	952	4±3	400±96	0.19±0.04
	970	9±5	301±96	0.16±0.03
AgSn	922	0.5±3	286±83	0.18±0.04
	978	2±2	232±38	0.17±0.03
	1051	7±3	139±49	0.13±0.02
	1106	4±3	236±51	0.18±0.03

not negligible, into account by fitting a polynomial of second order to the normalized data the resulting b_1 and b_2 values correspond well to those computed from the data of Faupel,⁸ which cover a larger range of concentration and, hence, indicate good agreement.

Within the error margins the G_{21} presented in Table III should be regarded as independent of temperature in the small temperature range of the present measurements. Thus we calculated a weighted mean value of $G_{21}=(0.175\pm 0.032)$ eV for AgSn.

The quantities G_{21} and ($g_{b_3}-g_{b_2}$) computed for AgSb and AgSn are quite similar within the experimental errors. Therefore it seems justified to use the same value of $\gamma=0$ in the case of AgSn, as found for AgSb. This yields by means of Eq. (24),

$$g_{b_2}-g_{b_1}=(0.175\pm 0.032) \text{ eV for AgSn.}$$

Obviously in AgSn as well as in AgSb alloys the binding free enthalpy of a second impurity atom to a vacancy-impurity pair $-(g_{b_2}-g_{b_1})$ is somewhat larger than the binding free enthalpy of a third B atom to a second-order complex ($g_{b_3}-g_{b_2}$) apparently due to impurity-impurity

interactions.

From these quantities g_{b_i} , Δ , W_1 , and P can be calculated as described above, using Eqs. (40), (41), (38), (17), and (33). The results are summarized in Table IV. The values for g_{b_1} and W_1 presented in Table IV are in good agreement with earlier determinations.^{7,8}

The binding free enthalpy ($-g_{b_1}$) can also be compared with theoretical calculations of the binding enthalpy ($-h_{b_1}$). Values of h_{b_1} reported in the literature vary between 0.063 and 0.17 eV in the case of AgSn and 0.077 and 0.23 eV in the case of AgSb.¹⁶⁻¹⁸ In all these treatments the relaxation of the impurity atom into the vacancy was neglected, which certainly will somewhat enlarge the value of h_{b_1} . Furthermore h_{b_1} does not contain contributions of the binding excess entropy ($-S_{b_1}$). First experiments on the enhancement of solvent diffusion at lower temperatures, employing ion beam sputtering, indicate a considerable influence of S_{b_1} , which also leads to h_{b_1} values substantially smaller than g_{b_1} .¹⁹ This will be discussed in detail in a forthcoming paper.

Recently Rockosch and Herzig²⁰ determined the binding free enthalpy ($-g_{b_1}$) in the framework of the five-frequency model using the assumption of a constant jump-frequency sum given in Eq. (4). They obtained $g_{b_1}=0.11$ eV in the case of AgSn.

From the data available we are able to estimate the ratio $(4w_1+7w_3+w_2)/(12w_0)$. In a nearest-neighbor approximation and neglecting changes in the correlation factor of the solvent atoms upon alloying (see below), one obtains

$$\frac{\langle w_{\text{eff}}^A \rangle_1}{f_0 w_0} \simeq \frac{4w_1+7w_3}{11w_0}. \quad (42)$$

According to Howard and Manning³ the jump-frequency ratio w_2/w_0 can be expressed as

$$\frac{w_2}{w_0} = \frac{D_{B^*}^A(0)}{D_{A^*}^A(0)} \frac{f_0}{f_2} \exp \left[-\frac{g_{b_1}}{kT} \right]. \quad (43)$$

TABLE III. Enhancement factors b_1 , b_2 , and b_3 of solvent diffusion and calculated values of G_{21} and G_{32} , as defined by Eqs. (24) and (25) for AgSb and AgSn alloys at different temperatures.

System	T (K)	b_1	b_2	b_3	G_{21} (eV)	G_{32} (eV)
AgSb	926	42	1426	32 200	0.16	0.17
	952	34±21	1579±1039	18 222±12 793	0.18±0.08	0.14±0.07
	1048	9	1103	19 737	0.23	0.19
AgSn	946	25±7	827±461		0.15±0.05	
	989					
	1046	13±5	861±540		0.20±0.07	
	1058					
	1108	9±7	544±152		0.19±0.05	
1145						

TABLE IV. Binding free enthalpies ($-g_{b_i}$), impurity-impurity interaction energy ($-\Delta$), normalized average effective jump frequency per A atom W_1 and parameter P , as defined by Eq. (31).

		System			Temperature range
	P	W_1 ($\alpha=0$)	Δ (eV)	g_{b_i} (eV)	
AgSb	$2.5^{+2.1}_{-1.1}$	$0.35^{+0.29}_{-0.17}$	-0.06	$g_{b_1}=0.20\pm 0.05$	870 K $\leq T \leq$ 1048 K
	($T=950$ K)	($T=950$ K)		$g_{b_2}=0.38$	
AgSn	$2.5^{+1.2}_{-0.8}$	$0.25^{+0.16}_{-0.10}$	-0.06	$g_{b_1}=0.20\pm 0.04$	922 K $\leq T \leq$ 1145 K
	($T=1050$ K)	($T=1050$ K)		$g_{b_2}=0.37$	

Combining Eqs. (17), (42), and (43) yields

$$g_{b_1} = kT \ln \left[\frac{1}{12} \frac{b_1 + 11 + [D_{B^*}^A(0)/D_{A^*}^A(0)]f_0/f_2}{(4w_1 + 7w_3 + w_2)/(12w_0)} \right]. \quad (44)$$

Taking $f_2=0.46$ from measurements of the isotope effect²⁰ and $D_{B^*}^A(0)/D_{A^*}^A(0)=5.8$ for $T=1043$ K (Refs. 21 and 22) g_{b_1} has been calculated as a function of the ratio $(4w_1 + 7w_3 + w_2)/(12w_0)$ with b_1 as a parameter. The re-

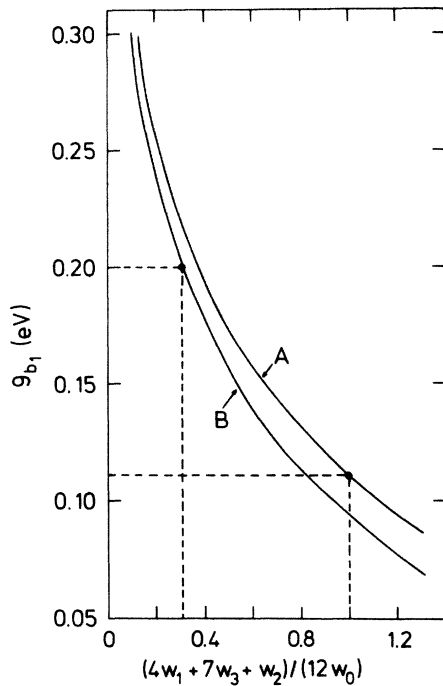


FIG. 2. The binding free enthalpy ($-g_{b_1}$) as function of the jump-frequency ratio $(4w_1 + 7w_3 + w_2)/(12w_0)$ with w_i defined as usual in the five-frequency model for 1043 K. Curve A was calculated for a linear enhancement factor $b_1=20.2$ taken from Köhler, Neuhaus, and Herzog (Ref. 15) and curve B for $b_1=13$ taken from Table III.

sults are shown in Fig. 2 for $b_1=20.2$, as computed by Köhler, Neuhaus, and Herzog from a linear fit,¹⁵ and $b_1=13$, taken from Table III for a second-order fit. It becomes obvious that g_{b_1} is very sensitive to variations of the ratio $(4w_1 + 7w_3 + w_2)/(12w_0)$, whereas changes in b_1 have only a much smaller influence.

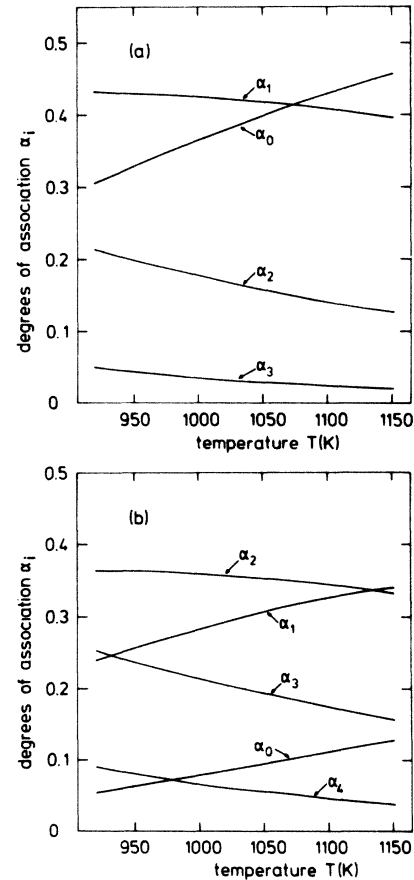


FIG. 3. Degrees of association α_i for an Ag at 1 at. % Sn alloy (a) and an Ag at 3 at. % Sn alloy (b) as a function of temperature.

By means of Eqs. (42) and (43), taking $\langle w_{\text{eff}}^A \rangle_1 / (f_0 w_0) \equiv W_1$ and g_{b_1} from Table III, we found

$$(4w_1 + 7w_3 + w_2) / (12w_0) \approx 0.3_{-0.1}^{+0.2}.$$

Obviously the mean jump frequency of a vacancy at a first nearest-neighbor site of an impurity is much more influenced by a decrease in the average exchange frequency with the eleven A atoms than by the increase in the exchange frequency with the impurity. Thus calculations based on Eq. (4) underestimate the value of g_{b_1} substantially.

From Eqs. (5) and (38) we have computed the complex population, introducing the degrees of association α_i of the different complexes

$$\alpha_i \equiv N_{v_i} / N_v. \quad (45)$$

As shown in Fig. 3(a), even at tin concentrations as low as 1 at. % second-order complexes have to be taken into account in AgSn. Figure 3(b) gives degrees of association for an alloy containing 3 at. % tin. There is considerable contribution of complexes with three B atoms, corresponding to a third-order enhancement of solvent diffusion.

V. THE RANGE OF VALIDITY OF THE COMPLEX MODEL

Whereas the five-frequency model, which is based on the Lomer approximation, is restricted to very diluted alloys with impurity concentrations of sometimes much less than 0.5 at. %, ⁷ the range of validity of the complex model of Dorn and Mitchell and its application to solvent and solute diffusion, as discussed in this paper, is much more extended. Nevertheless, at large impurity concentrations, changes in the binding free enthalpies ($-g_{b_i}$) upon alloying have to be considered.

According to Friedel,²³ interactions of point defects in alloys with B atoms of positive excess charge are independent of concentration as long as the Fermi energy remains unaltered upon alloying. Friedel introduced a critical molar fraction of impurities N_B^c . For $N_B < N_B^c$, to a good approximation, the Fermi energy does not depend strongly on N_B . For $N_B > N_B^c$ the Fermi energy increases almost as the square of the impurity concentration upon alloying, due to an increasing overlap of the screening clouds surrounding the impurities. The model of Friedel was corroborated by measurements of the nuclear Knight shift of many solute atoms of positive excess charge in fcc metals.

In the case of noble metals no change, within experimental error, was found in the Knight shift as a function of alloy concentration up to 5% solute.²⁴ Thus an almost constant Fermi energy is indicated up to $N_B^c \approx 0.05$, corresponding to constant values of the binding free enthalpies ($-g_{b_i}$).

Hehenkamp and Schlett²⁵ also took into account more than just electronic effects, leading to a concentration dependence of the interaction energy between point de-

fects, such as misfit and changes in the Debye frequencies upon alloying. In noble metal alloys, these authors found the electronic effects to be dominant.

Due to the very small molar fraction of vacancies in the whole range of temperature and concentration the overlap of the vacancy-impurity complexes can be neglected. One may also consider changes of the average effective jump frequencies upon alloying, due to changes of the jump frequencies themselves and of the correlation factors.

As far as the jump frequencies are concerned, they should be almost constant, to a good approximation, at impurity concentrations as low as $N_B < 0.05$.

The correlation factors of solvent and solute diffusion were studied by Manning,²⁶ employing a random alloy model. Schlett¹¹ pointed out that this model also applies for nonrandom alloys with vacancy-impurity attraction, even at concentrations of several at. % solute and, at least qualitatively, at lower concentrations.

According to Manning, almost no changes in the correlation factor of the solvent atoms are to be expected upon alloying for $N_B < 0.05$, in agreement with measurements of the isotope effect of solvent diffusion in CuZn alloys.²⁷

As for the correlation factor of the solute atoms, a slight increase upon alloying is expected. Measurements of the solute isotope effect in CuZn (Ref. 27) and CuGe (Ref. 11) show that the deviations from the value at infinite dilution—10% in the case of CuZn and 20% in the case of CuGe—are much smaller than the experimental errors in the average effective jump frequencies (Table IV).

Moreover the increase in the solute correlation factor is partly due to a change in the complex population upon alloying towards higher-order complexes, in which the mean solute correlation factor should be somewhat larger.

Thus the average effective jump frequencies of solvent as well as solute diffusion, to a good approximation, can be regarded as independent of concentration for $N_B < 0.05$.

For $N_B > 0.05$ the complex model should only be valid in a more and more qualitative sense mainly due to changes in the binding free enthalpies upon alloying.

Finally, employing Eq. (39) one is able to calculate the temperature range in which, according to Dorn and Mitchell, impurity atoms can be regarded as randomly distributed around a vacancy now.

Taking Δ from Table IV, one obtains $T > 725$ K for both systems AgSn and AgSb. It will be the purpose of a forthcoming paper to discuss the enhancement of solvent and solute diffusion at lower temperatures ($|\Delta/kT| > 1$).

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