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Investigation of the equilibrium concentration of lattice vacancies in silver and dilute silver–tin alloys with a differential dilatometer

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Abstract. The difference between relative changes in macroscopic length $\Delta L/L$ and x-ray lattice parameter $\Delta a/a$ has been measured over a wide temperature range from room temperature to 25 K below the respective melting point in pure silver and in some dilute silver–tin alloys between 0.25 and 8.60 at. % Sn. At higher temperatures, $\Delta L/L - \Delta a/a$ increases, showing an Arrhenius behaviour due to vacancy formation. The absolute vacancy concentration at the melting point increases continuously from 5.2×10^{-4} for pure silver to 2.5×10^{-3} for a Ag–8.6 at. % Sn alloy. The vacancy formation enthalpy decreases from 1.05 to 0.74 eV simultaneously. The binding enthalpy and entropy for the first vacancy–impurity complex were found to be $h_{B1} = 0.15 \pm 0.02$ eV and $s_{B1} = -(0.5 \pm 0.2)k_B$. The impurity–impurity interaction is repulsive and of the order of $\frac{1}{15}$ eV, similar to other noble metal alloys with positive excess charge. The binding Gibbs free energy of the first complex was determined as $g_{B1} = 0.20 \pm 0.02$ eV in good agreement with earlier measurements of resistivity and silver self-diffusion enhancement in silver–tin alloys but without some of their constraints since the vacancy concentration has been determined directly. All results can be interpreted within the framework of the model of Bérces and Kovács.

1. Introduction

Transport phenomena in solids mostly require the presence of vacancies. Therefore it is of great interest to determine the concentration of vacancies in solids. There are many indirect techniques for the detection of vacancies such as measurements of electrical resistivity (Meehan and Eggleston 1954, Hehenkamp and Sander 1979), specific heat (Brooks 1968, Kramer and Nölting 1972), self-diffusion enhancement (Hehenkamp, Schmidt and Schlett 1980, Hehenkamp 1982, Faupel and Hehenkamp 1984, Faupel 1985) or positron annihilation (Triftshäuser and McGervey 1975). Most of these techniques require a baseline construction, i.e. an extrapolation of the behaviour of the crystal at low temperatures to a vacancy-free crystal at high temperatures, that does not exist, and an assumption on the relationship of vacancy concentration and the measured quantity. The only known direct and absolute technique which does not need such an assumption or a baseline construction is the differential dilatometric measurement (Wagner and Bayer 1936, Gott 1942, Feder and Nowick 1958, 1967, Simmons and Balluffi 1960a, b, 1962, 1963). The difference in the change of microscopic and macroscopic density directly yields the concentration of extra lattice sites and takes the relaxation of the

lattice around the vacancy properly into account. In cubic crystals this can be written as (Flynn 1982)

$$c_v = 3(\Delta L/L_0 - \Delta a/a_0) \quad (1)$$

where L is the sample length and a the lattice parameter, the superscript 0 indicating measured values at a low reference temperature where the vacancy concentration can be neglected. The number of interstitials in thermal equilibrium, which would cause a decrease in the number of lattice sites is negligible compared with vacancy concentrations in noble metals and their alloys as their formation enthalpy is about 3 eV (Bauer *et al* 1982).

One difficulty associated with a differential dilatometric experiment is the extreme accuracy required for the measurement of sample length and x-ray lattice parameter. In many crystals the atomic fraction of vacancies is in the range 10^{-4} – 10^{-3} near the melting point. The precision that can be obtained in the measurement of $\Delta a/a$ by means of x-ray diffraction is at present about 10^{-5} and $(2-7) \times 10^{-6}$ for $\Delta L/L$ so that c_v can only be determined with reasonable accuracy at temperatures fairly close to the melting point. Furthermore the temperature difference between the two measurements must be kept to less than 0.2 K. This makes a simultaneous procedure in length and x-ray measurement necessary and hence increases the experimental effort.

The formation of vacancies requires enthalpy but produces entropy, so that the vacancy concentration in thermal equilibrium becomes

$$c_v = \exp(S_v/k_B - H_v/k_B T) \quad (2)$$

where S_v and H_v are the vacancy formation entropy and enthalpy, respectively.

For alloys, Dorn and Mitchell (1966) calculated the concentrations of vacancies that are surrounded by i B atoms and $z - i$ A atoms under the following assumptions.

(i) Only interaction between nearest neighbours has to be taken into consideration. This is not a severe restriction because the impurity shielding potentials are of very short range (Lazarus 1954, Alfred and March 1956, 1957).

(ii) There is no overlap of complexes. This holds because even near the melting point the vacancy concentration is very low so that vacancy–vacancy neighbourhoods are very unlikely.

(iii) A statistical distribution of B atoms at nearest-neighbour sites is only valid for not too low temperatures and for small impurity–impurity interaction as has been shown by Gollisch (1979) for Cu–Ge.

(iv) The Gibbs free energy g_i of formation is independent of impurity–concentration. Knight shift measurements (Lawrence and Mebs 1968) showed that this assumption should be true up to a critical atomic fraction of impurities of approximately 5%.

This leads to the following expression for c_{vi} , the number of vacancies surrounded by $z - i$ A atoms and i B atoms

$$c_{vi}(N_B, T) = \binom{z}{i} N_A^{z-i} N_B^i \exp\left(\frac{g_i}{k_B T}\right) \quad (3)$$

where N_A and N_B are the atomic fractions of A or B atoms, respectively. Summation of

all complexes and division by the vacancy concentration c_V in the pure metal ($N_B = 0$; T) yields ($g_{Bi} = g_0 - g_i$)

$$c_V^N = \sum_{i=0}^z \binom{z}{i} N_A^{z-i} N_B^i \exp\left(\frac{g_{Bi}}{k_B T}\right). \quad (4)$$

Bérces and Kovács (1983) eliminated the assumption that the impurity atoms are statistically distributed around the vacancy. Introducing an impurity-impurity interaction energy Δ they found

$$c_V^N = \sum_{i=0}^z \binom{z}{i} N_A^{z-i} N_B^i \exp\left(\frac{i(h_{B1} - Ts_{B1}) + \langle n_i^{BB} \rangle \Delta}{k_B T}\right). \quad (5)$$

Here $\langle n_i^{BB} \rangle$ is the average number of B-B nearest neighbourhoods and has been calculated by these authors for face-cubic-centred metals. Equation (5) reduces the number of adjustable parameters to three and allows the determination of h_{B1} , s_{B1} and Δ if the vacancy concentrations in the pure metal and the alloys are known. Whereas the earlier fits were performed at constant temperature as a function of concentration and had to be based on just as many points as different alloys were measured, the much higher numbers of the present investigation permit one to fit the results to data of one single concentration as a function of temperature. This offers the possibility of checking the consistency of the model and the range of applicability for the first time.

2. Experimental procedure

A differential dilatometer developed in our group in Göttingen has been used with only minor changes. For a more detailed description of the apparatus and a discussion of possible error sources of a differential dilatometer see Lüdecke (1981), Kluin (1989, 1991) or Hehenkamp *et al* (1992).

2.1. Specimen and furnace

The samples were prepared from 99.999% silver (Demetron, Hanau, Germany) and 99.999% tin (Koch Laboratories, Colnbrook, UK). They were melted several times in a medium-frequency furnace in a pure graphite mould. Then the specimens were annealed in an evacuated quartz capsule for 1000 h at $\frac{3}{4}T_m$, where T_m is the melting temperature. Electron microprobe analysis showed that all specimens were homogeneous after annealing. Then the final sample shape shown in figure 1 was obtained using spark erosion and lathe. The specimens were 20 mm long and 18 mm in diameter. The x-ray powder specimen was filed from the material removed with the lathe, so that it had exactly the same concentration as the massive sample. The x-ray powder specimen was placed exactly in the middle of the sample using a special press and then sintered for 1 d. To reduce the stress in the specimen produced by machining and pressing it was afterwards annealed again in the apparatus for approximately 48 h at 100 K below the melting point.

The furnace had three zones and was 20 cm long. The homogeneous part was more than 5 cm long. The specimen placed on a specimen holder was located exactly in the middle of the homogeneous zone. To avoid temperature gradients in the sample, the specimen holder was heated additionally. For measurement of the gradient in the

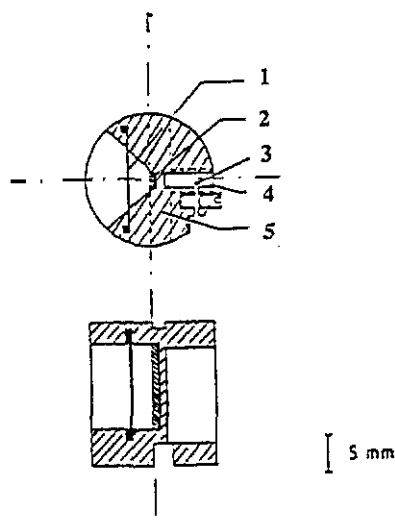


Figure 1. Specimen: 1, pyrolytic graphite window; 2, x-ray powder sample; 3, hole for molybdenum wire; 4, relief for specimen thermocouple; 5, T-shaped groove.

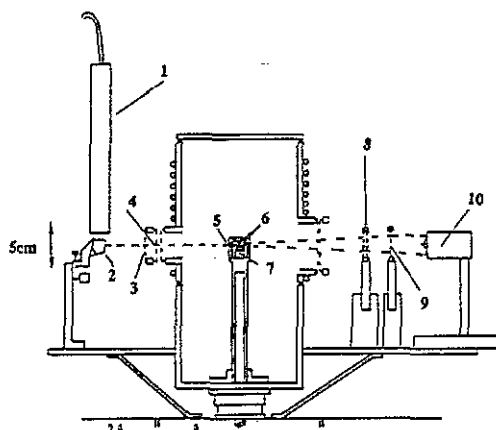


Figure 2. Vacuum chamber and optical path of laser slit dilatometer (The furnace is not drawn for reasons of simplicity): 1, laser; 2, pentagonal prism; 3, aperture; 4, quartz window; 5, graphite cage; 6, slit edges; 7, specimen; 8, interference filter (633 nm); 9, grey filter; 10, CCD sensor.

sample, two molybdenum wires were contacted with the specimen in a distance of 10 mm. The voltage of the differential thermocouple Mo–AgSn–Mo was kept always to smaller than $1 \mu\text{V}$, which corresponds to a temperature gradient of $0.05\text{--}0.15 \text{ K cm}^{-1}$ depending on the temperature and tin concentration.

The specimen, specimen holder and furnace were mounted in a vacuum chamber, equipped with a beryllium window for the x-ray spectrometer and two optically flat quartz windows for the laser interferometer. The chamber was evacuated to a pressure of 10^{-4} Pa before the measurement. A helium atmosphere at approximately 5×10^4 Pa during the measurement was found to be a good compromise between x-ray absorption and thermal coupling of sample and furnace.

2.2. Lattice expansion measurements

The lattice expansion was measured with a standard x-ray spectrometer. Ni $K\alpha$ radiation was used for the silver measurements instead of Cu $K\alpha$, that was used for investigations in the Cu–Ge system (Kluin 1989, 1991, Hehenkamp *et al* 1992), because larger diffraction angles lead to a higher precision in the lattice parameter determination. The sample preparation guaranteed the powder for the x-ray diffraction measurements to be placed exactly in the axis of the goniometer (MZIII, Seifert, Ahrensburg). The diffractometer was calibrated with a standard polycrystalline silicon sample supplied by Seifert, Ahrensburg. For each temperature the (311) and (420) reflections were analysed separately. Only measurements where the lattice parameter determined from the two reflections showed a difference of maximally 10^{-4} \AA were taken into consideration.

In order to prevent selective evaporation of alloy constituents from the powder part of the specimen a window of pyrolytic graphite was inserted in front of it, which permitted

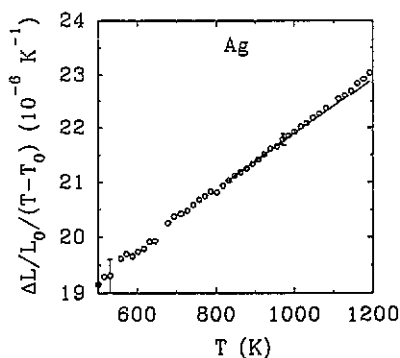


Figure 3. Length change in pure silver: —, fit through the corresponding lattice parameter change.

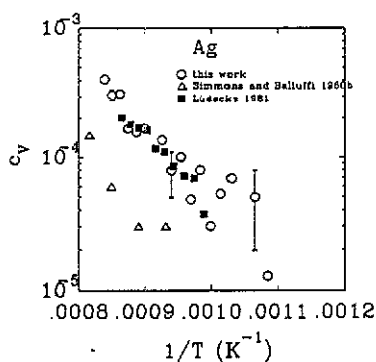


Figure 4. Arrhenius plot of the vacancy concentration in pure silver.

establishing equilibrium vapour pressure in front of the specimen. This precaution was of vital importance for the measurements since, under Bragg reflection conditions, only the very surface of the specimen is being sampled by the x-rays.

2.3. Length change measurements

The length change measurements were carried out using a laser slit interferometer. The optical path is shown in figure 2. The slit was formed by two edges prepared from amorphous graphite using spark erosion. The black colour prevented supplementary disturbing laser reflections. One of the edges was carried by the specimen, and the other by a graphite cage that was also placed on the specimen holder. The slit width measured with the dilatometer had to be corrected for the expansion of the graphite cage and the slit edges. For this purpose the interferometer was calibrated using a molybdenum sample identical with the actual specimen. In this high-melting material no equilibrium vacancies have been detected using positron annihilation below 2000 K (Maier *et al* 1979) so that differential dilatometric measurements in molybdenum should show no difference between $\Delta L/L$ and $\Delta a/a$. Occurring differences therefore must be due to the expansion of the graphite cage and the slit edges.

3. Experimental results and discussion

3.1. Vacancies in silver

Figure 3 shows the length change in the silver sample divided by the temperature difference. This representation is chosen because it is more sensitive to deviations from a linear behaviour. The full line is the corresponding fit through the lattice parameter data. Error bars represent an error of 2×10^{-5} in $\Delta L/L$; at higher temperatures they have the same size as the symbols on the graph. The difference between the two curves is the contribution of vacancies to the thermal expansion. In figure 4 the vacancy concentration derived from figure 3 is plotted semilogarithmically against $1/T$ together with the data of earlier direct measurements on pure silver carried out by Simmons and Balluffi (1960b) and Lüdecke (1981). The dilatometer used by Lüdecke was a first

Table 1. Vacancy formation data for pure silver obtained with different techniques: —, not known; *, estimated value.

Technique	H_V (eV)	$S_V(k_B)$	$c_V(T_M)(10^{-4})$	Reference
Absolute	1.05 ± 0.04	2.3 ± 0.8	5.2 ± 0.7	This work
Absolute	1.09 ± 0.1	$1.5 \pm 0.5^*$	1.7 ± 0.5	Simmons and Balluffi (1960b)
Absolute	1.04 ± 0.05	2.0 ± 0.7	4.2 ± 1.4	Lüdecke (1981)
Absolute	1.04 ± 0.05	2.1 ± 0.9	4.9 ± 0.8	Wolff (1990)
Absolute	1.07 ± 0.05	2.5 ± 0.8	5.2 ± 0.8	Wolff (1991)
Resistivity	1.06 ± 0.05	—	7 ± 2	Ascoli <i>et al</i> (1966)
Resistivity	1.10 ± 0.04	—	—	Doyama and Köhler (1962)
Thermopower	1.0 ± 0.03	—	—	Gertsriken and Novikov (1960)
Positron annihilation	1.13 ± 0.05	—	—	Schmüß (1985)
Positron annihilation	1.13 ± 0.03	—	—	Lühr-Tanck <i>et al</i> (1985)
Positron annihilation	1.13	—	—	Fukushima (1979)
Positron annihilation	1.16 ± 0.03	—	—	Triftshäuser and McGervey (1975)
Theoretical	0.92	—	—	Seeger and Bross (1956)
Theoretical	1.09	—	—	Schweitz and Vingsbo (1977)

version of the apparatus used in this work but with an inductive device to measure the length change instead of the optical employed here, which is much superior in performance. A linear fit through the data leads to the following values for the vacancy formation enthalpy and entropy:

$$H_V = 1.05 \pm 0.04 \text{ eV} \quad S_V = (2.3 \pm 0.8)k_B.$$

The vacancy concentration at the melting point is

$$c_V(T_M) = (5.2 \pm 0.7) \times 10^{-4}.$$

In table 1 these data are listed together with results from all known dilatometric measurements of vacancy concentrations in silver and values for the vacancy formation enthalpy obtained with other techniques. Our results are in good agreement with those of Lüdecke (1981) and recent measurements of Wolff (1990, 1991). The larger error margins and the difference in the vacancy concentration at the melting point in Lüdecke's (1981) measurement may be due to the smaller number of data points in the interesting temperature range. Moreover, the maximum temperature has been approximately 50 K lower than in this work so that extrapolation was necessary over an extended temperature range.

The value of Simmons and Balluffi (1960b) for the vacancy concentration at the melting point seems to be much too low compared with the other measurements. They calculated the vacancy concentration at the melting point by extrapolating their curves for the length and lattice parameter change up to the melting point because they have considered the error margin of a single data point as being too large to make a linear fit through the Arrhenius plot at a reasonable level of accuracy. Furthermore they have used an estimated value of $(1.5 \pm 0.5)k_B$ for the vacancy formation entropy as an input parameter to calculate the vacancy formation enthalpy since they were not able to determine it directly from the measurements. The present result that the value for $c_V(T_M)$ given by Simmons and Balluffi (1960b) is too low has been supported by measurements of

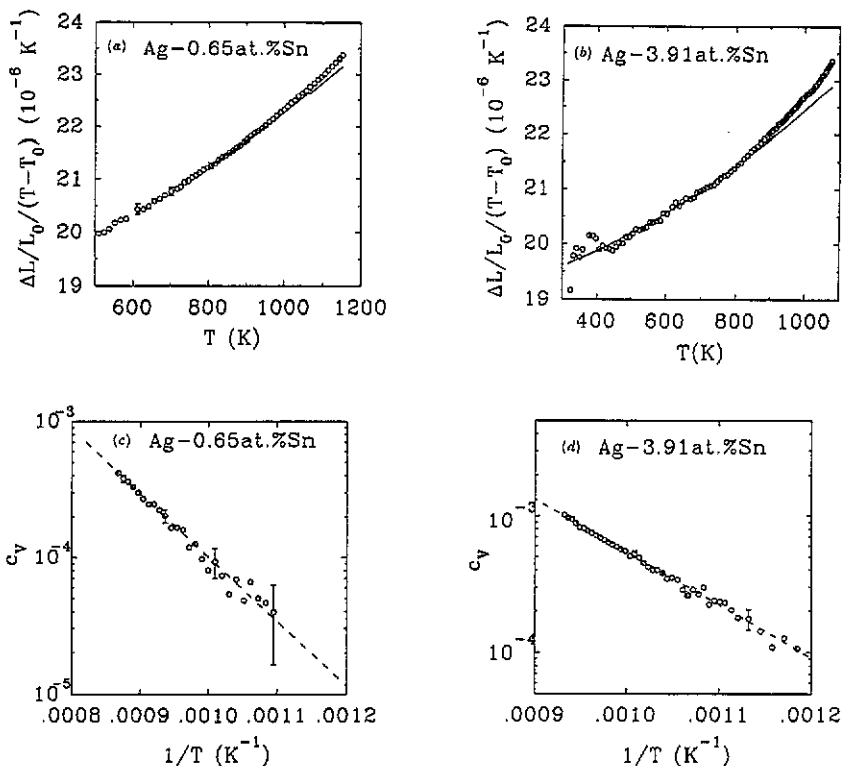


Figure 5. (a), (b): length change in (a) Ag-0.65 at.% Sn and (b) Ag-3.91 at.% Sn in the same form as in figure 3 for pure silver: —, fits through lattice expansion data. (c) and (d): Arrhenius plots belonging to (a) and (b): ---, linear fit through the data.

Ascoli *et al* (1966), who have estimated a value of $(7 \pm 2) \times 10^{-4}$ from the extrapolated extra resistivity at the melting point.

3.2. Vacancies in silver-tin alloys

Vacancy formation was studied in five specimens with tin concentrations of 0.25, 0.65, 2.07, 3.91 and 8.60 at.%. Figures 5(a) and 5(b) show typical examples of the specimen length change in Ag-0.65 at.% Sn and Ag-3.91 at.% Sn, respectively, in the same representation as in figure 3 for pure silver. The full curves represents a fit through the lattice expansion data. The corresponding Arrhenius plots are shown in figures 5(c) and 5(d). As in other noble metal alloys with impurities of positive excess charge, alloying obviously enhances the vacancy formation due to the attractive vacancy-impurity interaction.

The plot of all measured vacancy concentrations on a linear scale (figure 6) indicates a distinct decrease in the temperature where vacancies can be detected and an increase in the number of vacancies at the same temperature with increasing tin concentration. Alloying also leads to higher vacancy concentrations at the melting point, although the melting point as measured by the solidus temperature drops approximately 21 K (at.% Sn)⁻¹. This contradicts Górecki's (1983) assumption that the vacancy concentration is

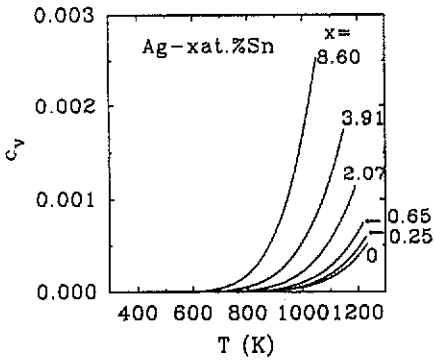


Figure 6. Linear plot of vacancy concentrations as a function of temperature for various silver-tin alloys.

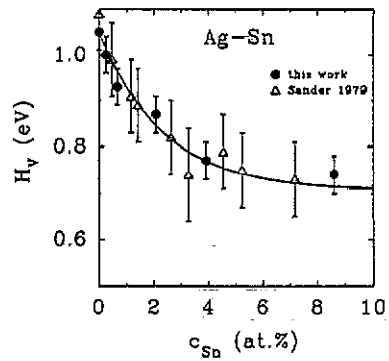


Figure 7. Vacancy formation enthalpies in silver-tin alloys as a function of tin concentration.

Table 2. Vacancy formation and complex binding data in Ag-Sn alloy.

c_{Sn} (at.%)	H_V^{eff} (eV)	S_V^{eff} (k_B)	$c_V(T_M)$ (10^{-4})	h_{B1} (eV)	s_{B1} (k_B)	Δ (eV)
0.00	1.05	2.3	5.2	—	—	—
0.25	1.00	2.0	5.9	0.16	-0.56	—
0.65	0.93	1.6	7.4	0.16	-0.51	-0.10
2.07	0.87	1.7	11	0.15	-0.51	-0.11
3.91	0.77	1.4	17	0.15	-0.49	-0.10
8.60	0.74	2.2	25	—	—	—

constant along the solidus line. The vacancy formation enthalpies computed from the measured data agree very well with those calculated by Sander (1979) and Hehenkamp and Sander (1979) from resistivity studies as figure 7 shows. In view of the assumptions involved in the resistivity measurements this agreement is remarkable. A summary of the vacancy formation values is given in the second third and fourth columns of table 2.

3.3. Vacancy-impurity interaction

The vacancy concentration relative to the pure metal was calculated for each specimen. For reasons of self-consistency the values of H_V and S_V from this work were used as a reference. The results are depicted in figure 8. The lines represent a weighted least-squares fit of equation (5) to the data for a set of h_{B1} , s_{B1} and Δ for each sample. For the Ag-0.25 at.% Sn specimen, only h_{B1} and s_{B1} could be fitted because in such a dilute alloy an impurity-impurity nearest neighbourhood is very unlikely. For the specimen with 8.60 at.% Sn the fit did not lead to reasonable results. This is to be expected as it is well known (Faupel 1985, Faupel and Hehenkamp 1986) that the assumptions for the complex model in silver-tin and other alloys with electropositive solutes should be valid up to an atomic fraction of impurities of approximately 5 at.% only. The results of the fits for

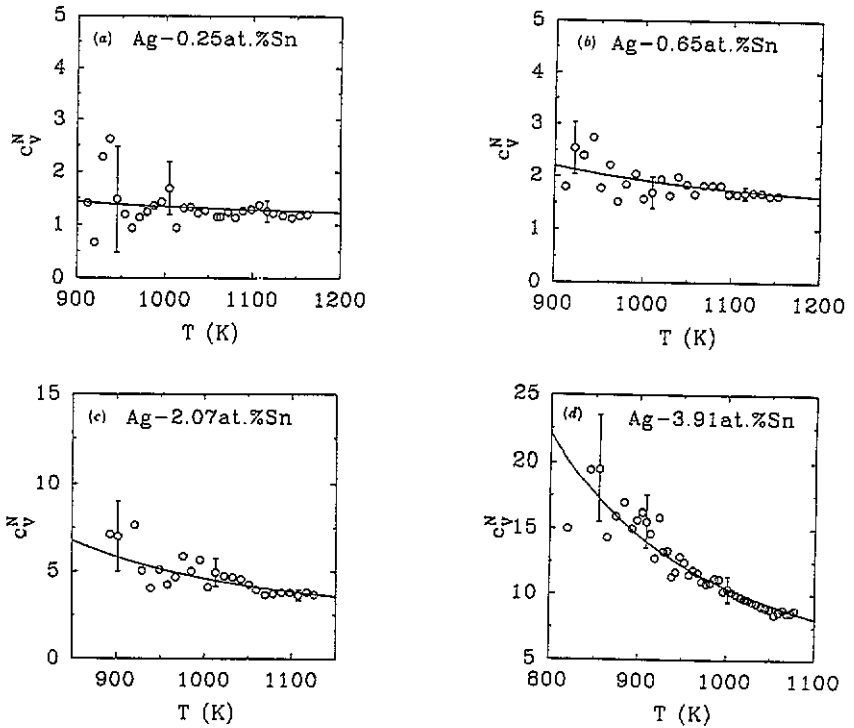


Figure 8. Vacancy concentrations relative to pure silver for four silver-tin alloys as a function of temperature: —, weighted least-squares fit to the data of equation (5).

every single specimen are listed in the fifth, sixth and seventh columns of table 2. Fitting one set of h_{B1} , s_{B1} and Δ to all data yields

$$h_{B1} = 0.15 \pm 0.02 \text{ eV} \quad s_{B1} = (-0.5 \pm 0.2)k_B \quad \Delta = -0.1 \pm 0.03 \text{ eV}.$$

This results in a value of the binding Gibbs free energy of the first complex at 1000 K of

$$g_{B1}(1000 \text{ K}) = 0.20 \pm 0.02 \text{ eV}.$$

Since all samples give almost the same results with rather small differences except 8.60 at.% Sn, this proves the validity and applicability of the model used.

In the literature, several values of g_{B1} in silver-tin alloys from resistivity or diffusion measurements are reported. Köstler *et al* (1987) have fitted a set of h_{B1} , s_{B1} and Δ to the values of the vacancy formation enthalpy obtained by Sander (1979) shown in figure 7 obtaining

$$g_{B1}(1000 \text{ K}) = 0.24 \pm 0.05 \text{ eV}.$$

Faupel and Hehenkamp (1986, 1987) have calculated vacancy-impurity and impurity-impurity interaction Gibbs free energy from self-diffusion measurements of silver in silver-tin alloys without the earlier assumption of a linear relation between normalized vacancy concentration and diffusivity. They obtained a value of

$$g_{B1}(1000 \text{ K}) = 0.20 \pm 0.05 \text{ eV}.$$

Both values are in good agreement with the results of this work. The particular values

Table 3. Vacancy binding data in silver-tin alloy.

h_{B1} (eV)	$s_{B1}(k_B)$	Δ (eV)	g_{B1} (1000 K) (eV)	Reference
Experimental				
0.15 ± 0.02	-0.5 ± 0.2	-0.10 ± 0.03	0.20 ± 0.02	This work
$0.11 \pm_{0.03}^{0.05}$	-1.5	-0.03	0.24 ± 0.05	Köstler <i>et al</i> (1987)
0.10 ± 0.03	-1.1 ± 0.4	-0.06	0.20 ± 0.05	Faupel and Hehenkamp (1986)
			0.110 ± 0.005	Köhler <i>et al</i> (1985)
			0.13	Hagenschulte and Heumann (1989)
Theoretical				
0.09				Blandin and Deplante (1962)
0.08				Gupta (1980)
0.17				Flynn (1962)
0.06				LeClaire (1962)

for h_{B1} , s_{B1} and Δ show some deviations, however. With respect to the results of Köstler *et al* (1987) this may be because these workers have based their evaluation on the concentration dependence of the effective vacancy formation enthalpy whereas in this work the fits were carried out as a function of temperature at a constant concentration so that concentration dependences of the Fermi surface or the screening potentials could have no effect on the results. On the other hand, the present results clearly show (table 2) that these concentration dependences are negligible in the range below 4 at. % Sn. Therefore, the aforementioned deviations in h_{B1} , s_{B1} and Δ appear to be due to slight differences between the absolute and resistivity data. As for the diffusivity measurements it seems that h_{B1} is underestimated and at the same time s_{B1} is overestimated. However, these quantities were estimated from an extrapolation over a temperature range of about 600 K. The quantity that was measured, the binding Gibbs free energy g_{B1} , is in good agreement with the present work.

Köhler *et al* (1985) and Rockosch and Herzig (1984) have evaluated

$$g_{B1}(1040 \text{ K}) = 0.110 \pm 0.005 \text{ eV}$$

from measurements of impurity diffusion. They obtained this value assuming that the sum of the jump-frequencies for the vacancy in pure metal and a dilute alloy are identical. This assumption was questioned by Faupel and Hehenkamp (1986).

Another investigation has been published by Hagenschulte and Heumann (1989), using the experimental data of Köhler *et al* (1985) and Hehenkamp and Faupel (1983). They have assumed that the relationship between normalized diffusivity and impurity concentration can be described to a good approximation by an exponential function. This procedure reduces the number of fitted parameters drastically to only one but implies a fixed relationship between the coefficients in a polynomial series expansion. This fixed relation is rather unlikely to hold generally. The physical model which has been proved to hold in this work to a high degree of precision describes the variation in the vacancy concentration as a function of impurity content of the alloy of course as a power series, the coefficients of which, however, depend on the configurational entropy and the Gibbs free energy of binding in the different complexes, which vary as well as the impurity-impurity interaction energy for different matrices and impurity atoms. This prevents a simple relationship of general nature between them as has been shown

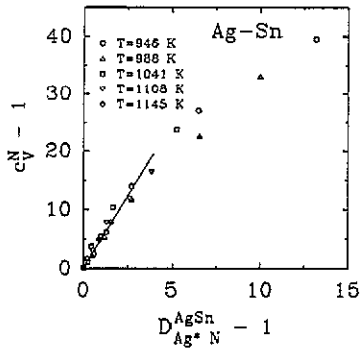


Figure 9. Normalized vacancy concentration against normalized self-diffusion coefficient in silver-tin alloys. The diffusion data are taken from Faupel and Hehenkamp (1986).

in some detail by Hentrich *et al* (1991) clearly. In the literature (Adda and Philibert 1966), usually two approximations for $c_v(x_B)$ are being used: a linear approximation or an exponential approximation. Whereas the linear approximation may be based on theoretical considerations at extremely low concentrations, the exponential has to be viewed as purely empirical with the consequences stated. While Faupel and Hehenkamp (1986) derived a value of 0.20 eV for g_{B1} from their own data these workers obtained a value of 0.13 eV with their method.

Finally the question of a possible linear relationship between normalized self-diffusion coefficient and normalized vacancy concentration shall be discussed. Figure 9 shows that a linear relationship holds up to a relative vacancy concentration of 15–20. For higher values of c_v^N , deviations from the linear behaviour can be observed. Thus the concentration range where the assumption of a linear correlation is valid depends on temperature. For 950 K it ranges from 0 to 6 at.% Sn. For temperatures exceeding 1100 K the linear correlation holds for the whole α -Ag-Sn region and is, as has been observed before (Hehenkamp and Faupel 1983) almost independent of temperature.

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