Atomic Distribution in Molten Silver-Tin Alloys*

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(Z. Naturforschg. **20 a**, 564—571 [1965]; received 28 January 1965)

Molten silver-tin alloys have been studied by x-ray diffraction technique, using a focusing Θ--Θ diffractometer with Mo-Kα radiation (quartz crystal monochromator in the diffracted beam). The scattered intensities $I_{\mathrm{eu}}^{\mathrm{coh}}$ in electron units and the interference function $I(K) = I_{\mathrm{eu}}^{\mathrm{coh}}/f^2$ (f being the scattering factor) have been measured in the range of $K = 4\pi \sin\Theta/\lambda = 1.4$ Å^{-1} to $K = 15$ Å^{-1} for 6 different alloy compositions at temperatures 100 °C above the liquidus line. Four alloys (from 62% to 82% Ag) were measured at 825 °C.

The positions of the first maximum of I_{eu} or $I(K)$ shift considerably with increasing silver content from $K = 2.25$ Å^{-1} for pure Sn to $K = 2.64$ Å^{-1} for pure Ag. The radial distribution function $4\pi r^2 \varrho(r)$ and the probability function $W(r) = \varrho(r)/\varrho_0$, where $\varrho(r)$ and ϱ_0 are the atomic and average atomic densities respectively, were obtained by Fourier transform of $I(K)$. The positions of the first maximum of $4\pi r^2 \varrho(r)$, (i. e., r_1) and of $W(r)$, (i. e., $r_1{}^1$) are a measure of the interatomic distances, and vary from $r_1{}^1 = 3.18$ Å for Sn to $r_1{}^1 = 2.86$ Å for Ag. The plot of r_1 vs. composition of the alloys shows a negative deviation from a linear law. A discontinuity appears in the curve in the range of 50—60% Ag. The coordination number Z increases rapidly on addition of Ag to Sn ($Z = 8.5$ for Sn) and reaches a value of about 11 beyond 60% Ag.

Diffraction studies of atomic distributions in molten alloys are relatively rare [1]. In order to learn more about the arrangements of atoms in liquid alloys the interatomic distances and the coordination numbers were measured in silver-tin alloys as a function of alloy concentration. Molten Ag-Sn alloys have not yet been studied by diffraction techniques, but other physical properties such as molar heat of mixing [2, 3], activities [4], densities [5], surface tension [6], viscosities [7], and electrical resistivities [8] have been determined for this system.

The availability of thermodynamic, mechanical and electrical data, although an important consideration, was only one incentive to study Ag-Sn alloys by x-ray diffraction techniques. The first consideration for the choice of the alloy system was that the two components should have similar scattering factors for x-rays. This condition is important for the normalization of the scattered x-ray intensities. The continuous background produced by the random arrangement of the two kinds of atoms in the liquid is thus greatly reduced when the atoms have similar scattering factors.

This can be easily shown by considering the coherent x-ray intensity $I_{\mathrm{eu}}^{\mathrm{coh}}$ scattered by a liquid with two kinds of atoms [9]:

$$I_{\mathrm{eu}}^{\mathrm{coh}} = \overline{f^2} + |\bar{f}|^2 \int_0^\infty 4\pi r^2 [\varrho(r) - \varrho_0]\,[(\sin K r)/K r]\,\mathrm{d}r\,, \tag{1}$$

$I_{\mathrm{eu}}^{\mathrm{coh}}$ = scattered intensity in electron units,

$$\overline{f^2} = c\, f_{\mathrm{A}}{}^2 + (1-c)\, f_{\mathrm{B}}{}^2, \tag{2}$$

$$|\bar{f}|^2 = |c\, f_{\mathrm{A}} + (1-c)\, f_{\mathrm{B}}|^2, \tag{3}$$

c = atomic concentration,
$\varrho(r)$ = atomic density function,
$4\pi r^2 \varrho(r)$ = radial distribution function,
ϱ_0 = average atomic density,

$$K = 4\pi \sin\Theta/\lambda\,, \tag{4}$$

λ = wavelength of the monochromatic x-rays.

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* This paper is based on a thesis presented by M. L. Joshi to the School of Engineering, Yale University, in partial fulfillment of the requirements for the degree of Doctor of Engineering, 1964.

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It can be shown that the interference function $I(K)$ is given by

$$\begin{aligned} I(K) &= I_{\text{eu}}^{\text{coh}}/|f|^2 \\ &= c(1-c)\,(f_A-f_B)^2/|f|^2 \\ &\quad + 1 + \int_0^\infty 4\pi r^2[\varrho(r)-\varrho_0]\,[\sin Kr/Kr]\,dr\,. \end{aligned} \tag{5}$$

If $f_A \cong f_B$, which is applicable in the Ag-Sn system, $(f_A - f_B)^2 \cong 0$ and

$$I(K) \cong I_{\text{eu}}^{\text{coh}}/f^2\,. \tag{6}$$

The second consideration for the choice of the alloy system was to estimate the importance of the size, electrochemical and valence factors on the atomic arrangement for the liquid alloy solutions. The tin atom is about 10% larger than the silver atom in the liquid state [10], and their electronegativities are almost identical [11]. Therefore, the valence difference of three electrons between silver and tin is the only factor that may appreciably influence the atomic arrangement in molten Ag-Sn alloys.

The fact that silver has a close-packed (face centered cubic) structure and tin has a more loosely packed (body centered tetragonal at higher temperature) structure in the solid state may be of some importance in evaluating the behavior of the molten silver-tin alloy system. In addition, immiscibility in the solid state is encouraged among metals of widely differing melting points [12]. In fact, the solubility of Ag in solid Sn is almost negligible whereas about 10% Sn are soluble in solid Ag. The phase diagram shows two peritectic reactions at ~12% Sn and 724 °C, and at ~25% Sn and 480 °C, and a eutectic reaction at ~96% Sn and 230 °C [13].

In order to investigate the effect of the valence, and the possible influence of the atomic size and the arrangement of the atoms in the solid state on the atomic distribution in the liquid, a series of six silver-tin alloys were measured at 100 °C above the liquidus temperature. In addition, four alloys with compositions between 62% and 82% Ag were measured at 825 °C. The primary objective was to determine the interatomic distances r_1 and the coordination numbers Z from the radial distribution functions as a function of alloy composition.

Experimental Procedure

The experimental arrangement for the measurement of the scattered x-ray intensities from the liquid is identical to the one described by WAGNER et al. [10]. The focussing diffraction geometry was realized with a $\Theta-\Theta$ diffractometer which allows the measurement of the scattered x-rays from an open surface of the liquid. A quartz crystal monochromator in the diffracted beam was used to eliminate the white spectrum, the K_β radiation, most of the COMPTON scattering, and the fluorescent radiation from the sample.

An "MRC High Temperature Diffractometer Attachment" [14] was modified to accommodate a crucible of 25 mm × 20 mm and to maintain temperatures in the sample up to 1200 °C in inert atmosphere [15] (90% He and 10% H) or in vacuum. A pyrolitic graphite crucible was heated by radiation using a pyrolitic graphite ristance element held between two copper electrodes.

The samples of the silver-tin alloys were prepared by melting appropriate amounts of Ag and Sn, both 99.999% purity, in 90% He − 10% H atmosphere in the MRC furnace. The melts were superheated about 300 °C, held at this temperature for about 3 hours and then rapidly cooled to room temperature. The solid sample surfaces were then cleaned very lightly with four 0 emery paper and mirror finished on a metallographic polishing wheel. Such samples retained their bright finish even after 12 hours in the molten state in the 90% He − 10% H atmosphere.

The temperature was measured with a chromel-alumel thermocouple, and calibrated by measuring the freezing points of pure In, Sn, Pb, Al and Ag and the change of the lattice parameter of tungsten with temperature. Both calibrations agreed to within ±10 °C; this value can be considered to be the accuracy of the temperature measurement in the molten samples.

The time required to count 4000 x-ray pulses was registered at definite angular settings of the scintillation counter in the range of $2\,\Theta = 10°$ ($K = 1.5$ Å^{-1}) to $2\,\Theta = 125°$ ($K = 15.7$ Å^{-1}) at intervals of 0.5° between 10° and 80° and at intervals of 1° between 80° and 125°, using Mo radiation.

Analysis and Results

The radial distribution functions were determined from the measured intensities with the aid of a program compiled for use with an IBM 709 computer [16].

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After correcting for the background scattering (i. e., counter noise), the measured intensities I_{meas} were divided by the proper polarization factor

$$P = (1 + \cos^2 2\,\alpha \cos^2 2\,\Theta)/(1 + \cos^2 2\,\alpha),$$

where $2\,\alpha$ is the diffraction angle of the monochromator, and by the absorption factor $A = 1/2\,\mu$. The corrected intensity $I_{\text{cor}} = I_{\text{meas}}/P\,A$ is proportional to the coherently scattered radiation $I_{\text{eu}}^{\text{coh}}$ in electron units. The COMPTON radiation $I_{\text{eu}}^{\text{inc}}$ was neglected since it is small enough at lower angles and is eliminated by the monochromator at higher angles. Therefore

$$I_{\text{eu}}^{\text{coh}} = \beta\, I_{\text{cor}} \tag{7}$$

where β is the normalization constant which was computed from the high angle method and the generalized KROGH-MOE–NORMAN method[10]. The atomic scattering factors for Ag and Sn given in Table 1 were dispersion corrected[17] and then used for converting the measured intensities into absolute intensities, i. e., I_{eu}.

$\sin\Theta/\lambda$	Ag[18]	Sn	Sn[20]	Sn[21]	Sn[22]
0.2	37.7	39.5	40.5	40.6	39.6
0.4	27.2	28.7	29.8	30.2	29.3
0.6	21.4	22.9	22.9	23.1	22.6
0.8	18.0	18.8	18.9	19.1	18.8
1.0	15.2	16.6	16.2	16.3	16.1
1.2	12.6	13.9	13.9	14.0	13.7

Table 1. Representative values of the scattering factors f of Ag and Sn used to convert the measured intensities into the interference function. Also given are recently published f values of Sn[20–22].

The scattering factors of Ag were calculated using the self-consistent field method[18]. The scattered intensity of pure silver was previously observed to match with the dispersion corrected f^2 values[10]. This was also observed for Cu[10] and Hg[10] where the atomic scattering factors evaluated with the self-consistent field method were used for the normalization of the measured intensities. A perfect matching was not possible for Sn, which was due to the lack of accurate values of the scattering factor. In this case, the measured intensities I_{meas} were converted into I_{eu} by using the normalization factors of Ag[10]. It can be shown[10] that for an infinitely absorbing material $\beta = 1/\Phi\,\varrho_0$ where ϱ_0 is the average atomic density and Φ is the proportionality constant converting measured x-ray intensities into absolute intensities. Φ is independent of the material used as a standard. Using the measured value of $\beta_{\text{Ag}} = 2.78 \cdot 10^{-4}$ Å^2/atoms and the density $\varrho = 6.90$ gm/cm^2 of liquid Sn at 335 °C[5] one obtains $\beta_{\text{Sn}} = 4.14 \cdot 10^{-4}$ Å^2/atoms.

The intensities I_{eu} of tin, measured at 335 °C follow very closely the dispersion corrected f^2 of JAMES and BRINDLEY[19] up to $K = 10$ Å^{-1}. Beyond this value of K, the measured intensities lie above the f^2 values. The values of the scattering factor of Sn above $K = 10$ Å^{-1} were then taken directly from the normalized x-ray intensities using $\beta = 4.14 \cdot 10^{-4}$ Å^2/atoms. Therefore, the scattering factors of Sn given in Table 1 are JAMES–BRINDLAY values modified for $\sin\Theta/\lambda > 0.8$.

After completion of this work, FREEMAN and WATSON[20], HANSON et al.[21], and CROMER et al.[22] calculated the scattering factors of tin using the self consistent field method. These values of f_{Sn} are also given in Table 1. It can be seen that the modified f_{Sn} values used in the present investigation are very close to the recently calculated scattering factors.

For the normalization of the intensities scattered from the molten alloys, the weighted average of the dispersion corrected f^2 values are used, i. e.,

$$f_{\text{alloys}}^2 = c\, f_{\text{Ag}}^2 + (1-c)\, f_{\text{Sn}}^2\,,$$

where c is the atomic fraction of Ag in the alloy. The quotient of the scattered intensity in electron units I_{eu} and the square of the scattering factor f is equal to the interference function $I(K)$ which is the FOURIER transform of the radial distribution function $4\,\pi\, r^2\, \varrho(r)$, equation (5).

The absolute intensities I_{eu} and the functions $I(K)$ are shown in the Figures 1, 2, and 3 for different alloy concentrations at 100 °C above the liquidus temperatures. The positions of the first, second, and third maxima of the $I(K)$ vs. K curve are given in Table 2. Also shown in this table are the positions of the peak maxima of the interference functions measured at 825 °C.

In the molten Ag-Sn alloys measured at 100 °C above the liquidus line, there occurs a systematic

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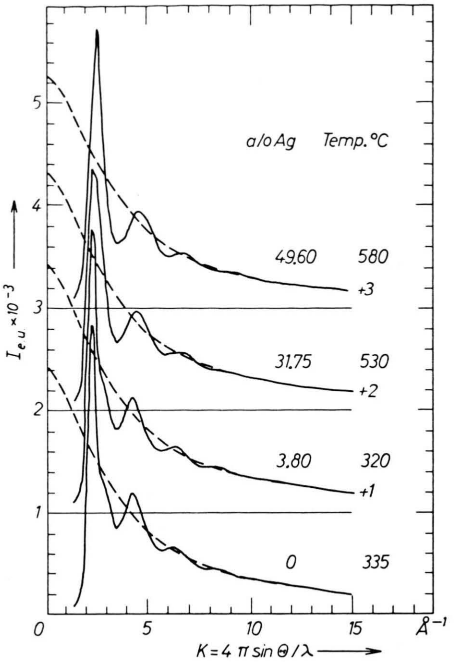

Fig. 1. Scattered x-ray intensities I_{eu} in electron units of molten Ag—Sn alloys with 0, 3.80, 31.75, and 49.60 a/o Ag, measured at 100 °C above the liquidus temperature.

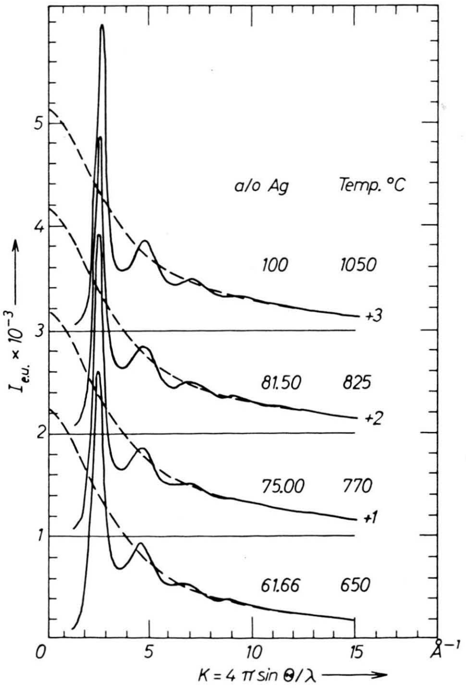

Fig. 2. Scattered x-ray intensities I_{eu} in electron units of molten Ag—Sn alloys with 61.66, 75.00, 81.50, and 100 a/o Ag, measured at 100 °C above the liquidus temperature.

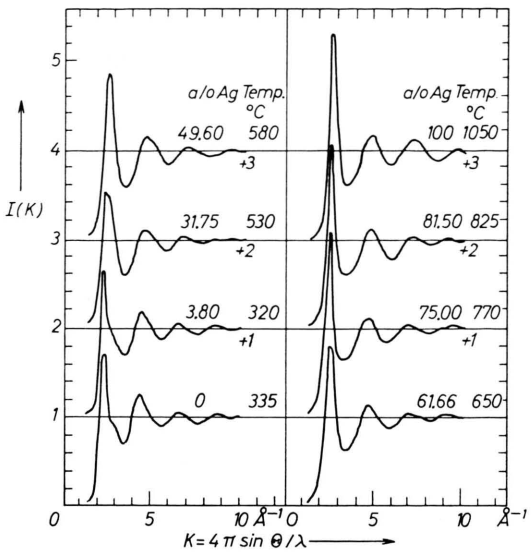

Fig. 3. Interference functions $I(K) = I_{\mathrm{eu}}/f^2$ of molten Ag—Sn alloys, measured at 100 °C above the liquidus temperature.

Composition a/o Ag	Temperature °C	K_1 Å^{-1}	K_2 Å^{-1}	K_3 Å^{-1}
0	335	2.25	4.22	6.45
3.8	320	2.22	4.35	6.42
31.8	530	2.34	4.60	6.74
49.6	580	2.51	4.63	6.90
61.7	650	2.53	4.66	6.90
75.0	770	2.58	4.82	7.10
81.5	825	2.59	4.88	7.10
100	1050	2.64	4.89	7.24
61.7	825	2.52	4.73	7.08
63.6	825	2.56	4.79	6.95
75.0	825	2.57	4.82	7.20

Table 2. Peak maxima $K_n = 4\pi \sin \Theta_n/\lambda$ of the interference function $I(K)$ for different molten silver-tin alloys.

shift of the maxima of the intensity functions towards higher values of $K = 4\pi \sin \Theta/\lambda$ as one passes from Sn to Ag. The diffraction patterns corresponding to the composition of 61.6 to 81.5% Ag measured at 825 °C show the same trend.

The radial distribution function $4\pi r^2 \varrho(r)$ was calculated from the interference function $I(K)$ by FOURIER transform.

$$4\pi r^2 \varrho(r) = 4\pi r^2 \varrho_0 + \frac{2r}{\pi}\int_0^\infty K[I(K)-1]\,(\sin r K)\,\mathrm{d}K\,. \qquad (8)$$

The integrand in the above equation assigns undue weight to the experimental intensities at high values of K[23], where the values of $I(K)$ are not very

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accurate. To minimize this effect and to reduce the ripple due to the termination error which is the consequence of the finite upper limit $K_{\max} = 12$ Å^{-1} in the integral, a damping factor of the form $\exp[-0.005\, K^2]$ was applied to the $K[I(K)-1]$ curves prior to the FOURIER inversions.

The radial distribution functions (RDF) $4\pi r^2 \varrho(r)$ are plotted in Figs. 4 and 5 for the alloys measured at 100 °C above the liquidus temperature. The probability functions $W(r) = \varrho(r)/\varrho_0$ are given in Figs. 6 and 7. The average atomic densities ϱ_0 needed for the evaluation of the RDF were obtained from the specific volume measurements by LAUERMANN and METZGER [5]. The values of the bulk densities at 100 °C above the liquidus temperature are given in Table 3.

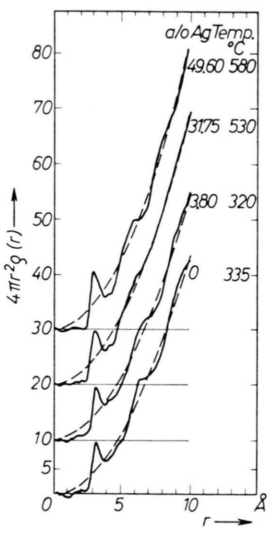

Fig. 4.

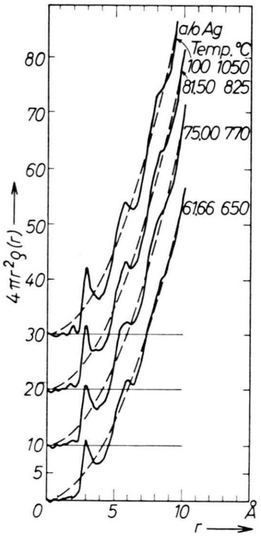

Fig. 5.

Fig. 4. Radial distribution functions $4\pi r^2 \varrho(r)$ of molten Ag—Sn alloys with 0, 3.80, 31.75, and 49.60 a/o Ag, measured at 100 °C above liqiudus temperature.

Fig. 5. Radial distribution functions $4\pi r^2 \varrho(r)$ of molten Ag—Sn alloys with 61.66, 75.00, 81.60, and 100 a/o Ag, measured at 100 °C above liquidus temperature.

Composition a/o Ag	Temperature °C	Density gm/cm^3
Sn	335	6.9
3.8	320	7.0
31.75	530	7.55
49.60	580	7.95
61.7	650	8.4
75.0	770	8.8
81.5	825	8.95
Ag	1050	9.25

Table 3. Values of the density of the liquid Ag—Sn alloys used to calculate the radial distribution function (from LAUERMANN and METZGER [5]).

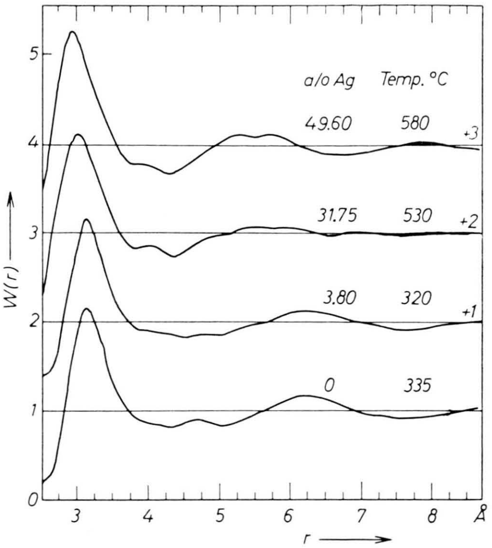

Fig. 6. Probability function $W(r) = \varrho(r)/\varrho_0$ of molten Ag—Sn alloys with 0, 3.80, 31.75, and 49.60 a/o Ag.

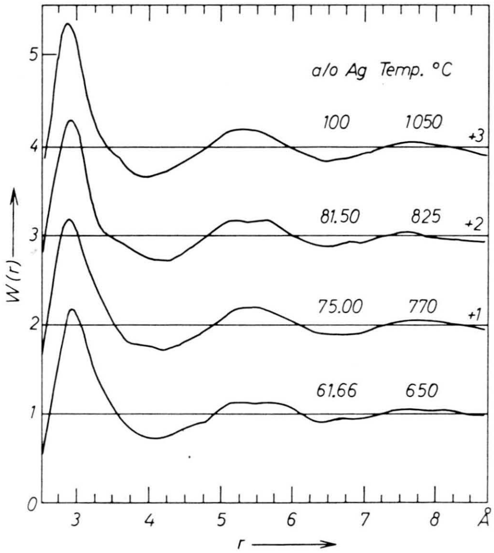

Fig. 7. Probability function $W(r) = \varrho(r)/\varrho_0$ of molten Ag—Sn alloys with 61.66, 75.00, 81.50, and 100 a/o Ag.

Table 4 summarizes the first interatomic distances and the first coordination number Z in the molten alloys measured at 100 °C above the liquidus temperature and at 825 °C. The values of the interatomic distance r_1 refer to the first peak maximum positions of the RDF obtained by extrapolating the midpoints of the peak to the peak maximum. The

Composition a/o Ag	Temperature °C	r_1^E (Ehrenfest [24]) in Å	r_1 RDF in Å	r_1^1 $W(r)$ in Å	Coordination number $Z = \int_{r_0}^{r_2} 4\pi r^2 \varrho(r)\,dr$		
					r_0 in Å	r_2 in Å	Z
0	335	3.42	3.20	3.18	2.66	4.02	8.5
3.8	320	3.47	3.19	3.16	2.65	3.94	9
31.8	530	3.28	3.06	3.02	2.50	3.93	10
49.6	580	3.06	2.97	2.94	2.49	3.93	11
61.7	650	3.04	2.98	2.95	2.46	3.85	11
75.0	770	2.98	2.93	2.91	2.42	3.80	11
81.5	825	2.97	2.92	2.90	2.40	3.75	10.5
100	1050	2.92	2.88	2.86	2.38	3.65	11
61.7	825	3.05	2.96	2.94	2.42	3.85	10.5
63.6	825	3.00	2.99	2.95	2.45	3.84	10.5
75.0	825	2.99	2.93	2.91	2.41	3.85	11

Table 4. Interatomic distances r_1 and coordination numbers Z in molten silver-tin alloys.

values r_1^1 are the first peak positions of the $W(r)$ curves. It is interesting to note that the interatomic distances obtained from the RDF and $W(r)$ differ slightly, i. e., $r_1 - r_1^1 \cong 0.02$ Å.

The first coordination number Z is the area under the first peak of the RDF, i. e.,

$$Z = \int_{r_0}^{r_2} 4\pi r^2 \varrho(r)\,\mathrm{d}r\,,$$

where r_0 is the value of r obtained by extrapolating the left side of the first peak to the abscissa and r_2 is the value of r at which the first minimum in the RDF occurs. r_2 is the intersection of the extrapolation lines drawn tangentially to the right side of the first peak and the left side of the second peak. The error in the first coordination number is estimated to be ± 0.5 atoms.

The values of r_1^1 and Z are plotted in Fig. 8 as a function of alloy composition. It can be seen that r_1^1 increases from 2.86 Å for Ag to 3.18 Å for Sn. The curve shows a significant deviation from a straight line (Vegard's law). As can be seen from Table 4, the value of r_1^1 of a given alloy is not sensitive to temperature. Only a broadening of the distribution peaks is observed with increasing temperature.

Discussion

The important result of the x-ray study of the molten Ag-Sn alloys is that the first interatomic distances r_1, when plotted as a function of the concentration c, show a negative asymmetric deviation from the linear relationship $r_1^* = r_{\mathrm{Ag}} - c(r_{\mathrm{Ag}} - r_{\mathrm{Sn}})$ corresponding to Vegard's law in solid solutions. The maximum deviation $\Delta r_1 = r_1^* - r_1$ occurs at about 50 to 60 a/o Ag which corresponds to an electron to atom ratio of e/a = 2.5 − 2.2 as shown in Fig. 8. The number Z of first neighbors about an arbitrary reference atom in molten Ag is about 11 and remains relatively constant in silver-tin alloys up to the value of e/a = 2.5. Above this e/a ratio, the coordination number decreases rapidly to about $Z = 8.5$ for molten tin. The addition of tin to liquid silver does not substantially loosen the closely packed structure until an e/a value of 2.5 is reached.

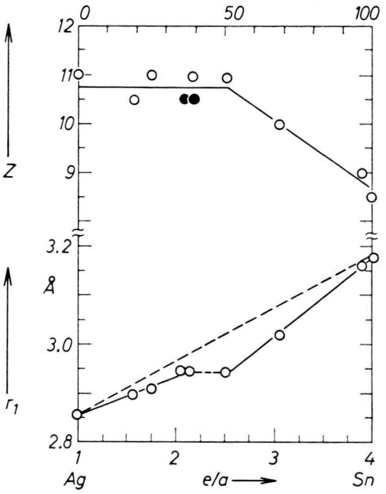

Fig. 8. Interatomic distances r_1 between nearest neighbors and coordination number Z in molten Ag—Sn alloys (○ measured at 100 °C above liquidus temperature, ● measured at 825 °C).

If the molten silver-tin alloys with less than 40 a/o Sn are indeed closely packed, EHRENFEST's equation [24]

$$K_1 = 4\,\pi \sin \Theta_1/\lambda = 7.7/r_1 \qquad (9)$$

should be valid, which predicts the interatomic distance r_1 directly from the position of the first interference maximum K_1 and vice versa. Indeed, the values of K_1 in the molten alloys with e/a $< 2.2 - 2.5$ are close to the corresponding values obtained from equation (9) using the distances of closest approach of the atoms in the corresponding solids [25] as shown in Fig. 9.

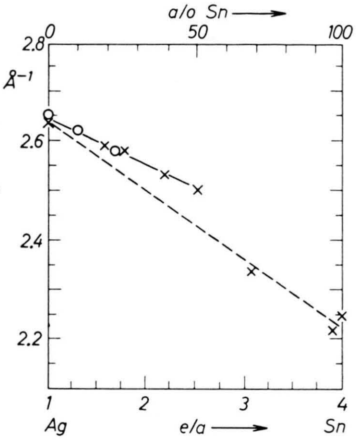

Fig. 9. Position $K_1 = 4\,\pi \sin \Theta_1/\lambda$ in Å^{-1} of the first interference peak of molten Ag–Sn alloys (×). The first diffraction peak in the corresponding solids is represented by ○.

The deviation of the interatomic distances r_1 from the linear relationship cannot be explained by the difference in sizes of the silver and tin atoms in the liquid state. The electrochemical factor is also expected to have little effect on the variation of the interatomic distance r_1 with concentration c. The most probable cause of the deviation from the linear relationship is the valence difference between silver and tin, the so-called valence factor [26].

It is well known [27] that the interatomic distances in solid solutions cannot be accounted for by assigning a fixed atomic diameter to each kind of atom, but that the apparent sizes of the atoms depend on the crystal structure of the particular alloy. The distance of closest approach of the atoms in the pure element A or B is called the atomic diameter. A linear extrapolation of the interatomic distances in the binary alloy of atoms A and B from the dilute region about B to pure A will yield an apparent atomic size of the solute A in the solvent B. Similarly, one can evaluate an apparent atomic diameter of solute B in solvent A.

In the molten silver-tin system the values of the atomic diameter are equal to $r_1{}^1$, i. e., 3.18 Å and 2.86 Å for Sn and Ag respectively. Extrapolating the initial slopes of r_1, versus c at Ag and Sn to Sn and Ag, respectively, leads to an apparent atomic diameter of 3.1 Å for Sn in Ag and 2.7 Å for Ag in Sn. These apparent atomic sizes are determined by the interplay of (1) the volume per valence electron V_{E} and (2) the ionic radii of the solute and the solvent. Using the values of r_1 which are very close to the GOLDSCHMIDT diameter of the corresponding atoms and assuming a closest packing in the liquid, one obtains a value of $V_{\mathrm{E}}(\mathrm{Ag}) = 17$ Å^3 for silver and $V_{\mathrm{E}}(\mathrm{Sn}) = 5.5$ Å^3 for tin. The PAULING ionic radii r_{i} are $r_{\mathrm{i}}(\mathrm{Ag}^+) = 1.26$ Å and $r_{\mathrm{i}}(\mathrm{Sn}^{+4}) = 0.71$ Å. If V_{E} of the solute is smaller than that of the solvent, we expect the apparent atomic diameter of the solute in the alloy to become larger than the corresponding atomic diameter. This V_{E}-effect can be considered as an attempt of the free electron gas to expand in order to reduce the FERMI energy. If, however, the ionic radius r_{i} of the solute is smaller than that of the solvent, the apparent atomic diameter should decrease.

In the molten Ag-Sn system, both the solutes Ag in Sn and Sn in Ag have a smaller apparent atomic diameter than the interatomic distances in pure Ag or Sn. This would mean that in the case of the solute Ag in the solvent Sn the V_{E} effect dominates, whereas in the case of Sn dissolved in Ag the ionic radii effect seems to be the predominant factor. An influence of any BRILLOUIN zone overlap, which is important in solids, on the apparent atomic diameter in liquid solutions is difficult to estimate. Its effect may be of importance in the composition range of 50 – 60 a/o Ag. Below and above this range, the interatomic distances seem to follow VEGARD's law if one uses the values of the apparent atomic size instead of the true size of the pure component atoms.

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Below 60% Ag the close-packed structure of the silver alloys seems to break up as shown in the decrease of the coordination number.

The nonlinearity of the first preferred interatomic distances seems to be reflected in the isothermal curve of the specific volume as a function of concentration at 1200 °C [5] as shown in Fig. 10. The plot of the volume of the first coordination sphere per nearest neighbor, i. e., $4\,\pi\,r_1^3/3\,Z$, versus concentration c (Fig. 10) shows a similar trend as the specific volume. This similarity between the concentration dependence of the atomic and macroscopic volume may seem fortuitous since r_1 vs. c was not measured isothermally at 1200 °C. It has been repeatedly shown that the interatomic distances r_1 in molten metals are not sensitive to variation in temperature. The coefficient of thermal expansion is of the order of $10^{-6}/°C$ in liquid metals. Therefore, even changes of a few hundred degrees in temperature should not appreciably change the interatomic distances in liquids in agreeement with results for liquid tin obtained by FURUKAWA et al. [28].

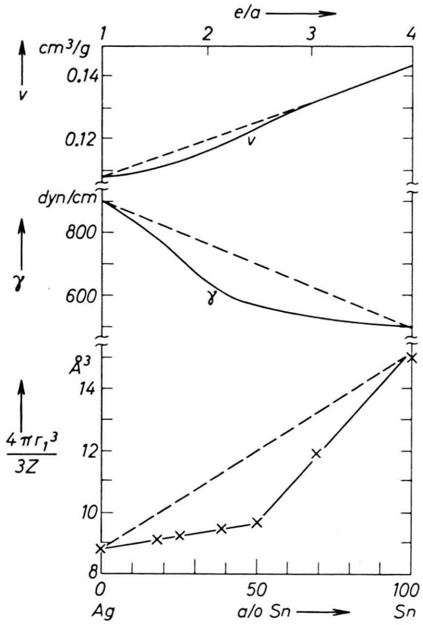

Fig. 10. Volume of the first coordination sphere per nearest neighbor $4\,\pi\,r_1^3/3\,Z$, surface tension γ (l. c. [6]) and specific volume v (l. c. [5]) of molten Ag—Sn alloys.

Thermodynamically, the molten Ag-Sn system deviates from the model of regular solutions. The heat of mixing [2, 3] is negative below about 70 a/o Sn and positive above this composition. The minimum occurs at 20 a/o Sn and the maximum at about 85 a/o Sn. The strong negative deviation of the surface tension in Ag-Sn alloys [6] from the linear relationship has been attributed to Ag-Sn intermetallic binding. The negative values of the heat of mixing below 60 a/o Sn indicate a preference of Ag-Sn grouping over Sn-Sn or Ag-Ag arrangement.

The curvature of the plot of the heat of mixing vs. composition is positive at 0 a/o Sn and negative at 100 a/o Sn which has been interpreted by FRIEDEL [29] as a valence effect. The heat of mixing is zero at about 70 a/o Sn, and it is at this composition that the x-ray diffraction pattern is most diffuse. The first peak of the interference function $I(K)$, Fig. 3, shows a considerable broadening compared to the other alloys and the modulations in $I(K)$ die out much more rapidly leading to a radial distribution function which shows only two distinct maxima.

Conclusions

The interatomic distances r_1 in molten Ag-Sn alloys were measured from the position of the first maximum of the radial distribution functions obtained by FOURIER transform of the experimentally determined interference functions $I(K)$. The plot of r_1 versus concentration c shows a negative deviation from a linear relationship between the values of $r_1(\text{Ag}) = 2.88$ Å and $r_1(\text{Sn}) = 3.20$ Å. This deviation is probably due to the valence difference between Ag and Sn, since their atomic size difference is less than 10% and the electronegativities are practically the same. This conlusion is in agreement with thermodynamical data. The coordination number, measured from the area of the first peak in the radial distribution function, is about 11 in Ag, remains constant up to about 50 a/o Sn and then decreases to about 8.5 in pure Sn.

Acknowledgment

The authors wish to thank Professor H. B. HUNTINGTON and Mr. H. OCKEN for helpful discussions and Doctors A. FREEMAN and R. E. WATSON for making available the scattering factors of Sn. This work was supported by the United States Atomic Energy Commission, Contract AT(30-1)2560.

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