Structure of Molten Sn-Zn-Alloys by Means of Neutron Diffraction

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Neutron diffraction experiments were performed with four molten Sn-Zn-alloys and the two molten elements Sn and Zn. The total structure factors and the pair correlation functions are given. The observed small angle scattering leads to the result that pairs of equal atoms predominate within the range of medium concentrations.

1. Introduction

As a continuation of diffraction work on melts from eutectic binary systems such as Al–Sn [1], Au–Co [2], and Bi–Cu [3] an investigation of melts from the eutectic system Sn–Zn by means of neutron diffraction will be described in the present work. The liquidus lines in the constitution diagrams of these systems always show a point of inflection, so that segregation tendency in molten state is to expected.

The Sn–Zn-melt with eutectic composition has already been investigated by means of X-Ray diffraction [4] with the result that partial segregation should exist within this melt.

2. Theoretical Outline

The coherent scattered intensity, the structure factors, and the pair-correlation-functions are described according to Ref. [5]. To obtain the coherent scattered intensity, all corrections known were applied to the measured intensity according to Ref. [6].

3. Experiments

Six different specimens were prepared for the neutron diffraction experiments. As initial substances, tin [99.995% (Sodipro)] and zinc [99.98% (Sodipro)] were used. The components were melted under vacuum and sealed into quartz tubes of 8 mm inner diameter and a wall thickness of 0.5 mm. The concentrations are indicated in Fig. 1, the temperature was 450 °C for all melts.

All specimens showed after the measurement a bright surface, so that the results are not influenced by oxide layers. Neutrons with the wavelength of $\lambda = 0.69$ Å were used in the D4-instrument of ILL, Grenoble. As furnace a cylindrical heating tube made from vanadium foil was used. The scattered neutron intensity was registered in the region $2^\circ \leqq 2\Theta \leqq 83^\circ$ corresponding to 0.3 Å$^{-1} \leqq Q \leqq 12$ Å^{-1} in steps of $\Delta 2\Theta = 0.3^\circ$ using pulse preset, the statistical error being less than 1%.

The coherent scattering lengths as taken from Ref. [8] are:

$$b_{\mathrm{Zn}} = 0.57 \cdot 10^{-12}\ \mathrm{cm} \quad \text{and}$$
$$b_{\mathrm{Sn}} = 0.61 \cdot 10^{-12}\ \mathrm{cm}\,.$$

The mean number densities for 450 °C as taken from Ref. [9] are:

$$\varrho_{0,\mathrm{Zn}} = 0.0603\ \mathrm{atoms/Å^3} \quad \text{and}$$
$$\varrho_{0,\mathrm{Sn}} = 0.0345\ \mathrm{atoms/Å^3}.$$

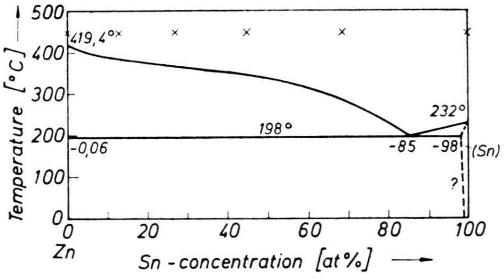

Fig. 1. System Sn-Zn: Phase diagram [7] (X = melts investigated during the present work).

4. Results and Discussion

Figure 2 shows the total structure factor for six melts from the Sn–Zn system. Starting from pure tin, the position of the main maximum shows a small shift from 2.24 Å^{-1} (100% Sn) to 2.30 (69% Sn) and to 2.40 Å^{-1} (45% Sn). More remarkable is the decrease in intensity. Starting from pure Zinc, the position of the main maximum also shows a

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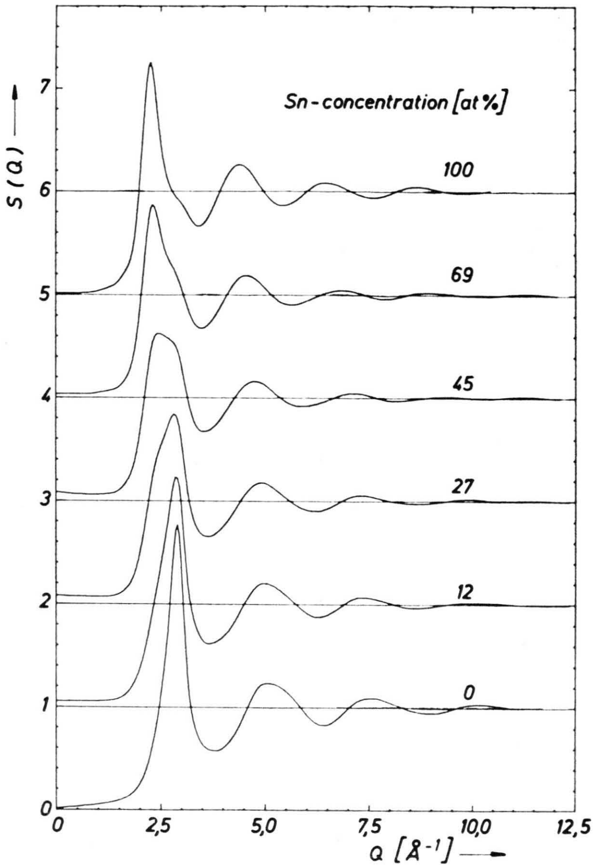

Fig. 2. System Sn-Zn: Structure factors for 450 °C.

small shift, namely from 2.89 Å^{-1} (100% Zn) to 2.85 Å^{-1} (73% Zn) which remains constant up to 55% Zn. Also for the main maximum of the intensity curve of molten Zinc a strong decrease in intensity is observed which leads to a nonresolved double peak for the structure factors obtained with melts from 31 up to 73% Zn.

The structure factor of the pure tin melt shows on the right hand side the shoulder well known for molten tin.

A small rise of the structure factor to zero scattering angle is observed for the melts containing 55 and 73% Zn, respectively, indicating an effect of small angle scattering which however is too weak as to be investigated in detail as was done in the case of Al–Sn or Bi–Cu systems.

By means of Eq. (1) (see Ref. [10]) it is possible to calculate from thermodynamical data the structure factor.

$$S(0)\big|_{\text{thermodyn.}} = \langle b\rangle^2 \varrho_0 k_{\mathrm{B}} T \beta_{\mathrm{is}} + (\langle b\rangle \delta - \Delta b)^2 \frac{c_2 a_1}{\partial a_1/\partial c_1} \qquad (1)$$

with

$\langle b\rangle = c_1 b_1 + c_2 b_2$,
$c_{1,2}$ = atomic concentrations ($c_1 + c_2 = 1$),
$b_{1,2}$ = neutron scattering lengths of the two species 1, 2,
ϱ_0 = mean number density,
β_{is} = isothermal compressibility,
$\delta = \varrho_0 (V_1 - V_2)$,
$V_{1,2}$ = partial molar volume,
$\Delta b = b_1 - b_2$,
$a_{1,2}$ = thermodynamic activity of component 1 or 2.

In Fig. 3 $S(0)\backslash_{\text{thermodyn.}}$ is compared with the structure factor $S(0)\backslash_{\text{extrapol.}}$ obtained from the measured values by extrapolation of

$$Q = 4\pi \sin\Theta/\lambda \to 0 .$$

Regarding the uncertainities in thermodynamic as well as in diffraction experiments, the accordance between both curves is satisfactory.

Figure 4 shows the pair correlation function $g(r) = \varrho(r)/\varrho_0$, obtained with the integration lengths of 10.4, 9.60, 9.95, 12.3, 12.3, and 10.88 Å^{-1}, respectively, for the melts with tin-concentrations of 100, 69, 45, 27, 12, and 0 at%, respectively.

The position of the main maximum shifts continuously from the value of pure Sn (3.14 Å) to that of pure Zn (2.73 Å). It is interesting to observe the mutual extinction of the oscillations beyond the main maximum especially in the case of the melt with 45% Sn.

Table 1 shows the coordination number N^{I} for the first coordination sphere, which was obtained

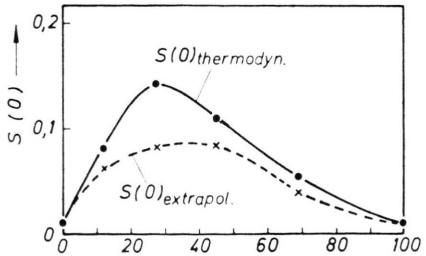

Fig. 3. System Sn-Zn: Comparison between $S(0)\backslash_{\text{thermodyn.}}$ and $S(0)\backslash_{\text{extrapol.}}$.

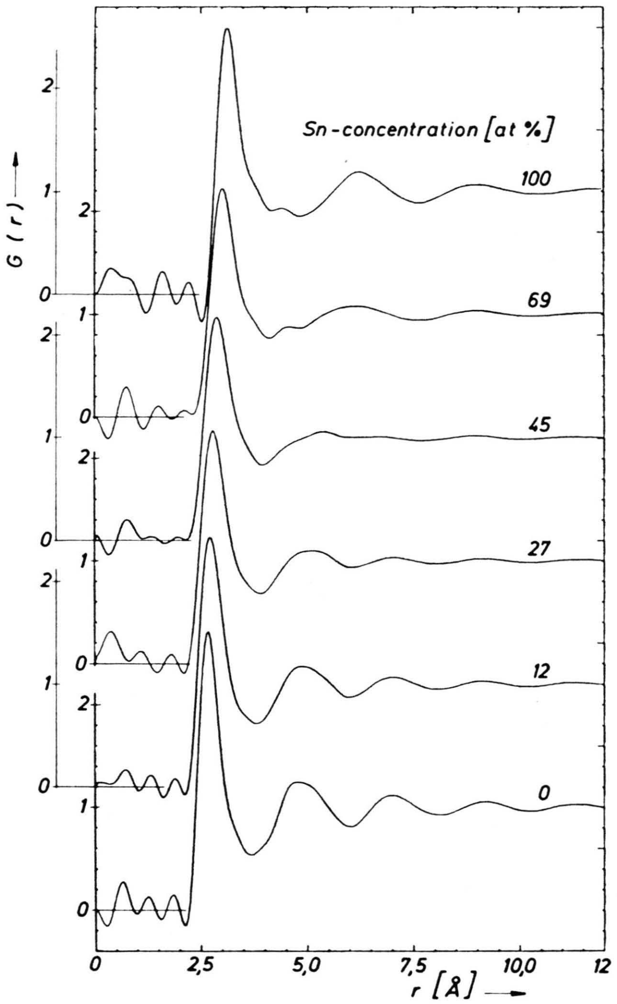

Fig. 4. System Sn-Zn: Pair correlation functions for 450 °C.

for each concentration from the area of the first maximum of the corresponding radial distribution function, limited by the tangents through the point of inflection. Furthermore, Table 1 contains the shortest neighbour distances r^{I} as obtained from the $g(r)$-curves.

Table 1. Sn-Zn-system: Experimental coordination numbers N^{I} and shortest neighbour distances r^{I}.

Sn-concentration [atomic fractions]	N^{I} [atoms]	r^{I} [Å]
0	9.7	2.70
12	9.7	2.73
27	9.4	2.80
45	9.3	2.90
69	8.8	3.03
100	8.1	3.13

As to be expected for a binary system with nearly equal scattering lengths b_{A} and b_{B} of the atoms of both components, N^{I} as well as r^{I} correspond to the values for statistical distribution, namely

$$N^{\mathrm{I}}_{\mathrm{stat}} = c_{\mathrm{A}}\, z_{\mathrm{A}} + c_{\mathrm{B}}\, z_{\mathrm{B}} \tag{2}$$

and

$$r^{\mathrm{I}}_{\mathrm{stat}} = c_{\mathrm{A}}\, r_{\mathrm{A}}{}^{\mathrm{I}} + c_{\mathrm{B}}\, c_{\mathrm{B}}{}^{\mathrm{I}}\,. \tag{3}$$

However, it should be mentioned that this does not justify the classification of Sn–Zn-melts as statistical case. Furthermore this statistical behaviour is simulated by $\Delta b \approx 0$, i.e. the non visibility of the concentration correlations in the present case.

The weak small angle scattering observed in Fig. 2 shows the Sn–Zn-melts to belong to the segregation type. This small angle scattering is determined not by Δb but by $\Delta(b\varrho)$, which in the present case is different from zero.

In a comparison of the results of the present work with those of the Au–Co-, Al–Sn-, and Bi–Cu-systems it is interesting to recognize that the main maxima of the structure factors of those systems are not double headed. Furthermore, in those melts these maxima shift continuously from their position corresponding to the first component to that corresponding to the second component.

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