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## Microstructure of binary metallic melts with limited components' solubility in solid state

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Binary metallic melts with limited mutual solubility of the components in the solid state have been investigated. It was established that all investigated alloys are micro-inhomogeneous at a microscopic level in the liquid state. Structural units for Ga-Sn, Ga-In, Ge-Sn and Bi-Sn liquid alloys have been defined. It was shown that mutual solubility of the components in the liquid state remains the same as in the solid state at the eutectic temperature.

**Keywords:** liquid metals and alloys, structure, X-ray diffraction, modeling.

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### I. Introduction

Physics and chemistry of liquid metals and alloys, in which the atomic arrangement is not spatially periodic in contrast to the case of crystalline materials, is now well-recognized as important and promising brunch for research and development. Liquid metals are known to play significant role in many metallurgical processes. Especially rapid quenching from the melt is a widely used method for production of metallic glasses. Structural and thermodynamic properties of the initial melt play important role in the processing of commercial amorphous ribbons and significantly affect their structure and optical, electronic, thermal, and magnetic properties.

Growing technological interest to the non-periodicity in the atomic arrangement of disordered materials, both in liquid and solid state, have led to an increasing need for a better description of their atomic scale structures.

The description of the atomic structure of disordered materials at a microscopic level as rule employs the pair distribution function  $g(r)$  indicating the probability of finding another

atom at a distance  $r$  from an origin atom. The information given by  $g(r)$  is only one-dimensional and it is difficult or even impossible to determine the fine structure, so-called compositional short-range order (CSRO), in multi-component disordered materials and thus it is hard to construct a realistic three-dimensional model structure.

For determining all partial pair correlation functions,  $g_{ij}(r)$ , of a multi-component system one needs as many independent diffraction measurements as the number of different pairs of particles in the system. In the case of a two-component system, for example, three experiments on the given system are necessary for separating the three ( $i-i$ ,  $i-j$  and  $j-j$ ) partial pair correlation functions, applying the traditional way of data evaluation (e.g. [1]). One reliable way for separating the partial functions is neutron diffraction with isotopic substitution technique [2]. On the other hand, the anomalous X-ray scattering method (AXS) [3] by utilizing the so-called anomalous dispersion effect near the absorption edge of the

constituent elements has recently received much attention. Undoubtedly, both these methods are powerful technique. However, the necessary number of measurements in the first case usually cannot be carried out, mainly because of the lack, or the unreasonably high cost, of suitable isotopes. The often insufficient absolute accuracy of the experimental data in the second case still prevents us from obtaining exact solutions of the simultaneous linear equations from the AXS measurements alone [4].

Taking into account all mentioned above it would be most welcomed if partial pair correlation functions could be at least approximated on the basis of a single measurement. Computer simulation is frequently used for these purposes. Recently a model describing the structure of multi-component liquid alloys has been developed [5]. Its rigorous mathematical formalism enables to obtain quantitative information on the distribution of different-sort atoms in the multi-component liquids. A method and procedure of performing diffraction experiments based on this model are proposed. Their full implementation allows drawing quite definite conclusions on the structure of multi-component liquid alloys.

## II. Description of the atomic distribution in the multicomponent melts

Let us consider in brief main principles of the micro-inhomogeneous model [5] concerning to binary melts. According to the model, binary liquid alloys are assumed to consist of micro-groupings (or clusters) of one or two different types, which are distinguished by composition and packing, and scatter X-rays independently. Depending on the characteristics of the system considered, the entire concentration range may be subdivided into several concentration intervals. The alloys located at the borders of these intervals (so-called reference alloys) contain atomic clusters of one type whose composition represents that of the alloy in question. The alloys placed between the borders contain the clusters of the two border types. The composition of the clusters remains constant if the alloy

composition changes, and only the relative number of each cluster-type is changed.

Such a representation of the constitution of liquid binary alloys enables one by experimentally measured diffraction functions, structure factors, and atomic density functions of reference alloys to calculate the respective functions for an alloy of arbitrary composition between the two border compositions. In [5] a complete derivation of the needed model equations is presented. The most simple equation is obtained for coherent intensity data  $I(Q)$  ( $Q=4\pi \sin\theta/\lambda$ , where  $\theta$  is half the scattering angle and  $\lambda$  is the radiation wavelength). If  $I^*(Q)$  and  $I^o(Q)$  are experimental coherent scattering intensities due to the border alloys then scattering intensity for an arbitrary alloy inside the concentration interval can be expressed as

$$I(Q) = \frac{c_x - c_i^o}{c_i^* - c_i^o} I^*(Q) + \frac{c_i^* - c_x}{c_i^* - c_i^o} I^o(Q). \quad (1)$$

Here  $c_i^*$  and  $c_i^o$  are the concentrations of the  $i$ -type atoms in the two cluster types and  $c_x$  ( $c_i^o \leq c_x \leq c_i^*$ ) refers to the concentration of  $i$ -type atoms in the alloy considered. Equation (1) can be subsequently transformed into a structure factor  $S(Q)$  and a number density function  $\rho(r)$ . If one has the measured functions of the border alloys such as  $I(Q)$ ,  $S(Q)$  and  $\rho(r)$  it is easy to calculate the corresponding functions of the alloy of question by the model, and comparison with experimental data may then be made.

The main problem is to define the border alloys. One of the methods is plotting the heights of the scattering intensity functions at different  $Q$  against the concentration. As it follows from Eq. (1), the intensity for any value of the diffraction vector between two border alloys should change linearly. If the model is suitable for system considered, then the plots consist of joined line segments, and the deflection points are the compositions of the border alloys.

Such approach has been used to explain the structure of liquid binary Ga-Sn and Ga-In alloys [6, 7]. The simple eutectic phase equilibrium diagrams characterize both Ga-Sn and Ga-In systems. Mutual solubility of the

components in Ga-Sn system is less than 1 at. %, and maximum solubility of Ga in In achieves 18,3 at. % at the eutectic temperature.

It has been shown that structure of molten Ga-Sn and Ga-In alloys can be well described on the basis of the micro-inhomogeneous model. Structural units in the Ga-Sn liquid alloys are clusters of two type enriched by one-sort atoms. The whole concentration range of Ga-In system divides into two intervals: first, from pure Ga to 81,7 at. % In (maximum solubility at the eutectic temperature in the solid state), and the second one, from this point to pure In. This means in the first concentration interval clusters of composition  $Ga_{18,3}In_{81,7}$  and pure Ga regions exist while in the second concentration interval clusters of composition  $Ga_{18,3}In_{81,7}$  are embedded in pure In.

Present work deals with structural investigations of two simple eutectic systems with limited mutual solubility of the components in solid state – Ge-Sn and Bi-Sn.

### III. Experimental details

X-ray patterns of the samples have been obtained in a high-temperature  $\theta$ - $\theta$  diffractometer with Mo- $K_{\alpha}$ -radiation at temperatures 960 and 1230 °C (Ge-Sn alloys) and 300 and 700 °C (Bi-Sn alloys). A graphite single crystal was used for monochromatization of X-rays scattered by the sample. Maximum value of diffraction vector was 12 Å<sup>-1</sup>. Statistical error of counting at the “tail” of the scattering curve did not exceed 1,5%. The samples were prepared from pure Ge, Sn and Bi (99,99 %) by melting at 1000 °C (Ge-Sn system) and at 500 °C (Bi-Sn system) for 2 hours in a helium atmosphere. The scattering intensity measured in arbitrary units was converted into the coherent scattering intensity per atom in electron units,  $I_{e.u.}^{coh}$ , using the generalized Krogh-Moe-Norman method [8, 9]. Compton scattering has been also corrected using the values given by Cromer and Mann [10]. Then the Ashcroft-Langreth total structure factor  $S(Q)$  was obtained from the scattering intensity as [11]:

$$S(Q) = \frac{I_{e.u.}^{coh}(Q)}{\langle f^2(Q) \rangle}, \quad (2)$$

with

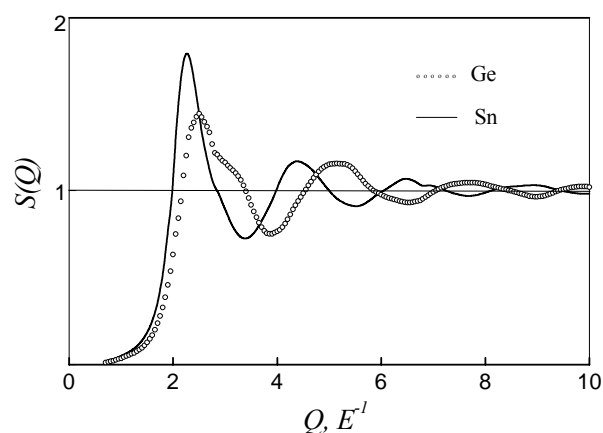
$$\langle f^2(Q) \rangle = \sum_j c_j f_j^2(Q). \quad (3)$$

## IV. Results and discussion

### 4.1. Structure of germanium-tin liquid alloys

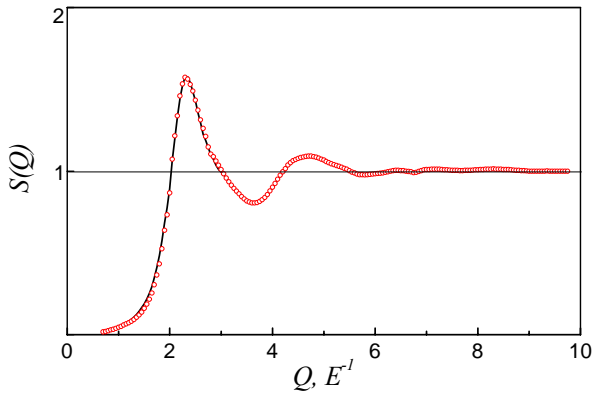
Mutual solubility of the components in Ge-Sn system is less than 1 at. % [12]. It has been assumed that this effect is preserved in the liquids. That is why the micro-inhomogeneous model has been used for interpretation of the experimental results.

Atomic sizes of germanium and tin are very different (2,82 Å and 3,23 Å, respectively) [13]. Therefore considerable differences in the features of structure factors and pair correlation functions of pure Ge and Sn are observed. Especially there is a shift of the positions of the maxima and the position of the third (it is about  $Q = 6 \text{ \AA}^{-1}$ ) and the higher maxima in the structure factor of Sn corresponds to positions of the minima in the structure factor of Ge (Fig.1).



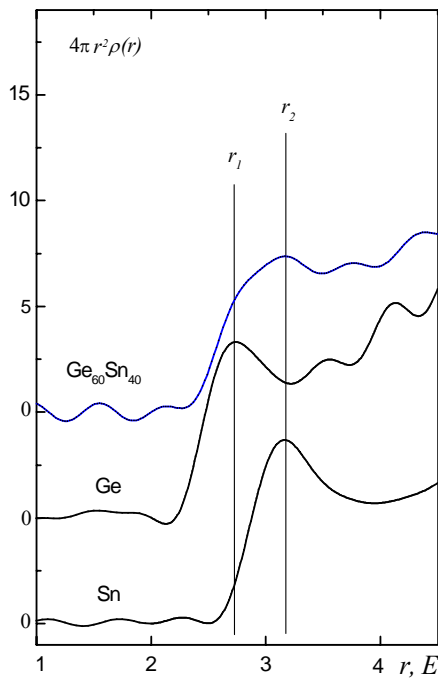
**Fig. 1.** Experimental structure factors of liquid tin and germanium at 1230 °C.

If there are clusters enriched by one-sort atoms in the Ge-Sn melts that scatter X-rays independently, then total structure factor of melts in which concentration of Sn is nearly 30–50 at. % should be equal unity beginning of  $Q \approx 6 \text{ \AA}^{-1}$ . Indeed,  $S(Q)$  of  $Ge_{60}Sn_{40}$  melt equals unity beginning from  $\sim 6 \text{ \AA}^{-1}$  of diffraction vector (Fig. 2).



**Fig. 2.**  $\text{Ge}_{60}\text{Sn}_{40}$  structure factor at 1230 °C: comparison with microinhomogeneous model; *full* line: X-ray dif-fraction results; *circles*: model.

Also it should be mentioned that structure factor of  $\text{Ge}_{60}\text{Sn}_{40}$  liquid alloy calculated on the base of structure factors of pure Ge and Sn (Eq. 1) is in a good agreement with experimental one (Fig. 2).



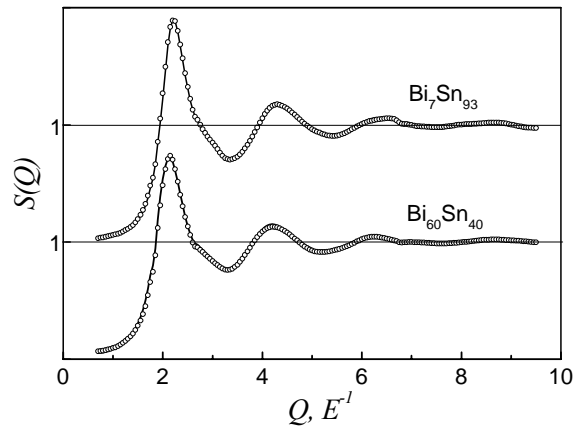
**Fig. 3.** Radial distribution functions  $4\pi r^2\rho(r)$  of liquid Ge, Sn and  $\text{Ge}_{60}\text{Sn}_{40}$  alloy at 1230 °C.

Another fact confirming this conclusion is the shape of the first maximum in the radial distribution function (*RDF*) of the  $\text{Ge}_{60}\text{Sn}_{40}$  melt. Fig. 3 shows the *RDFs* of  $\text{Ge}_{60}\text{Sn}_{40}$  melt and liquid Ge and Sn at 1230 °C. The first maximum of the *RDF* of binary melt is

subdivided into two peaks whose positions correspond to the positions of the main peaks of pure Ge and Sn. Such behaviour occurs only in case when binary Ge-Sn melts consist of clusters from atoms of pure Ge and Sn that scatter X-rays independently.

#### 4.2. Structure of bismuth-tin liquid alloys

Tin dissolves up to 13,1 at.% of bismuth at the eutectic temperature [13]. Taking into account our experience we considered two concentration intervals in this system: first – from pure Bi to  $\text{Bi}_{13,1}\text{Sn}_{86,9}$  alloy and second – from this alloy up to pure Sn. Five samples ( $\text{Bi}$ ,  $\text{Bi}_7\text{Sn}_{93}$ ,  $\text{Bi}_{13,1}\text{Sn}_{86,9}$ ,  $\text{Bi}_{60}\text{Sn}_{40}$  and Sn) have been investigated.



**Fig. 4.** Bi-Sn structure factors at 700 °C: comparison with microinhomogeneous model; *full* line: X-ray dif-fraction results; *circles*: model.

We have obtained experimental structure factors for all melts and calculated ones for  $\text{Bi}_7\text{Sn}_{93}$  and  $\text{Bi}_{60}\text{Sn}_{40}$  liquid alloys (Eq. 1) on the base of structure factors of reference alloys. Good agreement of experimental and calculated curves plotted on Fig. 4 shows that the microinhomogeneous model gives a satisfactory description of the melts of the Bi-Sn system. In the whole concentration region Bi-Sn melts are characterized by micro-inhomogeneous structure and contain clusters  $\text{Bi}_{13,1}\text{Sn}_{86,9}$  composition.

#### V. Conclusions

Four binary metallic systems with limited solubility of the components in the solid state

(Ga-Sn [6], Ga-In [7], Ge-Sn and Bi-Sn) have been investigated by X-ray diffraction.

Taking into account the experimental pair correlation functions and calculated ones by using equations of micro-inhomogeneous model it can be concluded the following: the structure of all investigated melts are micro-inhomogeneous over whole concentration range; mutual solubility of the components at a microscopic level in liquid state remains the same as in solid state at the eutectic

temperature;

the structure of the investigated melts is characterized by the coexistence of regions containing only the pure elements and clusters whose composition respects to maximum solubility of the components at the eutectic temperature in solid state;

the composition of the clusters remains constant if the alloy composition changes, and only the share of clusters is changed.

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## **Мікроструктура подвійних металічних розплавів з обмеженою розчинністю компонентів у твердому стані**

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Досліджено подвійні металічні розплави з обмеженою взаємною розчинністю компонентів у твердому стані. Встановлено, що всі досліджені сплави неоднорідні на мікрорівні в рідкому стані. Визначено структурні одиниці для сплавів Ga-Sn, Ga-In, Ge-Sn і Bi-Sn. Показано, що взаємна розчинність компонентів в рідкому стані залишається такою ж, як у твердому стані при температурі евтектики.