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SELF-ASSOCIATED ATOMIC GROUPS IN Ga–Sn LIQUID ALLOYS

The structures of a liquid eutectic alloy and one corresponding to the near-equatomic concentration in the phase diagram are investigated at different temperatures. The structure factors and pair correlation functions have been analyzed and interpreted. The temperature dependences of main structure parameters determined from these functions allowed us to suppose that the atomic distribution in both alloys is characterized by a tendency to the interaction of like-kind atoms. In addition, the structure data and the results on the density and surface tension are analyzed as well.

K e y w o r d s: Ga–Sn molten alloys, short-range order, surface tension, clusters, microsegregation.

1. Introduction

Due to the structure and properties atypical of liquid metals, gallium-based alloys have attracted the attention of many researchers. Ga-based systems are important components of electronic solid-state devices. They are the subject of numerous studies [1, 2]. Many alloys and compounds based on gallium are used in the semiconductor devices and superconductors [3] and the heat transfer agents in nuclear reactors [4]. Ga and its alloys have been proposed as replacements for Hg in dental filling materials [5–7] and high-temperature thermometers [8–10].

Alloys of binary Ga–Sn system are of interest due to their wide application as basic alloys for connecting elements in electronics. They are used also for the production of low melting temperature solder materials and as a matrix of such composites as ferrocoloidal suspensions. For instance, due to the solderability of a Ga–Sn molten eutectic alloy on an Au-coated copper substrate, the sandwich joints with good parameters were obtained [1]. For that reason, it is important to have a detailed information about the structure and properties of these alloys not only in the solid state, but also in the liquid one. Liquid constituent elements are of interest due to an anomalous profile of principal peaks of the structure factors (SF), which are asymmetric and reveal the shoulders on the right side. Such shoulder exists also in SFs for liquid Bi and Sb, being more pronounced in liquid semiconductors such as Ge and Si [11]. As follows from diffraction studies, this shoulder is attributed to the residual covalent bonds of of principal peakscrystalline solid turning into the melt, which results in the formation of the inhomogeneous structures of mentioned liquid metals. In them, due to some part of covalent bonds, the structure units with less packing density comparing with the rest atoms linked by means of metallic bonds are formed. For that reason, it is of importance to carry out detailed studies of the nature of such shoulder and its effect on structure formation processes in multicomponent alloys in the liquid, amorphous and solid states.

This work aimed to study the evolution of shoulders existing in SFs of liquid gallium and tin at the

formation of the structure of liquid alloys to clarify their effect on the total structure of binary melts. The main physical characteristics of Ga and Sn are in many respects similar. These two elements are the neighbors in the Periodic table of elements and have three valence electrons (Ga-$4s^2 4p^1$) and four electrons (Sn-$5s^2 5p^2$). The melting temperature for Ga is low (303 K) and significantly less than one for tin (505 K). Contrary to tin, gallium has a very large supercooling range (150 K). The structure parameters in the liquid state are in some respect similar.

Liquid alloys of the Ga–Sn system have early been studied in detail by means of the thermodynamics methods and the measurements of surface properties [12]. The authors used the method of quasichemical approximation and combined it with the quasilattice theory. Thermodynamic properties of this system deviate positively from Raolt's law. The energy of mixing was studied by means of the surface tension and surface composition measurements and calculations. It was shown that Ga–Sn liquid alloys show the tendency to the microsegregation not only in bulk, but also on the surface layers [13, 14].

It is known that the surface tension is a structurally sensitive value. Minor changes in the structure will greatly alter the surface tension. Therefore, changing the surface tension leads to changes in the structure, especially within near surface layers.

In [15], the surface tension of Ga–Sn alloys with a Sn addition in a wide concentration interval was investigated. In [16], the different changes in the surface tension were observed at a variation in the temperature.

2. Experimental

Samples have been alloyed from high-purity ingots of Ga and Sn (99.999%) in a furnace, installed in a chamber filled with argon to avoid the oxidation. In this work, Ga–Sn alloys with 8.5 and 43 at.% of tin were selected.

The structure of melts was studied by using a high-temperature X-ray diffractometer, as was reported in [17–19]. The sample was placed in a helium-filled chamber of a diffractometer to prevent its oxidation. The geometry of an incident Cu–Kα – radiation beam monochromated with the use of a LiF crystal, a center of the camera, and an inlet slit of the detector corresponded to the Bragg–Brentano type focusing geometry[20]. The accuracy of the measurement of the X-ray intensity was in the interval 2–3% and depended on the selected exposure time at each point. The temperature was measured and maintained with an accuracy of ± 2 K. Experimental dependences of the intensity were smoothed by the least squares method and then were corrected on the polarization, absorption, and anomalous dispersion. The normalization to electron units was carried out using the method described in [21]. After the normalization procedure, the structural factors have been calculated at different temperatures[22]. SFs have been analyzed by comparing the peak positions with similar peaks on constituent elements, and the interpretation of their temperature and concentration dependences was carries out. The pair correlation functions (PCF) and atomic distribution functions have been calculated from SFs using the integral Fourier transformation. These functions allowed us to calculate the main short-range-order parameters such as r – the most probable interatomic distances to the nearest neighbors.

The sessile drop method has been chosen for obtaining the density and surface tension. The installation for the research made it possible to obtain images of the droplet profile during the heating in an inert atmosphere.

The samples were heated using a nichrome electric furnace from the melting point up to 1000 K, and a molten drop was on a graphite substrate. The temperature control and measurements were performed using a platinum-rhodium thermocouple with an accuracy of ± 1 K. The images were obtained using a digital camera on a temperature interval $\Delta T = 40$ K. We have 3 images for each temperature, which allowed us to get representative values of the density and surface tension values. The surface tension and the density data were obtained with an accuracy of about $\pm 3\%$.

3. Results and Discussion

The SFs for liquid Ga–Sn of the eutectic concentration are shown in Fig. 1 and reveal the profiles atypical of simple liquids. The principal peaks show no symmetry and reveal a shoulder on the right-hand side. The position of this peak lies between such peaks for liquid Ga and Sn, has significant width, and, as a result, can be interpreted as an additive sum of curves corresponding to SFs for constituent elements. Therefore, the SF supposes that the eutectic melt consists

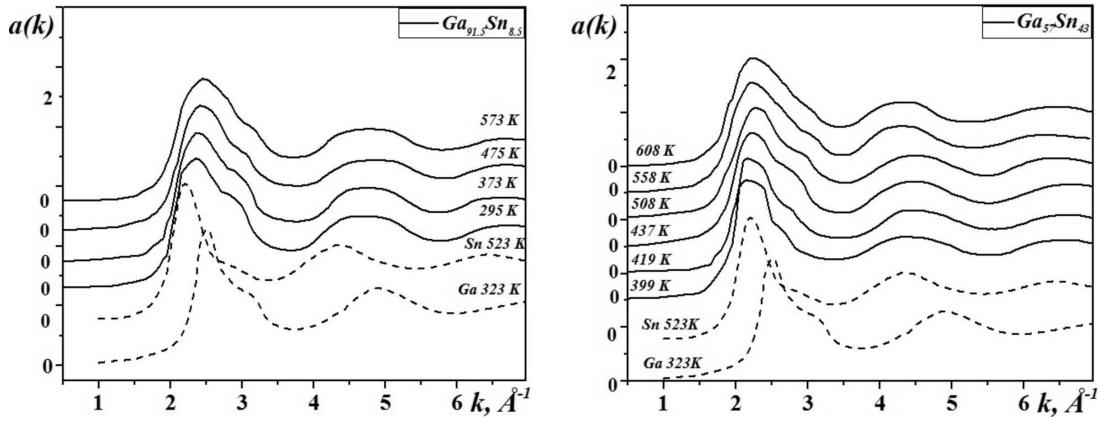

Fig. 1. Temperature dependences of SF for liquid Ga–Sn

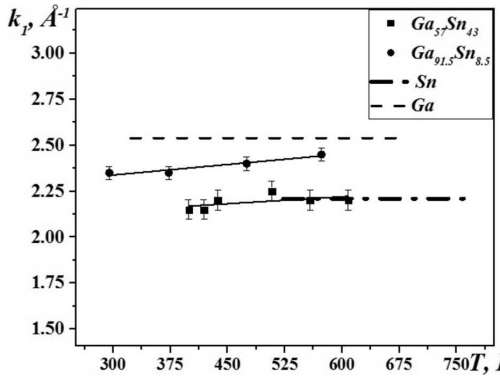

Fig. 2. Temperature dependence of peak positions in SF

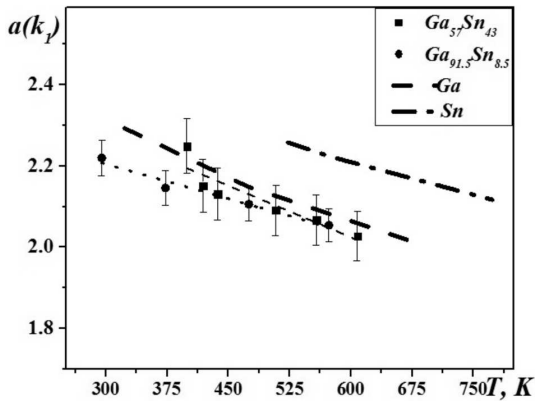

Fig. 3. SF principal peak height versus the temperature

of the structural units, with like-kind atoms. The stability of such kind structure is notably high, which follows from the temperature dependence of structure factors and parameters obtained from them.

For instance, the first peak positions are, in fact, unchangeable within a wide temperature interval (Fig. 2).

Another parameter obtained from SF is the principal peak height, which is commonly considered as a measure of the atomic packing density and decreases, as the with temperature increases (Fig. 3). The SF for the eutectic melt can be considered as an additive sum of SFs for liquid Ga and Sn, which allows concluding the existence of the tendency to a preferred interaction of like-kind atoms. The mean size of structural units as a function of the temperature for the eutectic melt is, in fact, unchangeable with the temperature (Fig. 4), which is the evidence of the high temperature stability of such structures. Slight temperature dependences are also observed for the

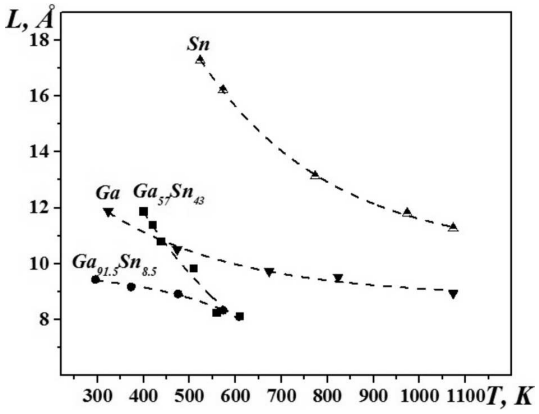

Fig. 4. Temperature dependence of cluster's size

distance to neighbor atoms, obtained from the pair correlation functions (Fig. 5).

Such decrease is related to an increase of the free volume in the atomic distribution at higher tem-

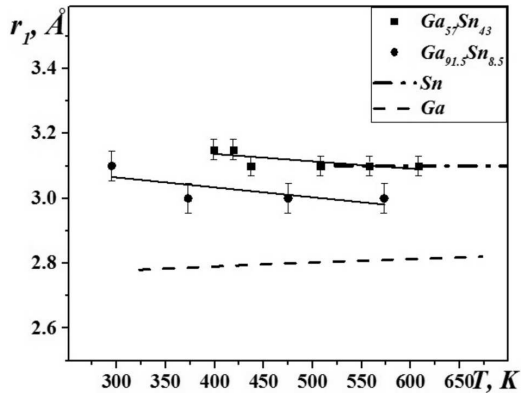

Fig. 5. Temperature dependences of the distances to neighbor atoms for Ga–Sn molten alloys

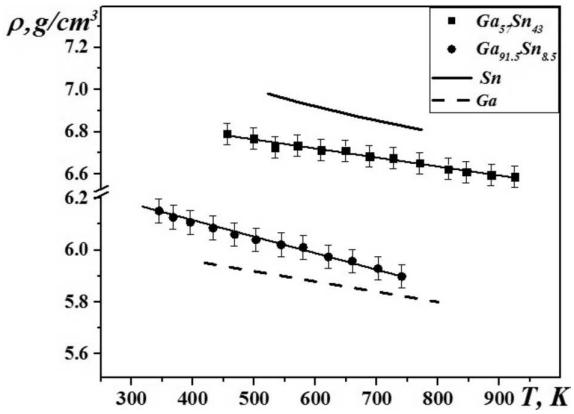

Fig. 6. Temperature dependences of the density for Ga–Sn molten alloys

peratures, as was early shown in [23]. The tendency to a microsegregation is most pronounced in melts with the miscibility gap and in eutectic melts. The binary Ga–Sn phase diagram, as well as those for other similar systems, reveals also the inflection point, which is commonly interpreted as a precursor to form the miscibility gap. The SF for the alloy corresponding to this inflection point (43 at.% Sn) (Fig. 1) reveals also wide peaks with shoulders on the right-hand side of the principal maximum for the eutectic melt.

It is seen that this distance is higher than the corresponding distance for liquid Ga, although the content of this element in the alloy prevails. For the melt corresponding to the inflection point, this parameter becomes higher and closer to the value for liquid tin. Therefore, this alloy also reveals the tendency to a preferred interaction of like-kind atoms, and it is

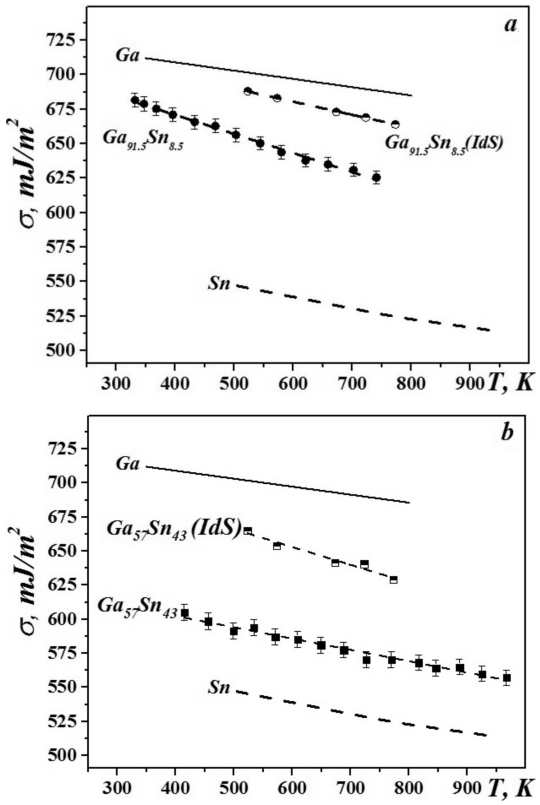

Fig. 7. Surface tension of Ga–Sn molten alloys

possible to conclude that the tendency to a microsegregation occurs within a wide concentration region.

It was found experimentally that the surface tension and the density of the pure liquid metals vary linearly with the temperature [24]. In the temperature interval under consideration, the temperature dependence of the surface tension (1) and the density (2) of all of the metals and alloys studied can be described by the following linear relations:

$$\sigma(T) = \sigma_0 + \frac{d\sigma}{dT}(T - T_m), \tag{1}$$

where T_m is the melting temperature, σ_0 is the surface tension at the melting point, and $d\sigma/dT$ is the temperature coefficient of the surface tension, respectively

$$\rho(T) = \rho_0 + \frac{d\rho}{dT}(T - T_m), \tag{2}$$

where ρ_0 and $d\rho/dT$ indicate the density at the melting temperature and its temperature coefficient, respectively.

The surface tension at the melting point and its temperature coefficient for investigated alloys according to the temperature dependence of the surface tension Eq. (1)

No.	Alloy	σ_0, mJ/m^2	$d\sigma/dT$, mJ/(K*m^2)
1	Ga	714.88	–0.06
2	$Ga_{91.5}Sn_{8.5}$	685.27	–0.13
3	$Ga_{57}Sn_{43}$	606.18	–0.079
4	Sn	547.32	–0.072

The temperature dependences of the density for Ga–Sn liquid alloys are shown in Fig. 6, and it is seen that they can be described by a linear relation. The presented results on $\rho(T)$ for the $Ga_{91.5}Sn_{8.5}$ eutectic composition are in good agreement with data obtained in [25]. As for the previous Ga–Sn molten alloy containing 43 at.% Sn, we can see a similar behavior: the density decreases, as the temperature increases. It is seen that the density of the eutectic melt is less, compared with the density of a melt with near-equatomic concentration. So, it can be noted that an addition of tin leads to increasing the density in the investigated alloys.

The temperature dependences of the surface tension of liquid Ga–Sn alloys are presented in Fig. 7. The ideal solution model has been used to calculate the surface tension of binary alloys of the Ga–Sn system. As we can see, the surface tension changes linearly with the temperature. The temperature dependences reveal a monotonic decrease, as the temperature increases. The obtained data for the surface tension of liquid Ga–Sn alloys were compared with the corresponding data for pure components. As is seen, the values for alloys are in an intermediate position between values for pure components.

The negative values for the temperature coefficient of the surface tension $d\sigma/dT$ were found for all alloys (Table). It is known that this coefficient is proportional to the surface entropy [26]:

$$S_\omega = -\left(\frac{d\sigma}{dT}\right)_{\omega,\,\mu,\,V}, \tag{3}$$

where ω is the surface area, V – liquid volume, and μ – chemical potential.

One can see that the surface entropy has a maximum value according to (3) for the eutectic melt and decreases with an addition of tin atoms. Therefore the variation of the atomic ordering related to the formation of self-associated atomic groups is observed not only in the bulk of the alloy, but also in surface layers. It should be noted that tin is a surfactant for gallium melts. The obtained results on the surface tension confirm our data of X-ray diffraction studies.

4. Conclusions

Liquid alloys of the Ga–Sn system with concentrations corresponding to the eutectics and the inflection point in a phase diagram have a structure, consisting of structural units (clusters) with a preferred interaction of like-kind atoms. Such structure shows the high stability at the heating. But, at higher temperatures (>450 K), the number of neighbor atoms decreases, whereas the size of clusters is, in fact, unchangeable. Such behavior is most probably due to an increase in the free volume at the heating.

Both the density and the surface tension slopes showed negative values in the temperature dependences and the linear temperature dependence in the investigated temperature regions. With the increasing Sn content in Ga–Sn alloys, the density and surface tension decrease, which conforms the tendency to a preferred interaction of like-kind atoms.

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САМОАСОЦІЙОВАНІ АТОМНІ ГРУПИ В РОЗПЛАВАХ Ga–Sn

Досліджувалась за різних температур структура рідких розплавів Ga–Sn евтектичної та біляеквіатомної концентрацій на діаграмі стану. Було проаналізовано і пояснено структурні фактори та парні кореляційні функції. Температурні залежності основних параметрів структури, визначені з цих функцій, дозволили припустити, що атомний розподіл в обох розплавах характеризується тенденцією до взаємодії односортних атомів. Також було отримано і проаналізовано дані густини та поверхневого натягу та їхні температурні залежності в цих розплавах.

Ключові слова: розплави Ga–Sn, ближній порядок, поверхневий натяг, кластери, мікросегрегація.