

Structure and short range order of liquid gallium

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The structure of liquid gallium in a wide temperature range has been studied. Analysis of data obtained by diffraction method allowed us to make some conclusions about the structural features of the liquid gallium. In particular there is a clear asymmetry of the first maximum of the structure factor (SF) and existence of shoulder on its right hand side. Also the temperature dependence of structural factors for liquid gallium in terms of its heterogeneous structure was analyzed. Interpretation was carried out under the assumption that the structure of liquid gallium consists of clusters with different distribution of atoms, as well as different types of chemical bonds between atoms. The structural units are sensitive to temperature. Splitting of the structure factor main maximum on the Gaussian partial curves, which corresponded to certain structural units of the melt, was also performed. Each structural component of the melt reveals a different nature of the temperature dependence. It is also assumed that the partial peaks for each cluster are described by Gaussian functions.

Keywords: structure factor, short range order, liquid gallium

Introduction. It is known that method of x-ray diffractions is effective in structure studies and it is widely used for investigation of liquid metals. Information, obtained with use of this method allowed to obtain the main conclusions about the structure of liquid metals. Unfortunately to now there are no complete understanding of nature of molten metals and structure variation with temperature. More detailed studies are needed to formulate the general theory of liquid metals, describing the behavior of experimental data, especially the temperature dependence of structure. Besides, up today there is no complete theory of the liquid state, capable also to explain the relation between the physical properties of melts and their structure. For this reason, it is necessary not only to accumulate the results of diffraction studies but also to find a new methods of their interpretation.. This is especially important for profile analysis of diffraction peaks in SF and pair correlation functions (PCF), calculated from them. Due to widely use of the models of micro inhomogeneous structure of metal melts, it is necessary to show how the parameters of such inhomogeneities are related with profile features of SFs and PCFs and to find a quantitative description of such microheterogeneous structure. In this work we attempt to obtain the some results on this problem.

Since the SFs are initial results contrary to PCFs, which are commonly calculated from SF we focused our attention on description of last. Other reason, which motivates further investigation of pure liquid metals is significant discrepancy of structure parameters, published by various authors.

Analysis of SF and PCF for most liquid metals is based mainly on quasicrystalline approach of structure or the hard-sphere model [1,2]. First of them supposes the similarity of atomic distribution in solid and liquid state, whereas the second one considers the structure of liquid metal as another than solid one. Hard sphere model supposes that atoms interact only by means of repulsive forces as hard balls and does not account the attraction forces. Using both models shown the restricted capability of them to describe the structure of various liquid metals over wide temperature range, especially those with inhomogeneous structure. Most of problems standing before researches are related with with analysis of the main structural characteristics and in particular the maxima profile in SF or RDF. Still is not fully understood the nature of the asymmetry of the first maximum and the presence of shoulder on its right hand side, wich is most pronounced in such metallic melts as Ga, Bi, Sb and Sn.

We have obtained the SF for liquid Ga by X-ray diffraction at different temperatures and then used them to calculate the PCF by Fourier transformation. Taking into account the asymmetry of principal peak in SF we assumed that asymmetry is caused by the presence a more complicated structure in comparasion with simple liquid metals, whose principal peaks show the symmetric shape. Taking into account numerous literature data on structure studies by diffraction methods and results on measurements of structure sensitive physical properties (viscosity, density, surface tension etc.) we suppose that in opposite to crystalline structure, describing by one kind of neighbor atoms arrangement in liquid state there is at least the two kind short range order structures. On that reason the structure should be displayed in profile of principal peaks in group of above mentioned metals. We also supposed that two kind structural units scatter x-rays at diffraction investigation independently. Therefore, it is possible to consider the profile of principal peak as the result of additive contributions from each kind structure units (clusters). According to such assumptions we have fitted the principal peaks of SF at different temperatures, using the Gaussian functions with different parameters.

1.Theoretical backgrounds

The structure studies of liquid metals by means of diffraction methods have a long history and main results, following from them are published in few monographs, among which most known are [1,4]. These results most effectively influenced the development of general postulates in physics of liquid metals. The approaches, based on similarity of liquid and crystalline phases are success to describe the structure and properties of metals with close packed atomic structure and metallic bonding (Cu, Al, Pb etc.). In this case the liquid metal is supposed to be as consisting crystal like clusters with short range order similar to crystalline cell. Some part of of atoms is supposed to be absolutely disordered as in gaseous phase and the fraction of this phase decreases with heating. Efforts to determine the fraction of clusters at any temperature and to describe the structure sensitive properties with using of this approach have not be successful on the different reasons but the main of them is that it is difficult to take

into account the change of structure of clusters and interaction between neighbor atoms upon transition from solid state to liquid or vice versa. One of the methods of this approach is Prince & Glauber method of interpretation of radial distribution functions of atoms [3]. This method is based on the procedure of transformation the atomic arrangement of ideal crystal cell into short range order distribution in liquid state by topologic and diffuse disordering. Unfortunately this model cannot describe the structure of less density packed in liquid state metals and revealing the shoulder in principal peak of SF as well having problems with description of structure temperature dependences.

Another model, which was already mentioned early, is based on the assumption that liquid has own features, by which cannot possess crystalline materials and gases. Interaction between atoms, considered as hard sphere of some diameter and distributed with some definite packing coefficient is written by formula:

$$\varphi(r) = \begin{cases} \infty, & r \leq \sigma \\ 0, & r > \sigma \end{cases} \quad (1)$$

where $\varphi(r)$ is pair potential, σ is hard sphere diameter, determined from experimental data on density.

This model allowed to obtain the solution of the equation of statistical theory of liquids in which pair potential is related with pair correlation function and to obtain the formula for SF. This formula was used to calculate the SFs for a lot of liquid metals which were compared with experimental SFs and showed good agreement in most cases. But as in case of crystal like approaches this model has a difficulties to describe the structure of liquid metals with shoulder in principal peak of SF. In other words it is difficult to describe the inhomogeneity in structure of liquid metals.

Thus, analyzing the results obtained by researchers with using the different methods, it can be argued that none of them is capable to give the general description and complete understanding of the structure of liquid metals. One of the main aim is not only to improve experimental research methods, but also finding the more effective ways of interpreting the results. This work was aimed to obtain some new results in this area of problems. For this reason, an investigation the structure of molten gallium was carried out attempting to interpret the fine features of the diffraction peaks.

Published data on structure studies of liquid gallium by means of diffraction methods (X-rays [4] and neutron diffractions [5]) indicate some differences between melt gallium and other liquid metals. The asymmetry of principal peak, revealed even as a shoulder is most pronounced at temperatures close to the melting temperature (323 K) and persists when temperature increases [6]. Upon strong supercooling this shoulder is transformed into clearly resolved maximum [7]. There are various assumptions about the nature of it [8-10], but now there is no clear explanation of the nature. Most researchers believe that is the expression of the structural inhomogeneities in liquid state, but no quantitative equations, evaluable to describe this relationship. The purpose of this paper was to make a small step in this direction.

2. Experimental

The experimental intensity curves were obtained in high-temperature X-ray diffraction camera for investigation of the metal melts. $\text{CuK}\alpha$ — adiation, monochromatized by single crystal graphite, installed into the primary beam according to Bragg-Brentano focusing geometry[11]. Experimental scattering curves were corrected on incoherent scattering and polarization according to the procedure described in [11]. After normalization procedure the structure factors have been calculated:

$$a(q) = \frac{I(q)}{N F^2(q)} \quad (2)$$

where $a(q)$ — structure factor, N — number of atoms, $F^2(q)$ — atomic scattering factor, $q = \frac{4\pi \sin \theta}{\lambda}$ — wave-vector, λ — wavelength of X-rays, θ — half scattering angle.

Atomic distribution functions have been calculated from SF by means of integral Fourier transformation:

$$4\pi r^2 \rho(r) = 4\pi r^2 \rho_0 + \frac{2r}{\pi} \int_0^{\infty} q [a(q) - 1] \sin(qr) dq \quad (3)$$

where r — is a distance from any atom to another one; ρ_0 — mean atomic density.

3. Results and Discussion

Structural factors for liquid gallium were obtained over wide temperature range and some of them are shown in Fig. 1. It can be seen that the peaks are not perfectly symmetrical, especially the first one. As in publications of other authors, we have observed clearly pronounced shoulder on the right hand side of the main peak, which is an evidence of structure another than in liquids with symmetric maximum. In order to interpret this maximum feature, related with structural inhomogeneities we approximate it as a sum of partial Gaussian curves, the such parameters of which as maxima positions and half — height width were determined and used to estimate the main structure parameters- most probable distances to neighbor atoms and medium size of clusters;

$$= \frac{7.73}{S_1} \quad (4)$$

$$= \frac{2\pi}{\Delta s} \quad (5)$$

The temperature dependence of the of the first and second subpeaks positions in SF indicate a decrease in these parameters with increasing temperature (Figure 2) that according to first formula correspond to increasing of distance to neighbor atoms in clusters. It should be noted that for second type of clusters temperature dependence of s_1 shows the anomaly in the temperature range 353-823 K. Thus, besides the topological disordering of atomic arrangement there is some transformation of structure in second kind clusters.

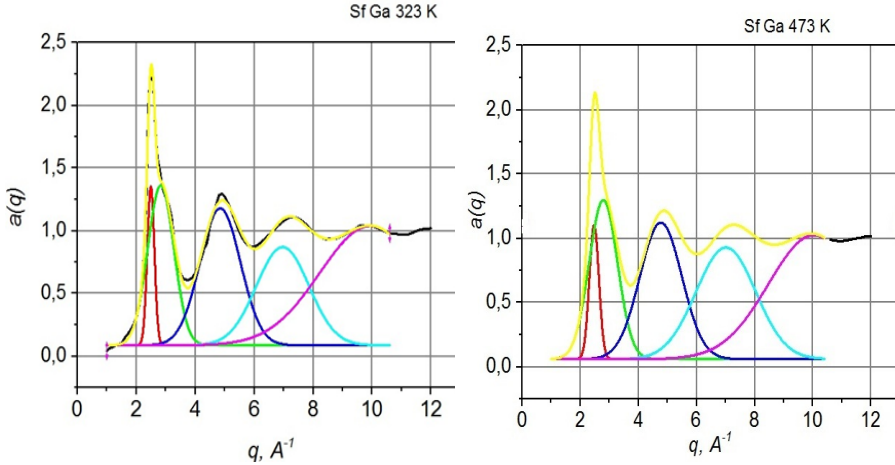


Fig.1. Interpretation of the SF for liquid gallium partial Gaussian curves at different temperatures

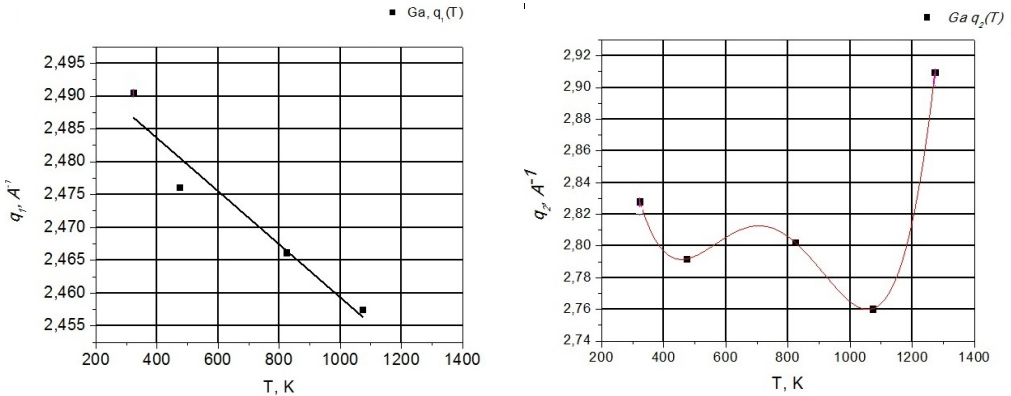


Fig. 2. The temperature dependence on the first maximum SF for clusters of two types.

For each type of structural units we have analyzed the temperature dependence of cluster size (Figure 3). As one can see at temperature, not far from melting temperature the size of first kind clusters is large enough and is about 2 nm, while at the same temperature the size of the second type clusters is approximately four times smaller. For the first type of cluster temperature dependence of their size reveals almost linearly function. Therefore the heating promotes the reduction of such cluster size due to growth of intensity of atomic vibrations causing moving of most active atoms out of clusters.

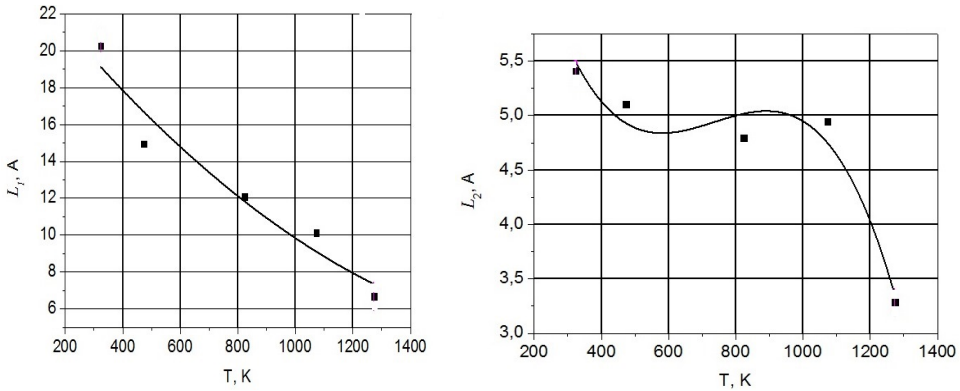


Fig. 3. The temperature dependence on the cluster size in the two types structural units.

In the second type of clusters not only the cluster sizes are notably smaller, but the temperature dependence of this size is different. We can see that with heating there is only a slight reduction in the size of the clusters, indicating their higher temperature stability. Therefore, these dependences allowed us to suggest that the structural units of the first type are the metal clusters with metallic bonding, whereas the structural units of the second type contain less number of atoms, which interact by means of covalent bonding. Clearly, that covalent bonding is stronger than the metallic one and on that reason in clusters this type there is no a rapid decrease in size as is the case with metal clusters. Thus the structure of liquid gallium is microinhomogeneous and the main its characteristic is the presence of clusters with different atomic bonding and with different numbers of atoms. Our data are in consistent with the analysis of structure data for liquid metals with asymmetric principal peak, reviewed in [1]. Our method of interpretation of structure data is fruitful for analysis of thermal dependences of physical properties of metals and their alloys. It is known that thermal expansion of liquid metals show some features, which are not observed in solid phases, namely many melts have negative thermal expansion coefficient that occurs due to dominant contribution of free volume in mechanism of thermal expansion. According to our data to our results some liquid metals can reveal complicated mechanism of thermal expansion and beside dominant contribution of free volume the change of interatomic distances in clusters and various of their size should be taken into account.

Conclusions. Asymmetry of the first maximum in SF of liquid gallium exists in a wide temperature range and is related with its microinhomogeneous structure. Principal peak of SF can be interpreted as additive sum of two maxima fitted to Gauss functions, parameters of which are different and depend on temperature. The analysis of the obtained values of partial structure parameters and their temperature dependences led to the conclusion that the structure of the liquid gallium consists of two kind clusters: the larger clusters with metallic bonding between atoms and the smaller ones with a covalent bonding. At heating the fraction of metallic clusters increases, whereas the fraction of second kind clusters simultaneously decreases. Temperature dependences of mean size in clusters of each kind are different that should influence the mechanism of thermal expansion in liquid gallium.

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Структура і ближній порядок рідкого галію

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Була вивчена структура рідкого галію в широкому інтервалі температур. Аналіз даних, отриманих методом дифракції, дозволив зробити деякі висновки про структурні особливості рідкого галію. Зокрема, є чітка асиметрія першого максимуму структурного фактора та існування плеча на його правому боці. Також проаналізовано температурну залежність структурних факторів для рідкого Ga за його неоднорідною структурою. Інтерпретація проводилася за умови, що структура рідини Ga складається з кластерів з різним розподілом атомів, а також різних типів хімічних зв'язків між атомами. Структурні одиниці чутливі до температури. Також було виконано розщеплення основного максимуму структурного фактора на парціальні криві Гауса, що відповідали певним структурним одиницям розплаву. Кожен структурний компонент розплаву показує інший характер температурної залежності. Також передбачається, що парціальні піки для кожного кластера описуються гаусовими функціями.

Структура и ближний порядок жидкого галлия

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Была изучена структура жидкого галлия в широком диапазоне температур. Анализ данных, полученных методом дифракции, позволил сделать некоторые выводы о структурных особенностях жидкого галлия. В частности, есть четкая асимметрия первого максимума структурного фактора и существование плеча на его правом боку. Также проанализирована температурная зависимость структурных факторов для жидкого Ga по его неоднородной структуре. Интерпретация проводилась при условии, что структура жидкости Ga состоит из кластеров с различным распределением атомов, а также различных типов химических связей между атомами. Структурные подразделения чувствительны к температуре. Также было выполнено расщепление основного максимума СФ на частичные кривые Гаусса, которые отвечают определенным структурным единицам расплава. Каждый структурный компонент расплава обнаруживает другой характер температурной зависимости. Также предполагается, что частичные пики для каждого кластера описываются гауссовыми функциями.

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