

## Correlation between diffraction and viscosity data for Bi–Ga molten alloys

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**Abstract.** Structure of Bi<sub>100-x</sub>Ga<sub>x</sub> molten alloys containing 38.5, 50, 70 and 91.5 at. % Ga has been studied by means of X-ray diffraction method and compared with viscosity measurements data. Significant changes in the structure factor profile were observed in vicinity of the concentration 70 at. % Ga. The dynamic viscosity coefficient was calculated by use of a statistical atomic distribution model and a Born–Green kinetic theory. The concentration dependence of viscosity is in agreement with change of structure parameters obtained from diffraction data.

**Keywords.** Bi–Ga alloys; structure factor; X-ray diffraction method; viscosity; melts.

### 1. Introduction

The main features of Bi–Ga system are an absolute insolubility of components in a solid state and limited in liquid, that is pronounced in presence of wide concentration and temperature area of immiscibility in liquid one. Studies of such systems in liquid phase are important for understanding of miscibility gap formation mechanism on microscopic scale and relation of this mechanism with structure changes. During the last few years, most of the researchers have focused on the study of physical properties in the vicinity of critical point, where they reveal an anomalous behaviour. However, results of diffraction studies as well as physico-chemical properties measurements are interpreted commonly separately of each other, because of limited availability of data, in which the relation between structure and properties is considered.

Constituents of this system, Bi and Ga being elements, their structures in liquid state have atomic distribution at which atomic volume decreases upon melting. Ga is more similar to typical metals in liquid state than Bi. Particularly its coordination number is higher than for Bi ( $Z_{\text{Ga}} = 10.8$ ;  $Z_{\text{Bi}} = 9.0$ ), indicating larger fraction of covalent bonds in liquid Bi upon melting than in Ga. Between them exists the large difference in atomic size (29.6) whereas the electronegativity difference is small (0.15). Hence, the conditions for atomic segregation are satisfied.

Interest in Ga–Bi system is also motivated by the fact that this is a unique system with large miscibility gap, whose both components are semimetals with above mentioned features

in structure and properties upon melting. The other binary systems with miscibility gap in the liquid state are Ga–Pb, Ga–Tl, Cu–Pb, etc.

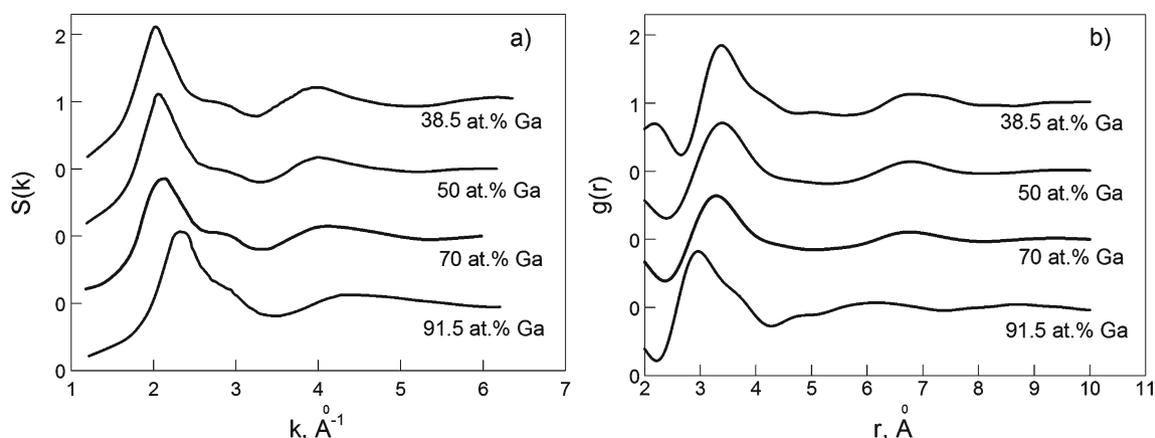
The structure and some kinetic properties (viscosity, diffusion) of liquid Bi–Ga alloys were investigated earlier (Buhalenko *et al* 1992; Inui and Takeda 1993; Vollmann and Riedel 1996; Sklyarchuk *et al* 2008; Yagodin *et al* 2008). However, only a few of them are available, viz. the ones having relation between structure and kinetic properties for systems with a miscibility gap. In particular, the correlation between local structure and thermodynamic properties has been studied by Inui and Takeda (1993) by means of diffraction method, ultrasonic velocity and density measurements. Unfortunately, up to now no similar studies on correlation between structure and viscosity exist for Bi–Ga liquid alloys.

Thus, the main aim of this work was to find out the correlation between the viscosity concentration dependence behaviour and structure features in molten immiscible alloys, viz. in Bi–Ga melts. For that reason, X-ray diffraction (XRD) investigations were carried out for Bi<sub>100-x</sub>Ga<sub>x</sub> liquid alloys ( $x = 8.5, 50, 70, 91.5$  at. %) with subsequent calculation of viscosity coefficient using the statistical approach based on the formalism of Iida *et al* (1976) and the kinetic theory of Born and Green (1947). The calculated results of viscosity were compared with available literature data and our earlier published results (Sklyarchuk *et al* 2008).

### 2. Experimental

Ingots of bismuth and gallium (both of 99.99% purity) were used to prepare the alloy samples.

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**Figure 1.** Structure factors (a) and pair correlation functions for Bi-Ga liquid alloys (b) at a temperature, 644 K.

The XRD measurements were carried out by means of an X-ray diffractometer using  $\text{CuK}\alpha$  radiation monochromatized with LiF single crystal, in the  $2\theta$  range from  $10^\circ$  up to  $140^\circ$ . A detailed description of the experimental technique was reported (Plevachuk *et al* 2009). The measuring of scattered intensity was done with an accuracy better than 2%. Main structure parameters obtained from structure factor (SF) and pair correlation function (PCF) were analysed.

### 3. Results and discussion

Experimental SFs and PCFs for liquid  $\text{Bi}_{100-x}\text{Ga}_x$  alloys of different Ga content are shown in figure 1. One can see that addition of Ga to Bi is accompanied with significant transformation of SFs. The change of their principal peak profile and shoulder on its right hand side is attributed to change in interatomic bounds which should cause the atomic redistribution. As it can be seen from this figure and table 1, the principal peak position in SF persists on addition of Ga up to 70 at. %. Moreover, in case of alloys containing 38.5 and 50 at. % of gallium, parameter  $k_1$  is even less than 1 for pure liquid Bi (2.11 Å, table 1). This parameter is the principal peak position in structure factor and is a characteristic of short range order in reciprocal space. Such behaviour has allowed us to suppose that the Bi-based structural units are not diluted by Ga-atoms. Most probably the Bi forms the self associated clusters. Tendency to segregation in atomic arrangement is also confirmed by the fact that shoulder is evidently pronounced in SF for each alloy, especially it is most pronounced for melt with 70 at. % of Ga. Drastic change of SFs is observed for molten alloy, where content of Ga is 91.5 at.%, revealing the transition to Bi-like structure.

Similar behaviour is also observed in concentration dependence of pair correlation functions (figure 1b). Significant increase of Ga concentration does not lead to corresponding decrease of most probable interatomic distance  $r_1$  and one can see only a small reduction of this parameter. The second interatomic distance  $r_2$  is also larger than in liquid Bi.

This distance is somewhat less for alloy with 91.5 at.% of Ga but it remains larger than corresponding value for liquid Ga. Therefore, the anomalous behaviour of interatomic distances is observed not only in first coordination sphere, but also in the next spheres. It should be noted that the increase of interatomic distance is not accompanied by simultaneous decrease of atomic packing density, because the number of neighbours ( $Z$ ) is large for most investigated alloys (table 1). Results obtained from analysis of diffraction data are in accordance with the results of Inui and Takeda (1993), where the remarkable change in the structure factors have been observed at a critical concentration of around 70 at.% Ga. Attempt to remain at a large distance to neighbouring atoms is evidence of large concentration fluctuations in these molten alloys. Certainly, that such fluctuations should be displayed in viscosity coefficient values. Existence of remarkable concentration fluctuations is confirmed by results of diffraction studies by Buhalenko *et al* (1992), where dependence of structure factors on time at  $T = 573$  K was investigated. It was found that atomic distribution significantly changes with time of holding at this temperature and the structure of melts is unchangeable when time of holding equals 2 h or more. Unfortunately the reason for such a behaviour is not analysed in this paper. From this work, existence of three concentration intervals for the structure is seen, but is not confirmed by our other studies.

**Table 1.** Structure parameters obtained from total structure factors and pair correlation functions.

At% Ga	$k_1(\text{Å}^{-1})$	$k_2(\text{Å}^{-1})$	$r_1(\text{Å})$	$r_2(\text{Å})$	$Z$
91.5	2.32	4.30	2.96	6.17	8.3
70	2.14	4.10	3.30	6.76	11.7
50	2.05	4.00	3.40	6.79	10.9
38.5	2.03	3.95	3.38	6.81	9.2
Bi	2.11	4.12	3.38	6.60	8.8
Ga	2.52	4.90	2.82	5.6	10.4

In order to understand the features of atomic distribution in these alloys it is also interesting to reveal the correlation between the data observed by means of diffraction method and viscosity results, which are highly sensitive to structure changes. For that reason, we have calculated the viscosity data using the statistical approach which is a most simple approach and the kinetic theory of Born and Green (1947). The last of them was by using the diffraction data and potential of pair interaction.

At first, the viscosity of binary ideal solution  $\eta^{\text{id}}$  was calculated according to additive approach:

$$\eta^{\text{id}} = \eta_1 x_1 + \eta_2 x_2, \quad (1)$$

where  $\eta_1$ ,  $\eta_2$ ,  $x_1$ ,  $x_2$  are viscosity coefficients and atomic fractions of pure elements, respectively.

The second step is to account for a nonideal contribution to viscosity:

$$\eta = \eta^{\text{id}} + \Delta\eta, \quad (2)$$

where  $\Delta\eta$  is the excess viscosity.

In order to calculate the excess viscosity we used the modified equation, which follows from the formalism of Iida *et al* (Terzieff 2008)

$$\Delta\eta = \Delta\eta_\sigma + \Delta\eta_M + \Delta\eta_S + \Delta\eta_V, \quad (3)$$

where  $\Delta\eta_\sigma$  is the hard sphere part contribution to viscosity, which is the function of diameters difference,  $\Delta\eta_M$  the hard sphere part contribution to viscosity, which depends on nuclear weights difference of components;  $\Delta\eta_S$  the soft sphere part of viscosity, which is determined by an attractive part in interatomic potential, and  $\Delta\eta_V$  the additional compo-

nent of viscosity, which is the dimensionless volume factor. The last equation can be written in following way:

$$\Delta\eta = (x_1\eta_1 + x_2\eta_2)^* \left( \alpha \frac{x_1 x_2 (\sigma_1 - \sigma_2)^2}{x_1 \sigma_1^2 + x_2 \sigma_2^2} + \beta \left[ \left( 1 + \frac{x_1 x_2 (M_1^{1/2} - M_2^{1/2})^2}{(x_1 M_1^{1/2} + x_2 M_2^{1/2})^2} \right)^{1/2} - 1 \right] \right) \left( + 2\gamma \Delta H / (RT) + 2\delta x_1 x_2 |V_1 - V_2| / (V_1 + V_2) \right), \quad (4)$$

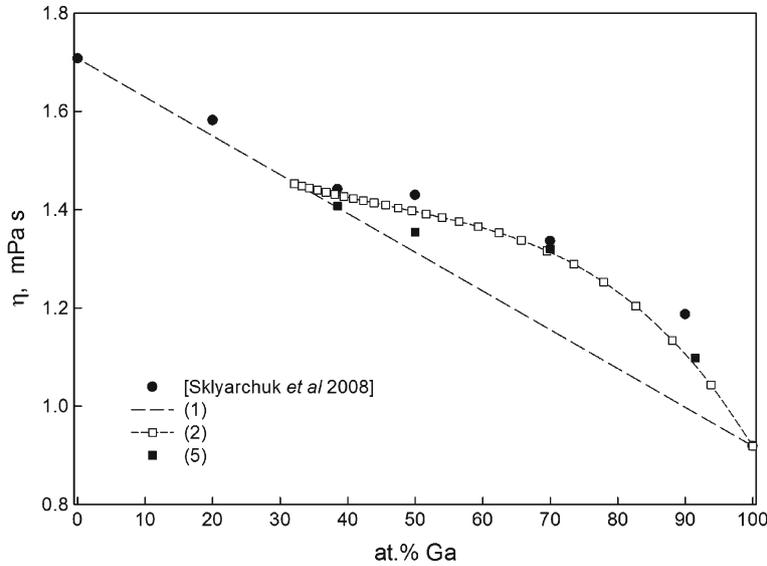
where  $V_1$ ,  $V_2$ ,  $\sigma_1$ ,  $\sigma_2$ ,  $M_1$ ,  $M_2$  are atomic volumes, hard sphere diameters and nuclear weights of components, respectively,  $\Delta H$  the enthalpy of mixing. The fitting parameters  $\alpha$ ,  $\beta$ ,  $\gamma$ ,  $\delta$  are as follows:  $\alpha = -4.05$ ,  $\beta = 12.0$ ,  $\gamma = -0.115$ ,  $\delta = -2.67$ .

Atomic volume and hard sphere diameter data were calculated using the density (Yagodin *et al* 2008) and packing fraction values (Ostrovskii *et al* 1988). Enthalpy of mixing values was taken from Huber *et al* (2008).

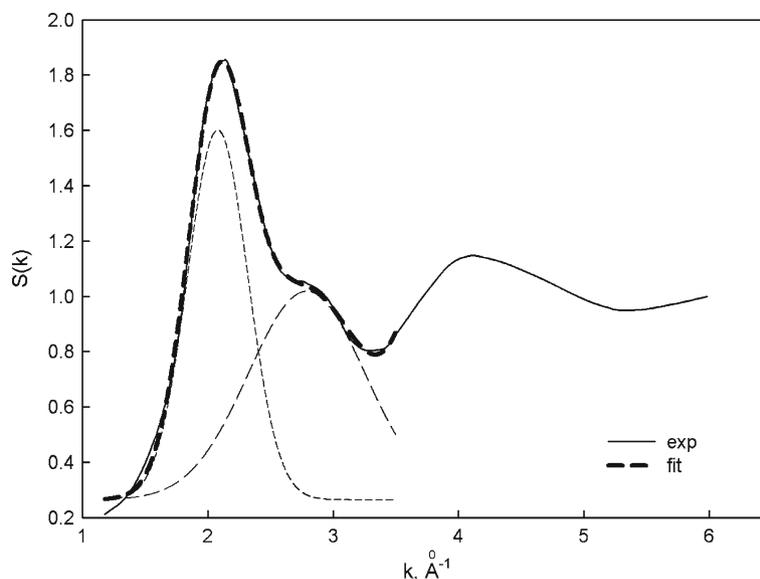
Born and Green (1947) derived a formula for viscosity of a liquid in frame of classic kinetic theory:

$$\eta = \frac{2\pi}{15V^2} \left( \frac{M}{kT} \right)^{1/2} \int_0^\infty g(r) \frac{d\varphi(r)}{dr} r^4 dr, \quad (5)$$

where  $V$  is the nuclear volume of liquid;  $M$  the nuclear weights of liquid;  $k$  the Boltzmann's constant;  $T$  the temperature;  $g(r)$  the pair correlation function and  $\varphi(r)$  the pair potential. The integral in (5) cannot be evaluated up to infinity limit, because we have the limited  $k$ -range of the experimental structure factors. On that reason some errors, which are known as cut-off errors are observed in  $g(r)$ . In order



**Figure 2.** Concentration dependence of viscosity for Bi–Ga liquid alloys at a temperature of 644 K.



**Figure 3.** Computer fitting of principal peak for  $\text{Bi}_{30}\text{Ga}_{70}$  liquid alloy.

to account for this error we have used special procedure (Kaplow *et al* 1965). In case of this model, we used the soft-sphere pair potential (Zelener *et al* 1981):

$$\varphi(r) = kT \ln(1 - \exp(-r^2/\sigma^2)). \quad (6)$$

By calculating the hard sphere diameters  $\sigma$  of alloys, the packing fraction value was found to be 0.53.

Results of viscosity calculation for above mentioned three models are shown in figure 2. One can see that experimental viscosity is in agreement with calculated ones by (2) and (5), and deviates from data obtained by means of (1). Thus, here we have also confirmation about deviation of atomic arrangement from random distribution that correlates with results of X-ray diffraction investigation. It can also be seen that the results obtained using (1), (2) and (5), respectively agree well with the experimental data in Bi-rich concentration region. The maximum deviation occurs in the interval from 50 at. % to 90 at. % of Ga which is also in agreement with the diffraction results. Therefore, significant viscosity increase within interval, corresponding to miscibility gap is supposed to be related with large size of Ga–Ga and Bi–Bi structural units.

Compared to earlier published works we focus more on the shape of principal peak. Taking into account the asymmetric profile of principal peaks in SFs for liquid alloys as well as for Ga and Bi we carried out computer fitting of these maxima in additive assumption. The result of such fitting for molten alloy, containing 70 at. % of Ga is shown in figure 3. As it can be seen from figure 3, the principal peak resulted from two kinds of structures: Bi- and Ga-like clusters (Wilson 1972).

We supposed that first of them corresponds to metallic clusters and second one to covalent clusters. Such param-

eters as peak positions and half height width have been determined from these partial maxima. The last of them was used for estimation of cluster size. It was found that metallic clusters for liquid Ga have a larger size than the ones for liquid Bi. Similar feature occurs for covalent clusters. On the other hand the parameters of both partial peaks are close to ones of liquid Ga within concentration interval from 0 to 50 at. Bi (near critical point) and then with the following Bi-content increasing, becomes more close to related parameters of liquid Bi. Therefore, one can note that observed behaviour of structure parameters as well as viscosity data at concentrations, corresponding to miscibility gap, is in correlation with less size of clusters in Bi-enriched melts. It should be noted, that results of structure analysis are based not only on analysis of typical parameters obtained from SF and PCF, but also by more detailed analysis of principal peak shape in SF.

#### 4. Conclusions

Structure of liquid  $\text{Bi}_{100-x}\text{Ga}_x$  alloys reveals the tendency of formation of self-associated atomic groups (clusters), especially at the concentrations, corresponding to miscibility gap. Shape of principal peak is analysed in more detail that confirmed the cluster structure in liquid state. The viscosity data, calculated using simple models, also indicate the specific behaviour within this concentration region. Use of diffraction data in order to calculate the viscosity coefficient yields good agreement between calculated and experimental data. Conclusions about tendency to self-association derived from diffraction data are in correlation with ones obtained from viscosity calculations.

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