Investigation of structural changes near the critical point in liquid Ga-Pb alloys using an acoustic method

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Abstract. The anomalous temperature dependence of the sound velocity above the liquid-liquid coexistence curve in the Ga-Pb system is associated with the critical fluctuations. A fit of the Fixman theory of the sound velocity data at the critical composition allows determination of the correlation length $\xi$. On the other hand, the temperature dependence of $\xi$ of the alloy with critical composition can be calculated in frames of the two-scale-factor universality hypothesis using interfacial tension data. Recently we proposed a new method of extracting the values of the liquid-liquid interfacial tension and densities of contacting phases along the coexistence curve from the results of acoustic measurements. The correlation length values determined from the sound velocity and interfacial tension measurements are in a good agreement to each other and in a reasonable agreement with the results of small-angle scattering experiments. All the critical exponents are determined by two exponents only, $\beta$ and $\mu$, which can be obtained from the coexistence curve, density and interfacial tension data.

1. Introduction
The increase in the concentration fluctuations near a critical point of the miscibility gap leads to anomalies in temperature dependences of the electrical resistivity, sound attenuation coefficient, specific heat and the coefficient of shear viscosity. The correlation length $\xi$ describes the spatial range of these fluctuations. The $\xi$ value can be obtained from the results of x-ray or neutron small-angle scattering experiments. However, these measurements are rather difficult for metallic systems. Therefore, it can be useful to calculate $\xi$ combining the results of measurements of the liquid-liquid interfacial tension temperature dependence and the theoretical hypothesis of the two-scale factor universality. Recently we proposed a new method of extracting the values of the liquid-liquid interfacial tension and densities of contacting phases along the coexistence curve from the results of acoustic measurements using the pulse phase technique [1].

The other way of the $\xi$ value determination is to fit the sound velocity data at the critical composition in accordance with Fixman theory. Before, we had measured temperature dependences of the sound velocity of Ga-Pb melts in the entire concentration range of their miscibility gap [2]. However, we could not perform these measurements for the sample with critical composition (41 ± 1 at. % Pb) near the
critical temperature $T_c$. In the present work the sound velocity in liquid Ga-40 at. % Pb alloy has been measured in the temperature range from $T_c$ up to 1100 K and corresponding $\xi$ value has been determined.

2. Experimental
The sound velocity in liquid alloy with 40 at. % Pb was measured in the range from $T_c$ up to 1100 K at a frequency $f$ of 30.3 MHz using a pulse phase technique with varying the acoustic path length. Details of the apparatus and the method of the sound velocity measurements in liquid alloys with a miscibility gap have been given in [2]. The accuracy of $v_s$ values is estimated to be $\pm 0.2\%$.

We have also used the acoustic method to determine the liquid-liquid phase separation curve for Ga-Pb system [2] and the liquid-liquid interfacial tension and the density of coexisting phases [1]. In particular, the method was used to measure temperature dependences of the interfacial tension in the Ga-Pb and Ga-Bi systems in the range from monotectic to critical temperatures. The data obtained are in a good agreement with literary data.

3. Result and Discussion
The temperature dependence of the sound velocity $v_s(T)$ for the investigated alloys is shown in figure 1. One can see that the sound velocity in the liquid Ga$_{60}$Pb$_{40}$ alloy deviates from a linear temperature dependence in a range of about 40 K above the critical temperature and decreases as the critical temperature is approached. According to [2] the anomalies near the phase separation curve in alloys with 30 and 50 at.% Pb have not been found. Thus it is reasonable to assume that the anomalous temperature dependence of the sound velocity above the phase separation curve is associated with the concentration fluctuations. According to Fixman [3] the sound velocity $v_s$ in the critical region is given by

$$\frac{(v_s - v_s^0)}{v_s^0} = -\frac{1}{2}HR(d),$$

where $v_s^0$ is the non-critical sound velocity; $H$ is a constant depending on the sound frequency $f$ and a critical temperature $T_c$; $R(d)$ is the real part of the definite integral which increases while $d$ decrease. The temperature dependence of $d$ is very simple: $d = d_0(T - T_c)$. $H$ and $d_0$ parameters satisfy the relation [3]:

$$H = (54 \cdot d_0 T_c)^{1/2} (\gamma_0 - 1) R(2\pi^2 C_p^0 n l^3)^{-1},$$

where $\gamma_0 = C_P^0/C_V^0$ is the specific heat ratio, $C_P^0$ and $C_V^0$ are the non-critical constant pressure and constant volume specific heats, $R$ is the gas constant, $n$ is the number density and $l$ is the Debye short-range correlation length. The $d_0$ and $l$ parameters are obtained by fitting experimental $v_s$ in accordance with (1). The theoretical $v_s$ is given as the solid curve in figure 1 with $d_0 = 1.3153$ K$^{-1}$ and $l = 10.27$ Å.

Using the Ornstein-Zernike-Debye approximation for the correlation length $\xi$ yields:

$$\xi = \frac{l}{\sqrt{6}}.\sqrt{1 - \frac{1}{2}}.$$
\[(\rho'' - \rho') = B(-\tau)\beta,\]  \hspace{1cm} (4)

\[(x'' - x') = C(-\tau)\beta,\]  \hspace{1cm} (5)

\[\sigma = \sigma_0(-\tau)\mu,\]  \hspace{1cm} (6)

\[\xi = \xi_0 e^{-\nu},\]  \hspace{1cm} (7)

where \(\tau = (T - T_c)/T_c\) is the reduced temperature, \(B, C, \sigma_0,\) and \(\xi_0\) are the critical amplitudes.

**Figure 1.** Temperature dependence of the sound velocity \(v_s\) in the liquid Ga\(_{60}\)Pb\(_{40}\) alloy. Solid curve is the theoretical values; dashed line is the experimental values extrapolated from higher temperatures; \(T_c\) is the critical temperature.

For the Ga-Pb system we have obtained \(\sigma_0 = 0.118 \pm 0.006\) J/m\(^2\) and \(\mu = 1.28 \pm 0.02\) [1] from acoustic measurements of the liquid-liquid interfacial tension. The critical exponent \(\beta\) derived from acoustic measurements [1, 2] is listed in table 1.

The critical exponents \(\alpha, \gamma, \eta\) and \(\nu\) are calculated by the following scaling relations in \(d\) dimensions:

\[\mu = (d - 1)\nu, \quad \alpha = 2 - d\nu, \quad \eta = (2\beta - \nu)\nu, \quad \gamma = (2 - \eta)\nu.\]  \hspace{1cm} (8)

Not all of these relations are independent. In fact, knowledge of two exponents suffices to determine the remaining ones. In table 1, we list a few of more frequently referenced exponents for the liquid Ga-Pb alloys together with theoretical estimations.

On the contrary, the critical amplitudes are not universal and depend on the microscopic parameters, and, therefore, on a considered system. Nonetheless, some ratios of amplitudes are universal. The standard amplitude combinations are considered in [5]. The amplitude of the correlation length can be estimated from the two-scale factor universality hypothesis which gives [5]:

\[\xi_0 = \left(\frac{k_BT_cR_{\sigma,\xi}}{\sigma_0}\right)^{1/2},\]  \hspace{1cm} (9)
where $k_B$ is the Boltzmann constant and $R\sigma_0\xi$ is a universal constant. Using obtained $\sigma_0$ and the amplitude ratio $R\sigma = (0.36\pm0.01)$ [6] the following value of the critical amplitude $\xi_0 = 1.93\pm0.08$ Å is obtained. The temperature dependence $\xi$ for liquid Ga-Pb alloys calculated by the equation (7) is shown in figure 2. The experimental $\xi$ values obtained from the neutron small-angle scattering experiments for the Ga-42.4 at.% Pb alloy [7] are also presented in figure 2. Correlation lengths calculated from the Fixman theory and from the scaling hypothesis are in a good agreement. The mixtures with 40 and 41 at.% Pb show a definite divergence of $\xi$ upon approaching $T_c$. The divergence of $\xi$ near the phase separation curve in the alloy with 42.4 at.% Pb is not found. It follows from these results and from sound velocity measurements that the critical phenomena exist only in a very small concentration range (~1-2 at.%)) and the temperature range of about 40 K above the critical temperature.

### 4. Conclusion

An anomalous temperature dependence of the sound velocity in liquid Ga - 40 at. % Pb alloy above the phase separation curve is associated with the concentration fluctuations. The Fixman theory can adequately explain this phenomenon. The correlation length values calculated from the Fixman theory and from the scaling hypothesis are in a good agreement.

### Acknowledgements

The author is thankful to the Russian Foundation of Basic Researches for the financial support of the work in frames of grants No. 07-02-96045

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### Table 1. Critical exponents for the Ga-Pb system, obtained from acoustic experiment, $\varepsilon$ - expansion and numerical modelling [4].

| Critical exponents | Acoustic experiment | $\varepsilon$ - expansion | Numerical modelling |
|--------------------|---------------------|---------------------------|-------------------|
| $\beta$            | $0.336 \pm 0.005^a$ | 0.333                     | 0.312 $\pm$ 0.003 |
|                    | $0.339 \pm 0.005^b$ |                           |                   |
| $\mu$              | $1.28 \pm 0.02^c$   | 1.166                     | 1.284 $\pm$ 0.003 |
| $\nu$              | $0.64 \pm 0.01^d$   | 0.583                     | 0.642 $\pm$ 0.003 |
| $\alpha$           | $0.080 \pm 0.001^d$ | 0.167                     | 0.125 $\pm$ 0.015 |
| $\gamma$           | $1.25 \pm 0.02^d$   | 1.167                     | 1.250 $\pm$ 0.003 |
| $\eta$             | $0.053 \pm 0.001^d$ | 0                        | 0.055 $\pm$ 0.010 |

$^a$ determined by fitting equation (4) to experimental data [1].
$^b$ determined by fitting equation (5) to experimental data [2].
$^c$ determined by fitting equation (6) to experimental data [1].
$^d$ calculated from relations (8).