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The viscosity of liquid Bi–Ga alloys

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Abstract. The shear viscosity of Bi–Ga melts in the entire concentration range was measured using an oscillating-cup viscometer. The viscosity data well above the temperature of phase separation can be represented by an empirical equation of the Arrhenius type. The activation energies of viscous flow are given. In the vicinity of the critical point the viscosity increases as the temperature decreases. This behaviour is analysed in terms of various models. The critical exponent γ is found to be $\gamma = 0.032 \pm 0.003$.

1. Introduction

The liquid Bi–Ga alloy system has a miscibility gap in the concentration range between 38.5 and 91.5 at.% Ga. The coordinates of the critical point are reported to be 70 at.% Ga and $T_c = 262^\circ\text{C}$ [1]. At the critical point a second-order phase transition occurs, which is similar to that at the liquid–vapour critical point of metals.

Few experimental studies concerning critical phenomena have been carried out for metallic alloys at elevated temperatures. This is also true for the Bi–Ga system, for which measurements on electrical conductivity [2], structure [3, 4], ultrasound velocity [3, 5, 6] and specific heat capacity [7] have already been reported. Commonly the measurements are not extended close enough to the phase separation line, and the temperature resolution capability is too low, to obtain information about critical phenomena. This is also true for viscosity measurements published before [8, 9].

This paper presents the results of viscosity measurements for liquid Bi–Ga alloys throughout the entire concentration range at temperatures ranging from the monotectic temperature up to 800°C with enhanced temperature resolution. Further it is shown that the method of the oscillating cup is suitable for investigating critical phenomena in metallic alloys with a miscibility gap at elevated temperatures.

2. Experimental details

Viscosity measurements were carried out using a computer-controlled oscillating-cup viscometer which is shown in figure 1. The oscillating system consists of a Kanthal wire of about 36 cm length with a diameter of 0.22 mm, supported by two chucks, as used in precision lathes, and a stainless steel rod in the upper low-temperature region with a removable inertial body. The lower part of the oscillating system consists of a thin aluminium rod, to which a stainless steel container with the cylindrical quartz cup inside is fastened. The viscometer furnace has a bifilar Kanthal resistance heater 500 mm long, the wire being led inside a Alsint core (of 60 mm inside diameter) in the axial direction, in order

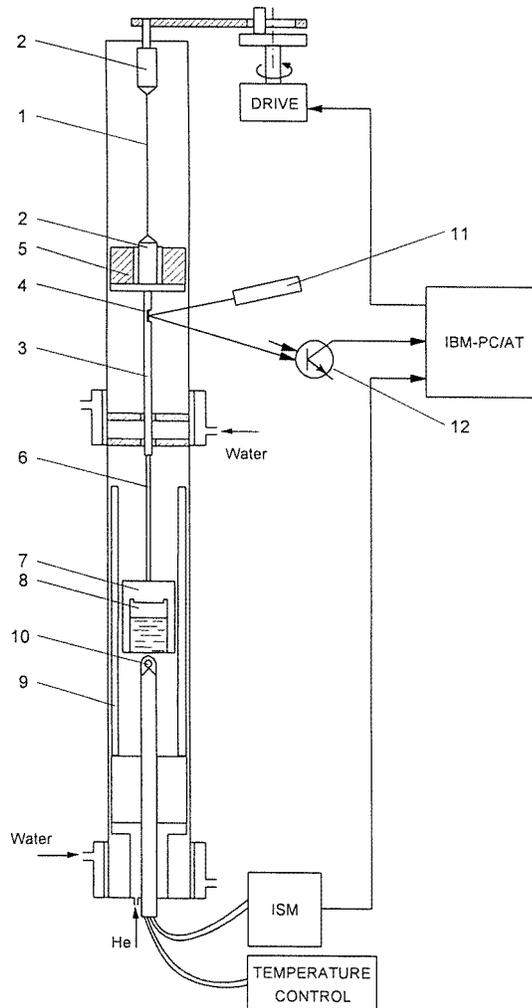


Figure 1. Oscillating-cup viscometer: 1, Kanthal wire; 2, chuck; 3, stainless steel rod; 4, mirror; 5, inertia cylinder; 6, aluminium rod; 7, stainless steel container; 8, quartz crucible; 9, electric heater (furnace); 10, thermocouple; 11, laser; 12, optical detector.

to minimize the influence of the remaining magnetic field. The temperature is measured with a (Pt–Rh)–Pt (S-type) thermocouple, arranged just below the cup and calibrated by measuring the viscosity of samples of pure (99.999%) elements Pb, Sb and Ag at their melting points. This way an accuracy better than 0.5 K in the whole temperature range was achieved. The voltage of the thermocouple is recorded, digitized and transmitted to the PC by an intelligent sensor module (ISM). The mechanical oscillation initiator consists of a drive with a limiting switch, controlled by the PC. The period and logarithmic decrement of the oscillations are determined with an optical system. A laser is directed onto the mirror on the pendulum. The reflected beam strikes twice, for each oscillation, a photodiode fixed on a free position apart from the oscillation zero and gives impulses, which are transmitted to an internal clock in the PC. Here the corresponding times are measured and stored. The

period and logarithmic decrement of the oscillations are then obtained by an optimization procedure, given in detail elsewhere [10, 11]. The initiation of torsional oscillations, data collection and reduction as well as determination of viscosity are controlled and saved by a PC.

The viscosity η is calculated using Roscoe's [12] equation for cylindrical samples with radius R , height H and a free upper surface, modified in the following way.

(1) The damping Δ_0 of the oscillating system without the liquid sample (logarithmic decrement δ_0 in terms of 2π) was taken into consideration in a correct way (see equation (1)).

(2) The second term of coefficient a_0 (see equation (3)) reads correctly, $-3\Delta/2$ instead of $-1\Delta/2$ as given in [12].

The equations then are

$$\eta = \left(\frac{2J(\Delta - \Delta_0)}{R^3 H z} \right)^2 \frac{1}{\pi \rho \tau} \quad (1)$$

$$z = \left(1 + \frac{R}{4H} \right) a_0 - \left(\frac{3}{2} + \frac{4R}{\pi H} \right) \frac{1}{p} + \left(\frac{3}{8} + \frac{9R}{4H} \right) \frac{a_2}{2p^2} \quad (2)$$

$$a_0 = 1 - \frac{3\Delta}{2} - \frac{3\Delta^2}{8} - \frac{\Delta^3}{16} \quad (3)$$

$$a_2 = 1 - \frac{\Delta}{2} - \frac{\Delta^2}{8} - \frac{\Delta^3}{16} \quad (4)$$

$$p = R \sqrt{\frac{\pi \rho}{\tau \eta}} \quad (5)$$

$$H = \frac{m}{\pi R^2 \rho} . \quad (6)$$

Here J is the moment of inertia of the oscillating system with the empty crucible, $\Delta = \delta/2\pi$ is the logarithmic decrement in terms of 2π , τ is the period of oscillations of the system with liquid sample, ρ is the density of the sample and m is the mass of the sample. The damping correction term $\Delta_0 = \delta_0/2\pi$ contains the damping due to internal friction of the wire and the damping due to the surrounding gas and was determined in accordance with Shvidkovski [13] from the damping δ'_0 of the system containing a solid sample, the moment of inertia of the solid sample being J' . Then δ_0 is given by

$$\delta_0 = \delta'_0 \sqrt{\frac{J + J'}{J}} . \quad (7)$$

Equations (1)–(6) correspond to the three-term working equation given by Brockner *et al* [14] for a similar experimental situation, if the period of oscillations of the empty system is assumed to be equal to τ . The equations give a computational accuracy of better than 0.1% in the large-cup limit for $p > 5$. The required densities of the alloys are determined from the densities of the components, the latter being taken from the literature [15].

The measurements were carried out in two experimental sets, which gave almost identical results within the limitations of experimental uncertainty. Typical values for the parameters of the two experimental arrangements at room temperature are given in table 1.

Typical values for the logarithmic decrement of the oscillating system with a liquid sample are of the order of $(40\text{--}60) \times 10^{-3}$. The viscometer was tested with distilled water and mercury at room temperature. An absolute accuracy of 0.3% was reached for water, and 1.2% for mercury.

Table 1. Typical parameters for the experimental sets at room temperature.

Set	m (g)	R (cm)	J (g cm ²)	$\delta_0 \times 10^3$	τ (s)
1	45	0.75	105	2.4 (Ar)	4.5
2	120	1.1	418	1.4 (He)	5.36

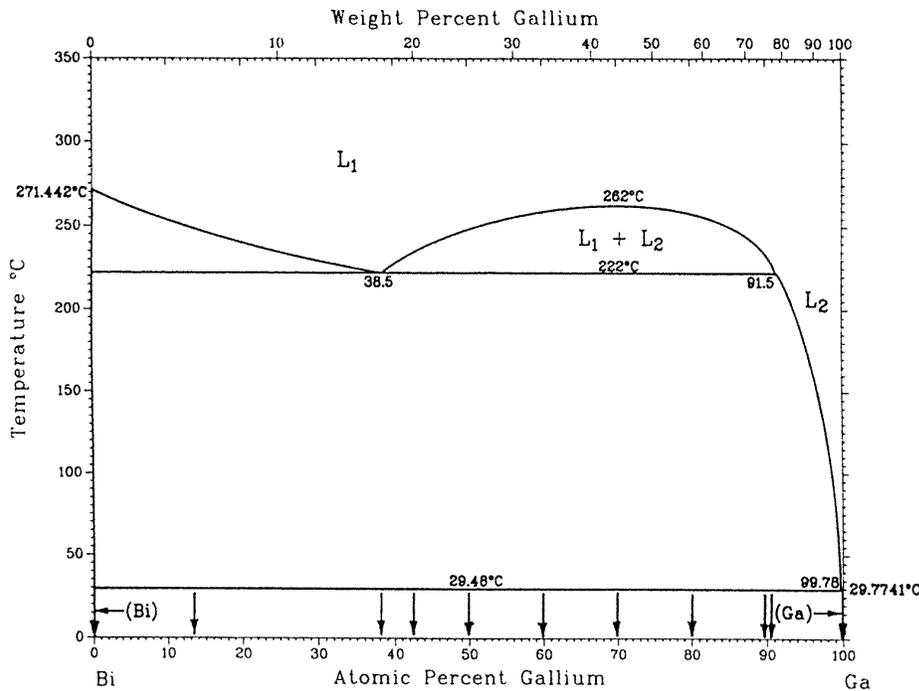
**Figure 2.** Phase diagram of the system Bi–Ga (after Massalski). The arrows indicate the chemical composition of the investigated alloys.

Figure 2 shows the phase diagram [16] of the Bi–Ga system; the composition of the investigated alloys is indicated by arrows. The Bi–Ga samples were prepared from pure (99.999%) elements in evacuated and sealed quartz tubes and quenched in water in order to obtain homogeneous samples. The measurements were performed in an atmosphere of pure Ar (set 1) or He (set 2). The samples were placed into the cylindrical quartz cups, the latter being covered with quartz lids and sealed with a ceramic glue. After melting, the samples were homogenized for 10–80 h at about 300 °C. Experimental data were obtained, starting measurements at the maximum working temperature for a given run with a cooling rate of 0.09–0.4 K min⁻¹ and a rate of 25 measurements per hour. The maximum shear rate was estimated to be of the order of 1 s⁻¹.

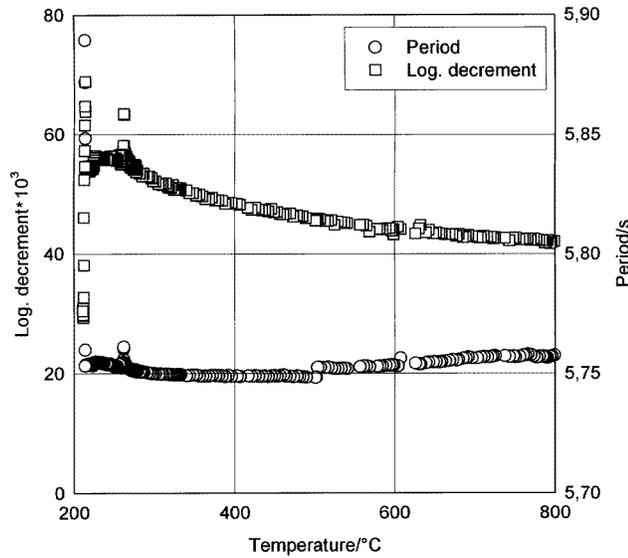


Figure 3. Period and logarithmic decrement measured for liquid $\text{Bi}_{30}\text{Ga}_{70}$ as functions of temperature. The peaks observed at $262\text{ }^\circ\text{C}$ and $222\text{ }^\circ\text{C}$ indicate the onset of phase separation into two liquids and crystallization.

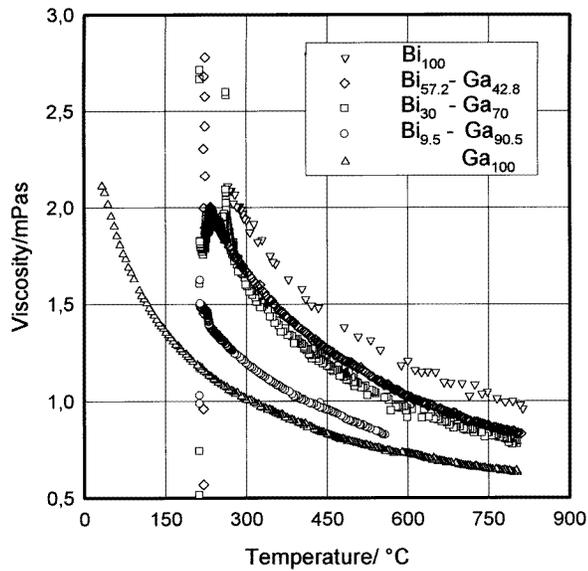


Figure 4. Viscosities of liquid Bi, Ga and three melts of the Bi–Ga system with a chemical composition within the miscibility gap as functions of temperature.

3. Results

Figure 3 shows the logarithmic decrement and the period of oscillations of the viscometer for a sample of critical composition $\text{Bi}_{30}\text{Ga}_{70}$ as a function of temperature. The measurement

was performed with a cooling rate of 0.4 K min^{-1} at elevated temperatures and 0.09 K min^{-1} near the critical temperature T_c . The logarithmic decrement increases with decreasing temperature. At a characteristic temperature it reaches its maximum value. Here the macroscopic phase separation begins. The onset of crystallization at the monotectic temperature also gives a pronounced change in the logarithmic decrement. The period of oscillations is determined by both the properties of the pendulum and the viscosity of the liquid sample. The decrease in the period with decreasing temperature at elevated temperatures is related mainly to the decrease in moment of inertia of the metallic container and the cup, located in the high-temperature region of the furnace. Only at temperatures below $300 \text{ }^\circ\text{C}$ is this effect overcompensated by the increasing inertia of the melt. As can be seen in figure 3, phase separation and crystallization can be detected easily by the changes in the period of the oscillations too. Finally, both effects disturb the harmonic oscillations, which gives further information about phase transitions in the liquid sample. In figure 4 the viscosities for samples of various compositions as well as for the pure elements are shown as functions of temperature. The temperature dependences of the viscosities are in general the same as for the logarithmic decrement. For samples with critical composition the viscosity increases with decreasing temperature and passes through a maximum value at the liquid–liquid phase separation. The viscosity values given for temperatures below this point should be interpreted as effective values. Some increase in the viscosity near the phase separation temperature is observed in melts of non-critical composition too; the effect vanishes gradually with increasing distance from the critical composition.

At elevated temperatures and in the concentration range near the critical composition the viscosity is almost independent of composition. So only three plots for the concentration range within the miscibility gap are given. In general some increase in viscosity is observable, if the Bi content of the melt is increased.

4. Discussion

At elevated temperatures the dependence of the viscosity on temperature can be described by an Arrhenius-type empirical equation:

$$\eta = \eta_0 \exp\left(\frac{Q}{RT}\right) \quad (8)$$

where η_0 is a constant or has a very weak dependence on temperature, Q is the energy of activation of viscous flow and R is the ideal gas constant.

Such behaviour is illustrated in figure 5, where the viscosity of a sample of critical composition ($\text{Bi}_{30}\text{Ga}_{70}$) as a function of temperature is given in a plot of $\ln \eta$ versus the reciprocal of the temperature, $1000/T$. The experimental data can be fitted by a straight line. A temperature dependence of this type for the viscosity is often found in melts of simple metals, if the properties of the melt can be well described by a hard-sphere model. Values of the activation energy of viscous flow for all investigated samples were determined by LSR fits of the experimental data to equation (8). These values are presented in figure 6. As can be seen from figure 6 for some compositions there is a remarkable scatter of computed values. The solid curve in figure 6 shows a fit of all obtained values by a polynomial of fourth order. The activation energy Q of viscous flow corresponds to the liquidus temperature; for melts with a low Ga content it is almost constant and decreases in the Ga-rich composition region. This result agrees well with the data found for simple metals [17] and solutions [18], where the energy of activation of viscous flow increases with increasing temperature of the melting point or the liquidus temperature. Values for the constant η_0

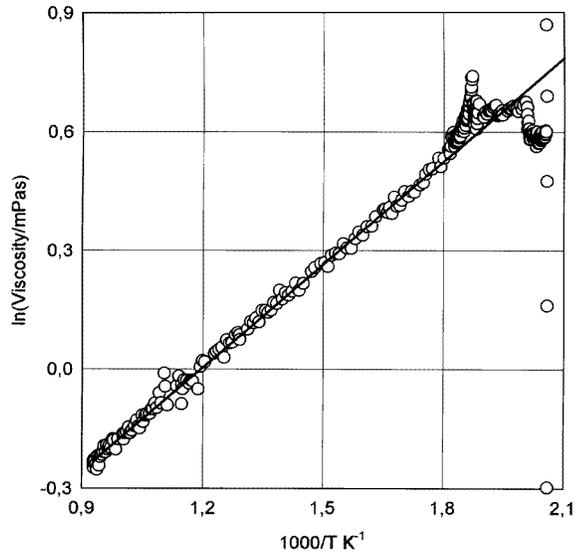


Figure 5. Natural logarithm of viscosity for liquid Bi₃₀Ga₇₀ versus reciprocal absolute temperature. The deviation from the straight line at lower temperatures is due to concentration fluctuations within the liquid. The maximum indicates the onset of phase separation.

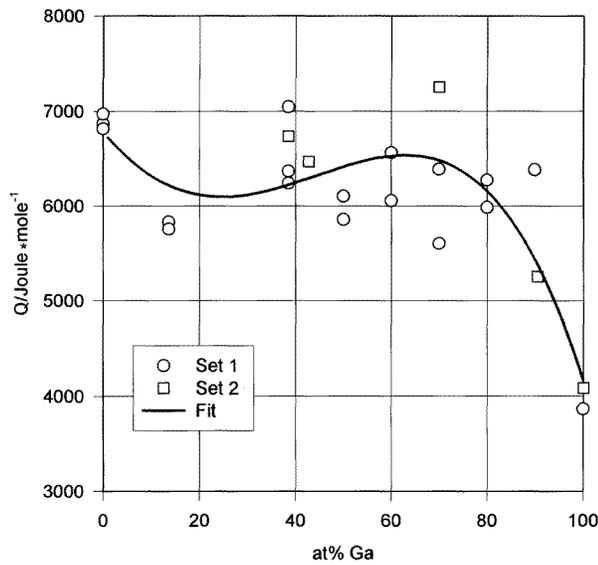


Figure 6. Energy of activation of viscous flow of the Bi–Ga system as a function of composition. The solid curve shows the fit of the values obtained by a polynomial of fourth order.

range between 0.35 and 0.6 mPa s and no remarkable dependence on composition was found.

In figure 5 it can be seen that, in a temperature range of some kelvins just above the critical temperature T_c , we observe a pronounced deviation in the viscosity from the

Arrhenius type of behaviour, which is caused by a correlated motion of the atoms. Although the model calculations of Singh *et al* [19] as well as structure investigations [3,4] gave evidence for the existence of self-correlation in Bi–Ga melts at temperatures far above the critical temperature T_c , the influence on viscosity seems to be insignificant, except in the very small temperature range near T_c , as mentioned before. It is usual to describe the viscosity increase near T_c by a power law of the form [19]

$$\eta = \eta_0 \exp(B\varepsilon)\varepsilon^{-y} \quad (9)$$

where $\varepsilon = |(T_c - T)|/T_c$ is the reduced temperature and η_0 , B and y are constants. The expression $\eta_0 \exp(B\varepsilon)$ represents the non-critical part of the viscosity while the term ε^{-y} describes the divergence of the viscosity introduced by concentration fluctuations within the melt near T_c , i.e. for $\varepsilon \ll 1$. Here y is the critical exponent. Equation (9) is based on the assumption that the critical behaviour of the viscosity near T_c can be described by adding to the temperature coefficient B of the non-critical part of the viscosity a term $-y(1/\varepsilon)$, which diverges at T_c :

$$\frac{1}{\eta} \frac{d\eta}{d\varepsilon} = B - y \frac{1}{\varepsilon}. \quad (10)$$

Usually the number of available data points in the range $\varepsilon \ll 1$ is too small to determine all four parameters of equation (9) with a satisfactory confidence level. Table 2 shows the result of fitting the data in figure 5 in the temperature range of 10 K above T_c (31 data points) to equation (9). This fit, called fit 1, gives a value for the parameter y of most interest, $y = 0.026$. This value is smaller than the expected theoretical value of 0.033 [20]; however, the theoretical value lies well within the error limits of this fit, which are rather high. If one fixes one of the parameters, say T_c , the situation is not really changed, because the fitting procedure always responds very sensibly to minor changes in T_c , say of the order of 0.1 K. As a consequence the fitting parameters η_0 , B and y will depend strongly on the fixed value T_c . We tried to use more data points for the present analysis by including such data for which $\varepsilon \ll 1$ no longer holds. Fit 2 in table 2 summarizes the results of a fit of all 112 data points in a temperature range of 240 K above T_c to equation (9). The statistical uncertainties of the parameters are significantly reduced, but the critical exponent y now is too high in comparison with the expected theoretical value. So in a further test we fitted the same data to a more realistic expression than equation (9), namely

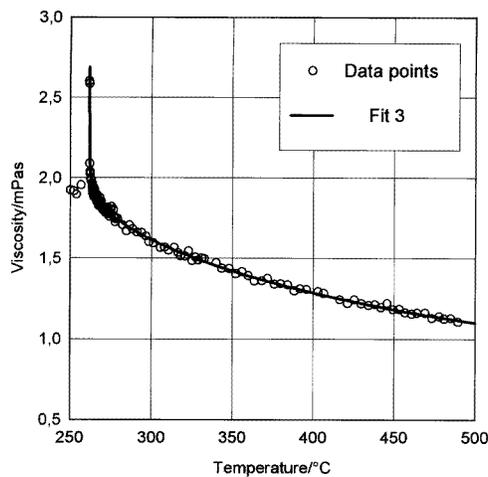
$$\eta = \eta_0 \exp\left(\frac{Q}{RT}\right)\varepsilon^{-y}. \quad (11)$$

The first two terms of equation (11) exactly describe the temperature dependence of the viscosity for the alloys under investigation in a wide temperature range as given by equation (8), while the last term of equation (11) takes into account the divergence of the temperature coefficient of viscosity near T_c in just the same manner as for equation (9). The result of fitting the same experimental data as in the case of fit 2 to equation (11) is given by fit 3 in table 2. The statistical uncertainties of the parameters are of the same order as for fit 2. The critical exponent y was found to be $y = 0.032 \pm 003$ in good agreement with the theoretical value. The solid curve in figure 7 shows the resulting curve of fit 3. Note that the energy of activation of viscous flow now is reduced from $Q = 7250 \text{ J mol}^{-1}$ as obtained from equation (8) to $Q = 5912 \text{ J mol}^{-1}$.

It should be mentioned finally that for all the fits given in table 2 the data point at 261.7°C with maximum viscosity (one of two open circles in figure 7 at $\eta = 2.6 \text{ mPa s}$) was omitted as the phase separation started here.

Table 2. Results of various fits of viscosity data from a Bi₃₀Ga₇₀ melt to equation (9) and to equation (11).

	Parameter	Value	Standard deviation	Coefficient of variation (%)	Dependency
Fit 1	η_0 (mPa s)	1.68	0.18	10.8	0.997
	B	-1.96	2.91	149	0.95
	y	0.026	0.017	66.6	0.997
	T_c (°C)	261.9	0.1	0.036	0.97
Fit 2	η_0 (mPa s)	1.57	0.02	1.1	0.96
	B	-0.936	0.036	3.8	0.78
	y	0.0367	0.0023	6.4	0.95
	T_c (°C)	261.889	0.002	0.001	0.60
Fit 3	η_0 (mPa s)	0.429	0.018	4.2	0.997
	Q (J mol ⁻¹)	5912	241	4.1	0.998
	y	0.0321	0.0029	9.0	0.97
	T_c (°C)	261.89	0.03	0.01	0.78

**Figure 7.** Viscosity of liquid Bi₃₀Ga₇₀ near the phase separation into two liquids. The solid curve indicates the quality of the fit to equation (11) (see text).

The analysis of the viscosity data in a wide temperature range, assuming a realistic temperature dependence of the non-critical viscosity, seems to be appropriate to obtain more valid values of the critical parameters of metallic melts with a miscibility gap. Further progress may be obtained by decreasing the cooling rates and increasing the accuracy of temperature and viscosity measurement.

5. Conclusions

In the entire composition range at temperatures well above the phase separation line, binary Bi–Ga melts show a temperature dependence of viscosity, which can be well described by an empirical expression of the Arrhenius type. The activation energy of viscous flow

depends only slightly on the composition of the melts and some correlation with the liquidus temperature is observed. The onset of the phase separation can be detected by these viscosity measurements using the oscillating-cup method. Near the critical point we observe a marked increase in viscosity, which is correlated with concentration fluctuations near T_c . Using experimental viscosity data in a wide temperature range and a correct temperature dependence of the so-called non-critical viscosity an experimental value of the critical exponent, $\gamma = 0.032 \pm 003$, was found which agrees very well with the expected theoretical value.

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