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Pressure–temperature diagram of liquid bismuth

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Abstract. The transitions in the Bi melt were found under high pressures. These transitions were accompanied by anomalies of electrical resistivity and volume. The (P, T) phase diagram of liquid Bi was investigated up to 7.7 GPa and 1020 K.

1. Introduction

Recently Tsuji and co-workers [1, 2] have developed a method for x-ray diffraction investigation of liquids under high pressures. In melts of Se, Cs and Bi, essential changes in short-range order structure were found under pressures up to 8 GPa.

The behaviour of the properties of these liquids seems to be rather complicated under high pressures and obviously cannot be described by simple models.

Bismuth is known to exhibit a number of polymorphic phase transitions under high pressures (about eight different crystalline phases), but still little is known about the behaviour of liquid Bi under high pressures. In [2], some transformations of the short-range order structure of liquid Bi between 4.7 and 7.3 GPa were found.

In this work the anomalies of the relative electrical resistivity and of the volume in liquid Bi were obtained. The volume changes were studied by means of the thermobaroanalysis (TBA) previously developed by Brazhkin *et al* [3] to investigate the non-metal-to-metal transition in liquid Se.

2. Experiment

To produce a high pressure a device of the 'toroid' type was employed [4] which had been calibrated using well known phase transitions in Bi (2.25, 2.7 and 7.7 GPa) and in Ce (0.75 GPa).

Figure 1(*a*) shows the cross section of the high-pressure 'toroid' chamber. The chamber consists of two anvils of special form and a pipe stone gasket between the anvils. The gasket transmits pressure to the sample cell placed at the centre of the chamber. Two different types of sample cell were used in the pressure apparatus.

When the anomalies of the relative electrical resistivity were investigated, a sample of Bi (3 mm in diameter and 4 mm long) was enclosed in a tantalum ampoule to prevent chemical reaction between Bi and the pipe stone surrounding the sample (see figure 1(*b*)). The sample was heated by passing an AC through the ampoule and the sample.

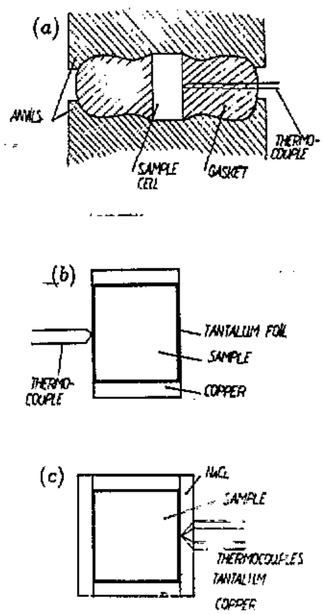

Figure 1. High-pressure chamber. (*a*) Schematic diagram of the device which was of the toroid type. (*b*) Sample cell for recording resistance anomalies. (*c*) Sample cell for TBA measurements.

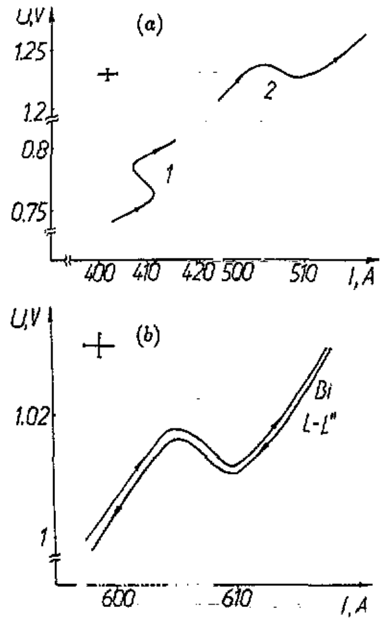

Figure 2. Anomalies in the voltage–current curve: (*a*) curve 1, the Sn(I)–Sn(III) transition ($\Delta\rho/\rho = 4\%$) at $P = 6$ GPa and $T = 500$ K (the sample was enclosed in a tantalum ampoule); curve 2, the Te(II)–Te(III) transition ($\Delta\rho/\rho \simeq 2.5\%$) at $P = 3.7$ GPa and $T = 600$ K (the sample was enclosed in a graphite ampoule); +, noise level of the measurements; (*b*) the L–L″ transition in Bi at $P = 4.2$ GPa and $T = 800$ K (the sample was enclosed in a tantalum ampoule).

Anomalies of the relative resistance were seen in the voltage–current curve. This method is often used to investigate phase transitions in metals at high pressures. For example see the investigation of solid Bi (P, T) diagram in [5]. Figure 2(*a*) shows the anomalies in the voltage–current curves obtained during well known solid-phase transitions under high pressures in Sn and Te [6, 7]. In figure 2(*b*) the anomaly in the voltage–current curve for liquid Bi is presented.

The TBA method is based on the influence of pressure on the thermo-EMF of thermocouples (as described by Getting and Kennedy [8]). All jumps in pressure caused by changes in the sample's volume are accompanied by anomalies in the thermo-EMF. We used chromel–alumel and Pt–(Pt + 10% Rh) thermocouples having dependences of thermo-EMF on pressure of different values and signs [8]. Drawing the thermo-EMF curve of one of the thermocouples versus that of the other during heating of a sample, one can see anomalies corresponding to volume jumps in the sample.

Special experiments were undertaken to eliminate the influence of phase transitions in the pressure-transmitting medium (pipe stone). The transitions in the pressure-transmitting medium were obtained by TBA in a chamber containing only pipe stone and a graphite cylindrical heater (graphite does not show any transition in the ranges of pressures and temperatures in which the experiments were carried out). The junction

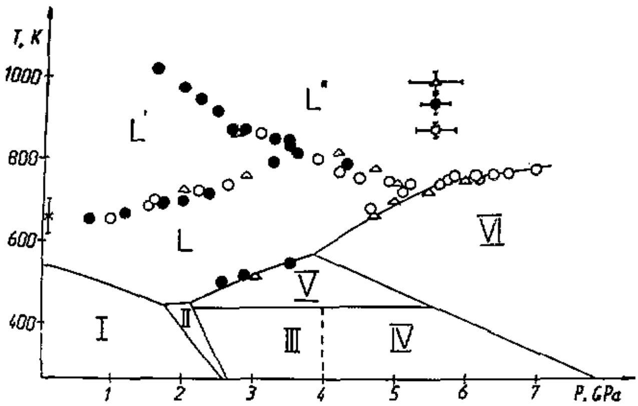

Figure 3. (P, T) phase diagram of bismuth: ——, melting temperature and phase boundaries in the solid state; △, anomalies in the electrical resistivity; ●, TBA signals (P = constant); ○, TBA signals (T = constant); ⫲, Derivatograph measurement datum. The values of the experimental errors are shown in the right upper corner of the figure.

of the two thermocouples was located near the heater. It was found that a thin (1.5 mm) NaCl tube surrounding the heater and the junction of the thermocouples eliminates the influence of the transitions in pipe stone on TBA signals.

The high-pressure cell used for TBA is shown in figure 1(c). A sample of Bi placed in a tantalum ampoule is surrounded by a NaCl damper. The junction of the thermocouples is located near the ampoule. This assembly is placed in a pipe stone gasket and is enclosed by two copper spacers to improve electrical contact between the cell and the anvils. After the chamber has been assembled, it was compressed, and the sample was heated by an AC. To ensure that the rate of heating does not influence the value of the anomalies, every experiment was repeated three to five times with different heating rates of 5–15 K min^{-1}. No influence on the value and on the (P, T) location of the anomalies within the accuracy of the experiments was found.

Errors in the measurements of the thermo-EMF were found to be about 0.25%. Errors for determining the (P, T) location of all anomalies are shown in the resulting phase diagram.

To investigate the behaviour of liquid Bi at room pressure, a computer-controlled Derivatograph C (MOM, Hungary) was used.

3. Experimental results and discussion

The experimental results are presented in figure 3 where the solid phases of Bi are also shown. There are three parts in the liquid region of the diagram for Bi which are separated by quite remarkable reversible anomalies of the relative electrical resistivity and by the TBA signals. Both the signals and the anomalies were obtained in rather narrow temperature and pressure intervals (50 K; 0.5 GPa). We believe them to be connected with some transformation in liquid Bi at high pressures.

Figure 4 shows examples of the curves obtained directly from experiment. The triple points are listed in table 1. The transitions discussed seem to be rather sharp and this feature was found previously for the non-metal-to-metal transition in liquid Se [3]. The

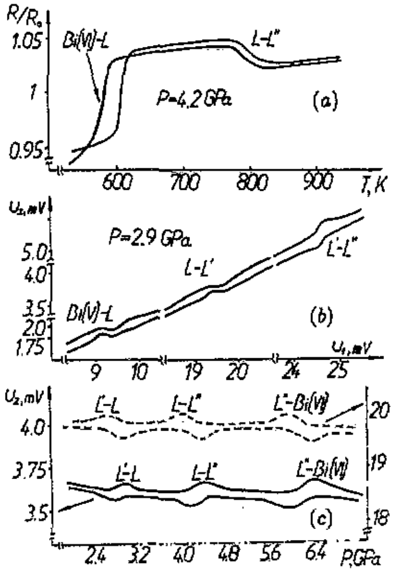

Figure 4. (*a*) Relative electrical resistivity versus temperature at $P = 4.2$ GPa showing the melting Bi(VI)–L and L–L″ transitions. (*b*) Thermo-EMF U_2 of the Pt–(Pt + 10% Rh) thermocouple versus the thermo-EMF U_1 of the chromel–alumel thermocouple at $P = 2.9$ GPa. (*c*) Thermo–EMFs of the Pt–(Pt–10% Rh) thermocouple (——) and of the chromel–alumel thermocouple (– – –) versus pressure when the temperature is constant (about 770 K). One can see three anomalies in both curves, which correspond to the L′–L and L–L″ transitions and the L″–Bi(VI) crystallization. All transitions are accompanied by a decrease in volume but the signs of the anomalies are different for different thermocouples because of the opposite signs of their pressure derivatives.

Table 1. The triple points of liquid Bi.

Triple point	P (GPa)	T (K)
L–L′–L″	3.5 ± 0.2	815 ± 10
L–L″–solid	5.3 ± 0.2	710 ± 10

L–L′ transition was accompanied by a decrease in electrical resistivity and an increase in volume. Both L′–L″ and L–L″ transitions were accompanied by a decrease in resistivity and a decrease in volume.

At pressures up to 1.6 GPa the TBA signals were so smooth for L′–L″ that it was not possible to measure them.

As to the L–L′ transition it was impossible to measure the behaviour of the melt at $P < 0.7$ GPa using our high-pressure apparatus. However, if we extrapolate the L–L′ curve to room pressure, we find the corresponding transition to occur at $T \simeq 630$ K. The investigation of liquid Bi at room pressure was carried out using the Derivatograph and indicated a small reversible endothermal peak ($H \simeq 1.2$ kJ mol^{-1}) in the temperature interval 640–710 K.

As was shown in [2], liquid Bi under a pressure of about 7.3 GPa has a short-range order structure like a BCC crystal (solid phase VI). We believe the liquid L″ to have the same structure. However, it is very difficult to say anything about the structure of the liquid L′. The short-range order structure of Bi melt even at room pressure is still under discussion.

We believe the data presented on the properties of the Bi melt under high pressures together with the data on the Se melt [3] allow us to propose that there may be transformations in liquids similar to first-order phase transitions in solids. This has been proposed on theoretical grounds previously by Mitus and Patashinskii [9].

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