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1994 J. Phys.: Condens. Matter 6 4625

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Pressure–temperature diagram of gallium antimonide melt

A G Umnov

Institute for High Pressure Physics, 142092 Troick, Moscow Region, Russia

Received 21 July 1993, in final form 6 January 1994

Abstract. Pressure–temperature diagram of gallium antimonide has been studied at $p = 3\text{--}8$ GPa and $T = 300\text{--}1000$ °C. Measurements of the melting temperature have been carried out up to 8 GPa. The transition with changes in the volume and electrical resistivity was detected in the GaSb melt. This transformation is apparently connected with the change in the short-range order structure of the mutual arrangement of molecules. The non-metal–metal transition in amorphous GaSb has been explained. Analogous transformations in amorphous Si and Ge are predicted.

1. Introduction

Compounds of $A^{\text{III}}B^{\text{V}}$ type (GaAs, GaSb, InSb, etc.) have been studied throughout the world for the last three decades because of their unique electromagnetic, optical and other properties [1]. Experiments with single crystals, thin films as well as with amorphous samples of these materials are numerous. Nevertheless, only a few attempts have been made to study the liquid state of these materials (see, e.g., [2, 3], where the discovery of dissociation of GaSb molecules at $T = 1100$ °C and normal pressure has been reported). The pressure–temperature (p – T) phase diagram of solid GaSb at pressures up to 10 GPa and the melting curve up to 6.5 GPa have been studied in [4, 5]. The non-metal–metal transition takes place at room temperature and $p = 6.5$ GPa [5] in crystalline GaSb. As for the melting curve, there is a strange sharp change in the slope of the curve at $p \simeq 4$ GPa [5].

Amorphous samples were obtained in [6] by solid state amorphization at normal pressure and in [7] by ‘quenching from the melt under a high pressure’. Recently bulky amorphous species of GaSb were obtained by ‘solid state amorphization’ under a high pressure [8]. Detailed study of the amorphization process in GaSb under a high pressure [8] demonstrates, that there are two kinds of amorphous sample of GaSb with different electrophysical properties. The first was obtained by quenching at $p = 9$ GPa from an initial temperature $T \leq 800$ °C down to room temperature, while the second was quenched from $T \geq 800$ °C. The study of the short-range order structure showed that, in the first kind of sample (non-metal), atoms of Ga, as a rule, have atoms of Sb as the nearest neighbour while, in the second type (metal), there are separate regions with excess concentrations of Ga and Sb atoms. The presence of two different kinds of amorphous sample was termed the non-metal–metal transition in amorphous GaSb [8], although direct transformation of the non-metal state into the metal state and vice versa has not been observed.

2. Experiments

The experiments on the measurements of volume anomalies (thermobaric analysis (TBA)) and relative electrical resistance were carried out in a high-pressure chamber of ‘toroid’ type.

The high-pressure cell for TBA experiments is shown in figure 1. The sample was placed in the centre. It was enclosed in the graphite heater. The common junction of chromel–alumel (CA) and Pt–(Pt + 10%Rh) (PPR) thermocouples was located near the external wall of the heater. A NaCl damper was placed round the heater to eliminate the influence of the phase transitions in pipe-stone (pressure-transmitting medium) on the junction. The sample was closed by graphite spacers and was heated by an AC flowing through the heater and the sample.

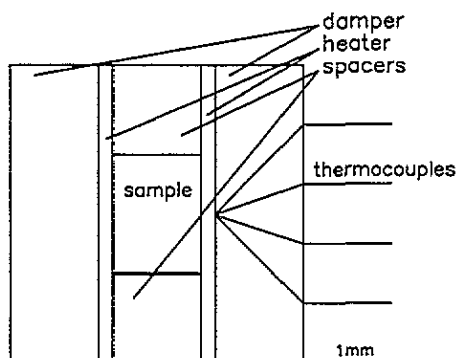


Figure 1. Cell for TBA measurements. The same cell in the absence of the damper and the PPR thermocouple is used for the relative electrical resistivity experiments.

The increase in the volume of the sample induces an increase in the pressure in the cell. The CA and PPR have identical temperature and different pressure dependences of their thermoEMFs [9]. Recording the thermoEMF of one thermocouple versus that of another during the heating and cooling of the sample, one can detect the increase in the pressure in the cell and, therefore, the volume anomaly in the sample.

The TBA cell in the absence of the damper and PPR thermocouple was used for the relative electrical resistivity measurements. Recording the voltage–current curve of the whole cell during heating and cooling of the sample, one can detect a phase transition with the change in the electrical resistivity ρ in the sample. All the materials of the cell, excluding the sample, were chosen so that they do not induce any volume or resistivity anomaly. That is why every detected anomaly could be assigned to the sample. However, evidence of the accuracy of both methods, a more detailed description and typical anomalies during the well known phase transitions have been given in [10, 11].

The investigations were carried out at $p = 3\text{--}8$ GPa and $T = 300\text{--}1000^\circ\text{C}$. After the experiments the samples were subjected to an x-ray study. No chemical impurities such as graphite and pipe-stone were found in the sample. However, a great deal (about 80%) of GaSb was in the amorphous state after unloading, i.e. solid state amorphization really takes place under pressure.

3. Results and discussion

The pressure–temperature diagram of GaSb melt (figure 2) is the main result of TBA and relative electrical resistivity measurements. There are two regions in the liquid part of the diagram. They are separated from each other by reversible and marked volume and

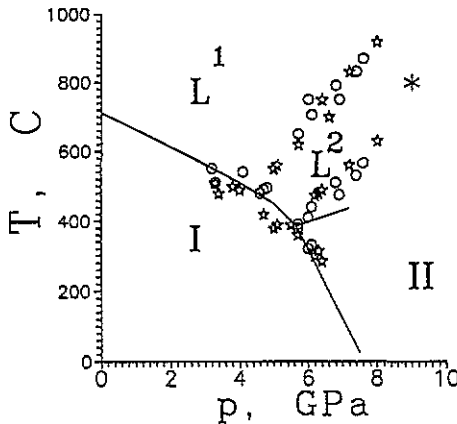


Figure 2. Pressure–temperature diagram of GaSb: —, phase boundaries in GaSb, according to [5]; I, II, crystalline phases of GaSb; ☆, τBA anomalies; ○, electrical resistivity anomalies; L¹, L², states of the GaSb melt; *, point of synthesis of amorphous GaSb [8], where a sharp change in the properties of samples takes place.

resistance anomalies. These anomalies remain rather distinct throughout the whole pressure and temperature ranges.

Measurements of the melting temperature at pressures up to 8 GPa have also been made. The slope of the melting curve of GaSbII was found to be equal to 80 K GPa⁻¹. This value is larger than previously obtained [4, 5]. Probably, it is due to the revision of the high-pressure scale [12].

The coordinates of the triple points are as follows: 4.2 GPa and 480 °C for L¹–L²–S, and 5.0 GPa and 380 °C for I–II–L², with the errors of determination of *p* and *T* as ±0.3 GPa and ±25 °C, respectively. The signs of the jumps of density and resistivity during the transitions are given in table 1.

Table 1. Signs of the increases in density and resistivity during transitions. The upper sign in the cell denotes the change in the density *d*, while the lower sign denotes the increase in the electrical resistivity *ρ*. For example, *d*(GaSbII) > *d*(GaSbI), sign +; *ρ*(GaSbII) < *ρ*(GaSbI), sign –.

State	Sign for the following states			
	GaSbI	GaSbII	L ¹	L ²
GaSbI		+	+	+
		–	–	–
GaSbII	–		–	–
	+		+	+
L ¹	–	+		+
	+	–		–
L ²	–	+	–	
	+	–	+	

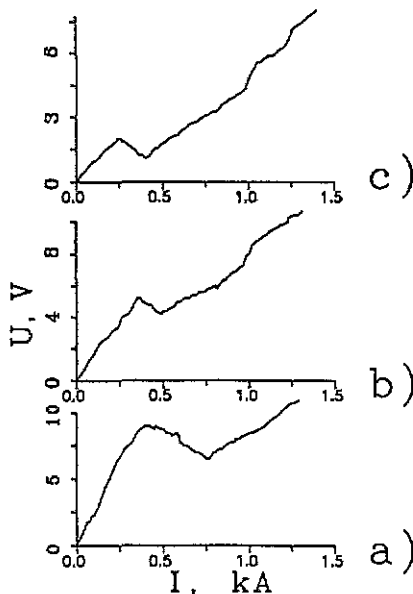


Figure 3. Typical experimental voltage–current curves showing transitions: (a) $p < 4.2$ GPa, melting; (b) 4.2 GPa $< p < 5.0$ GPa, melting and L^1 – L^2 ; (c) $p > 5.0$ GPa, I–II, melting and L^1 – L^2 . A change in the slope of the direct line, starting from the point (0,0), takes place during a transition. The temperature was controlled independently.

Typical voltage–current curves, taken directly from the experiments on the measurements of ρ , are shown in figure 3. The anomalies in the GaSb melt proved to be rather wide (about 50 K), unlike Bi [10] and Te [11], where the experimental width of transition did not exceed 20 K. It could be connected, for example, with some kinetic effect.

Revision of the high-pressure scale [12] has led to an essential decrease in the pressures of transitions, especially above 6 GPa. All p – T diagrams, obtained before 1970 (including [4, 5]), should be corrected. However, Demishev *et al* [8] have used the melting temperatures of GaSb taken directly from [5] and found that quenching at 9 GPa from initial temperature of firstly 800 °C and above and secondly 800 °C and below results in different conductivities of the samples. According to the present data on the melting temperature, the first kind of sample was quenched from the melt while the second was quenched from the solid state. It was quenching from different initial phases that led to the non-metal–metal transition in amorphous GaSb [8] (in fact, to the preparation of samples with essentially different properties).

The presence of regions with excess concentrations of Ga or Sb atoms in the samples, quenched from $T \geq 800$ °C [8], becomes clear also. In fact, there are similar regions in the melt, and it is not surprising that the same regions occur in amorphous samples quenched from the melt. Contrarily, quenching from an initial solid state leads to a more homogeneous mutual distribution of Ga and Sb atoms.

Probably, both L^1 and L^2 are molecular states of the GaSb melt. At normal pressure the molecules of GaSb break to form atoms at $T > 1100$ °C [2]. Therefore, the GaSb melt is in a molecular state near the melting curve (i.e. only very few GaSb molecules are dissociated). In this way, L^1 is apparently the molecular state of the GaSb melt. On the other hand, L^2 is apparently a molecular state as well. In fact, L^2 is a low-temperature state

in relation to L^1 . The formation of molecules (in L^1) from atoms of Ga and Sb (in L^2) upon increase in T seems to be unlikely. Thus, the detected transition is due to the change in arrangement of molecules in the GaSb melt.

Dissociation of I_2 molecules in the iodine melt has been detected recently (the transition $L'-L''$ in [13]). In that case, as assumed, the high-temperature state L'' is atomic. The non-metal-metal transition in liquid iodine [13] is another example of transformation in the molecular melt.

GaSb was chosen as the subject of study, for the properties of this substance (set of phase transitions, resistivity of phases, etc) are similar to those of Si and Ge (see, e.g. [1, 3, 4, 5]). Bulky amorphous samples of Si and Ge were obtained recently [14] by solid state amorphization at about 77 K. One can expect that amorphous species of Si and Ge quenched at high temperature from the melt to liquid-nitrogen temperature would exhibit a non-metal-metal transition, like the transition in amorphous GaSb [8].

4. Conclusion

The pressure-temperature phase diagram of the GaSb melt as well as the melting curve has been studied at $p = 3-8$ GPa and $T = 300-1000^\circ\text{C}$. A transition with changes in the volume and electrical conductivity was detected in the melt. The melting temperature of GaSb was defined more exactly up to 8 GPa.

A simple physical consideration shows that the transition is apparently connected with the change in the short-range order structure of melt, with both liquid 'phases' in the molecular rather than the atomic state. Transitions of the same type take place in the melts of Bi and Te [10, 11]. These data were confirmed recently by independent x-ray study [15, 16], which exhibited sharp changes in the short-range order structures of the Bi and Te melts in rather narrow p and T intervals. Additional x-ray investigation of the GaSb melt in the vicinity of the L^1-L^2 transition is also necessary.

The non-metal-metal transition in amorphous GaSb [8] has been explained. Quenching of the samples of Si and Ge from the melt to liquid-nitrogen temperature at pressures higher than location of their triple points I-II-L (11 and 9 GPa [17, 18]) could lead to a similar non-metal-metal transition in amorphous Si and Ge.

Acknowledgments

This work was supported in part by a Soros Foundation grant awarded by the American Physical Society. The author is very grateful to Dr V V Brazhkin and Dr A G Lyapin for useful discussions.

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