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Bulk amorphous Zn–Sb under normal and high pressures: phase transformations and relaxation phenomena

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Abstract

Processes occurring upon heating of the high-pressure δ-$Zn_{41}Sb_{59}$ phase at atmospheric pressure were studied on bulk samples using scanning calorimetry and dilatometry in the temperature interval 170–573 K which includes the temperatures of amorphization and subsequent crystallization. Irreversible relaxation of the amorphous state followed by a heat release and elongation of the sample of the order of 1/4 of those found upon amorphization were observed at 325–425 K. At room temperature the effect of pressure on the electrical resistance of the amorphous $Zn_{41}Sb_{59}$ samples ($P \leqslant 70$ kbar) and on their volume ($P \leqslant 28$ kbar) was investigated. The resistance decreased with pressure by approximately five orders of magnitude displaying two falls at approximately 20 and 49 kbar characteristic of first-order phase transitions. The former transition was found to be reversible and is accompanied by an approximately 0.8% decrease in volume.

1. Introduction

During the last decade new methods have been developed to obtain materials in an amorphous state employing solid state reactions. These include ball milling [1], annealing of film multilayers [2], hydrogenization [3–5], irradiation by high energy ions [6] and spontaneous amorphization (SA) of high pressure phases produced by thermobaric quenching [7–9]. This method enables amorphous samples to be obtained in bulk form under easily reproducible and controllable conditions, which is advantageous for further investigation of their properties.

The SA method has been successfully applied to obtain semiconducting amorphous phases in the Cd–Sb, Ga–Sb, Zn–Sb and some other systems [8, 9]. The present paper reports on the effect of heat and baric treatments on the properties of the $Zn_{41}Sb_{59}$ bulk amorphous alloy.

As for the effect of pressure on the properties of amorphous semiconductors, the behaviour of the electrical resistivity ρ of a large variety of systems is already known (germanium, silicon [10, 11], InSb [12], arsenic [13], selenium [14], tellurium [15], As–Te, As_2Se_3, As_2S_3 [16, 17] etc.). The main feature of the observed $\rho(P)$ dependences was a decrease in ρ (gradual and/or stepwise) with increasing pressure by many orders of magnitude, down to the values characteristic of semimetals and metals. Most of the studied semiconductors crystallize upon transition to the metallic state; of the above amorphous elements and compounds, only As_2Te_3 [18] seems to be an exception.

None of the amorphous materials produced by the SA method have been studied at high pressures.

2. Sample preparation and experimental details

There are three compounds, Zn_4Sb_3, Zn_3Sb_2 and ZnSb, known in the Zn–Sb system at atmospheric pressure; all are semiconductors [19]. These phases decompose with increasing pressure, and a new metallic δ-phase forms, stable over a rather narrow concentration interval in the vicinity of $Zn_{41}Sb_{59}$, and at $P > 65$ kbar the δ-phase is the only intermediate phase in the system [20]. The δ-phase can be "quenched" under high pressure and then stored at atmospheric pressure in liquid nitrogen. Having been heated at atmospheric pressure, it transforms into an amorphous semiconductor which remains amorphous at room temperature for an indefinitely long time. The reasons why the final product is amorphous are discussed thoroughly in ref. 21.

In the present work, samples of δ-$Zn_{41}Sb_{59}$ in the form of bars $1 \times 1.5 \times 4$ mm^3 for the electrical measurements and in the form of discs 5 mm in diameter and 1.5 mm thick for other measurements were prepared

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by exposure of the samples of this composition (a mixture of ZnSb and antimony at normal conditions) to $P=70$ kbar and 623 K for 24 h with subsequent rapid cooling ("quenching") under pressure down to 100 K. Toroid type chambers with Teflon as a pressure transmitting medium (the pressure being measured accurate to ±3 kbar, the temperature to ±5 K) were used both for this purpose and for further study of the samples transformed into an amorphous state at atmospheric pressure.

An X-ray analysis of the samples was performed at 100 K by a phototechnique using a DRON-2.0 diffractometer with Cu Kα radiation. Thermal and dilatometric analyses were carried out with the use of a PE DSC 7 differential scanning calorimeter and a PE TMA 7 thermomechanical analyser. The samples were loaded into the apparatus without warming above 100 K.

The effect of pressure up to 28 kbar on the volume of the amorphous samples was measured at room temperature with a piston-cylinder type piezometer using lead as a pressure transmitting medium [22]. The apparatus permitted repeated runs of increases and decreases in pressure, the pressure being determined with an accuracy of ±0.3 kbar. Relative changes in the sample volume were estimated as accurate to ±0.1% by a differential method [23].

Electrical resistance was measured by a conventional d.c. four-probe technique with copper electrodes pressed against the sample. The electrical resistivity of the samples under pressure was estimated using their initial dimensions at atmospheric pressure.

3. Results and discussion

3.1. Calorimetry and dilatometry

Amorphization of the δ-phase and subsequent crystallization of the resultant amorphous phases in the Zn–Sb system were studied in ref. 24 by scanning calorimetry in the temperature intervals 77–300 K and 420–520 K correspondingly, on samples of composition $Zn_{43}Sb_{57}$. The amorphization was shown to be an exothermic process occurring in a wide temperature range from approximately 170 to 290 K for the chosen rate of heating of 0.5 K min^{-1}. According to the X-ray data, the samples treated this way remained amorphous up to approximately 420 K.

In the present work, we measured temperature dependences of the heat flow and elongation of the sample while heating single-phase δ-$Zn_{41}Sb_{59}$ at a rate of 5 K min^{-1} in the temperature interval 110–573 K which includes the temperatures of both amorphization and crystallization processes. Some representative results are given in Fig. 1 and Table 1.

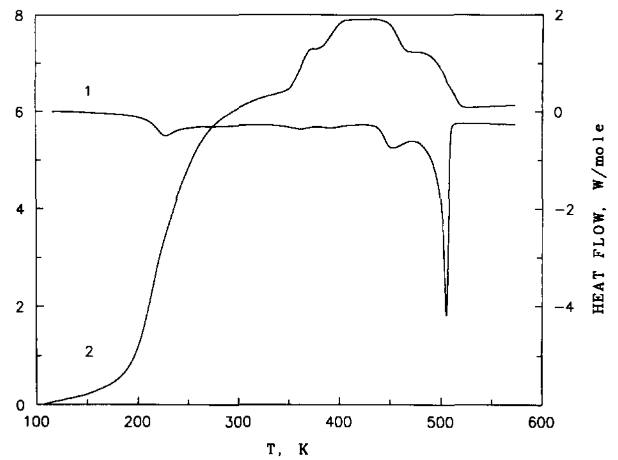

Fig. 1. Relative elongation $\Delta l/l_0$ (curve 2) and heat flow (curve 1) upon heating of quenched δ-$Zn_{41}Sb_{59}$ samples at a rate of 5 K min^{-1}.

As is seen from Fig. 1, curve 1, all the processes occurring in the sample below approximately 520 K are exothermic and therefore associated with relaxation of thermodynamically non-equilibrium states. Five minima in the heat flow (which are the maxima in the heat release) dependence are clearly observed. The positions of these minima are close to those of the steepest changes in the sample length l (curve 2), thus allowing one to suggest that the anomalies in both dependences reflect the same processes. The peaks of the curve 1 are stretched over large temperature intervals which makes it difficult to determine correctly the thermal effects Q. The Q-values presented in Table 1 were estimated by the areas below straight lines connecting the points of the curve 1 at the temperatures indicated in Table 1, the last but one column, and close to the positions of corresponding minima in the slope of the $l(T)$ dependence. The Δl values in Table 1 refer to the same temperature intervals.

An X-ray examination of the samples obtained by heating of the δ-phase from 110 K to 300, 413 and 573 K with the same rate 5 K min^{-1} showed that the two former samples were amorphous and the latter consisted of a mixture of crystalline ZnSb and antimony. Thus, the leftmost peak of curve 1 corresponds to amorphization of the δ-phase and the two rightmost peaks are associated with crystallization of the amorphous phase, which is in agreement with the data of ref. 24.

In fact, the values of Q and the width of the leftmost peak nearly coincide with those of the corresponding peak in ref. 24, and its position is only somewhat shifted towards higher temperatures, which could be accounted for by the increase in the rate of heating (from 0.5 K min^{-1} in ref. 24 to 5 K min^{-1} in the present work). The parameters of the two rightmost peaks are nearly the same as those of crystallization in ref. 24.

TABLE 1. Heat release Q, linear $\Delta l/l_0$ and volume $\Delta V/V_0$ expansions measured upon heating of the δ-phase in the Zn–Sb system

	DSC peak position (K)	Q (kJ mol^{-1})	$\Delta l/l_0$ (%)	$\Delta V/V_0$ (%)	Temperature inverval (K)	Heating rate (K min^{-1})
$Zn_{41}Sb_{59}$	228	2.0	6.3	20	110–326	5
	364 393	0.5	1.5	5	326–425	5
	453 506	6.6	−1.8	−6	425–530	5
$Zn_{43}Sb_{57}$ [24]	210	1.9	–	–	170–290	0.5
	447 505	6.7	–	–	420–510	4

$\Delta V/V_0$ values were calculated in an isotropical approximation.

As for the two new peaks of curve 1 in the temperature range 324–425 K where the sample is amorphous, their presence suggests that the amorphous state of the sample changes with temperature and that at least some of the changes are spasmodic. The behaviour of curve 2 indicates that such changes could be considered as transitions between the stages characterized by different specific volumes.

If heating of the samples was stopped at $T_a = 300$ K or 420 K and they were cooled down to 100 K again, no anomalies were then seen at $T \leqslant T_a$ in the $l(T)$ and DSC dependences obtained in the second run of the temperature increase. Thus, the processes occurring in the δ-samples being heated for the first time are irreversible and can be considered as a gradual relaxation of the initial metastable δ-state and also the amorphous phase.

3.2. Temperature and pressure dependences of electrical resistivity

The amorphous Zn–Sb alloys are known to be semiconductors displaying an activation type of electrical conduction, $\rho = \rho_0 \exp(\Delta E/T)$, over a wide temperature range [7].

Values of resistivity of the amorphous $Zn_{41}Sb_{59}$ samples obtained by heating the δ-samples under the same conditions were not well reproduced, *e.g.* heating to room temperature could result in $50 \leqslant \rho(293\ \text{K}) \leqslant 500$ Ω cm. For each sample, however, an increase in the annealing temperature always led to an irreversible increase in ρ, with both ΔE and the pre-exponential factor increasing. As an example, Fig. 2 presents two temperature dependences of ρ for the sample primarily annealed at $T_a = 293$ K (curve 1, $\Delta E = 0.28$ eV) and then at 383 K (curve 2, $\Delta E = 0.30$ eV); each dependence was measured below the corresponding T_a.

Pressure dependences of ρ for the amorphous $Zn_{41}Sb_{59}$ samples were measured using a step-wise increase and decrease in pressure at room temperature.

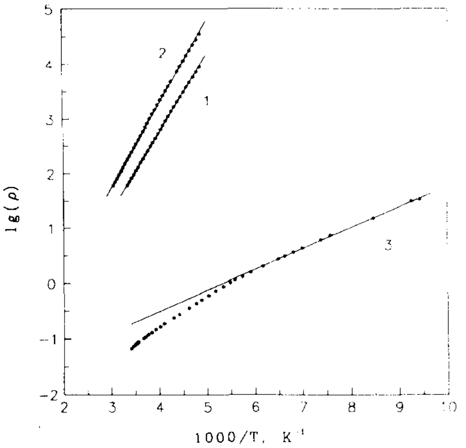

Fig. 2. Decimal logarithm of electrical resistivity ρ (Ω cm) *vs.* inverse temperature for amorphous $Zn_{41}Sb_{59}$ samples: curve 1, $P = 1$ bar, sample obtained by annealing of δ-phase at 293 K for 15 min; curve 2, $P = 1$ bar, the same sample after additional annealing at 363 K for 2 h; curve 3, $P = 35$ kbar, sample obtained by annealing of the δ-phase at 293 K for 24 h.

The samples were exposed to each fixed P until termination of the ρ temporal drift (if any) and the final value of ρ was plotted in the figure. Representative results are shown in Fig. 3.

Upon application of increasing pressure up to 70 kbar, the resistivity fell by approximately five orders of magnitude. Along with intervals of steady decrease, two rather narrow steps of the curve were observed. The positions of the steps varied from sample to sample in the ranges 16–23 kbar for the first step and 43–53 kbar for the second step. The height of the first step also changed noticeably (compare Fig. 3 and the inset) whereas that of the second step remained nearly the same for all the samples studied.

Temporal drift of ρ occurred at every given pressure and continued for 1–3 h in the vicinities of the steps and for 15–30 min in the other pressure intervals. A considerable increase in the duration of the resistance

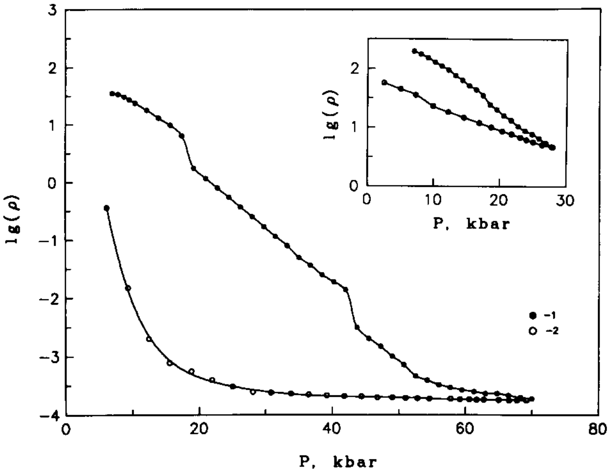

Fig. 3. Decimal logarithm of electrical resistivity ρ (Ω cm) *vs.* pressure at room temperature for amorphous $Zn_{41}Sb_{59}$ samples obtained by annealing of the δ-phase at 293 K for 24 h (main figure) and at 373 K for 30 min (inset): curve 1, increasing pressure; curve 2, decreasing pressure.

drift at pressures close to the positions of the steps allows one to associate these two steps with two first-order phase transitions ($a \to a'$ and $a' \to a''$ hereafter), most probably of a thermoactivated nature.

The behaviour of ρ with decreasing pressure differed from that observed with a pressure increase. After lowering the pressure, the time drift of ρ ceased in 2–4 min which was a characteristic time for equalization of the pressure over the working zone of the high-pressure chamber. As is seen from Fig. 3, the $\rho(P^{\downarrow})$ dependences obtained did not coincide with the $\rho(P^{\uparrow})$ dependences from the very beginning, even at points lying a long distance from the steps of the $\rho(P^{\uparrow})$ curve. Taken together with the presence of the temporal drift of ρ at every fixed pressure during its previous stepwise increase, this irreversibility is indicative of the fact that the first run of increase in pressure is followed by a gradual relaxation of the starting amorphous state of the samples, noticeably contributing to the total slope of the $\rho(P^{\uparrow})$ dependence.

Upon lowering the pressure after its increase to 28 kbar (inset to Fig. 3), an inflection was once observed in the $\rho(P^{\downarrow})$ curve near 8 kbar. One could speculate that this inflection and the step of the $\rho(P^{\uparrow})$ curve at approximately 18 kbar are associated with a reversible $a \to a'$ first-order phase transition displaying a hysteresis of the order of 10 kbar.

If the sample was subjected to a pressure of 70 kbar (Fig. 3), a subsequent decrease in the pressure down to approximately 30 kbar did not lead to any visible changes in its resistance. At lower pressures, the resistance began to rise more and more steeply, the resultant $\rho(P^{\downarrow})$ dependence being smooth within experimental error. The behaviour of the resistance thus shows that hysteresis of the $a' \to a''$ transition (which manifests itself by a step in the $\rho(P^{\uparrow})$ dependence at $P \approx 43$ bar) is large, not less than 20 kbar.

At $P = 35$ and 70 kbar, $\rho(T)$ dependences were measured at $110 \leqslant T \leqslant 293$ K on the amorphous samples exposed, prior to the measurement, to a chosen pressure at room temperature for 24 h. No temporal drift of ρ arose after changing the temperature, and the $\rho(T^{\uparrow})$ and $\rho(T^{\downarrow})$ dependences coincided within experimental error.

Dependences $\rho(T)$ of the starting amorphous $Zn_{41}Sb_{59}$ samples at atmospheric pressure were of activation character like those shown in Fig. 2, curves 1 and 2. At $P = 35$ kbar, the sample remained semiconducting, but its $\rho(T)$ dependence was not exponential (Fig. 2, curve 3; the solid line with $\Delta E = 0.075$ eV has been drawn to make the non-linearity of the experimental dependence clearly visible). As is seen from Fig. 4, this $\rho(T)$ could be well fit with the dependence $\rho(T) \propto (T/T_0)^{0.35} \exp(T_0/T)^{1/4}$, characteristic of conduction by variable-range hopping amongst localized states near to the Fermi energy [25] (in our case, $T_0 = 7.5 \times 10^7$ K). At $P = 70$ kbar (Fig. 5, curve 1), judging by the magnitude of ρ and its temperature dependence (a small but noticeable increase with T at lower temperatures), the sample became semimetallic.

One possible explanation of the observed behaviour of ρ could be that, with increasing pressure, a gap in the electronic spectrum of the amorphous $Zn_{41}Sb_{59}$ becomes narrower, the tails of localized states begin to overlap more and more and their density at the Fermi level becomes high enough for conduction by variable-range hopping to predominate over that by interband excitation, and then the gap nearly vanishes. Similar phenomena seem to be typical of many amorphous semiconductors under pressure [26].

In order to prove that our $Zn_{41}Sb_{59}$ samples remained amorphous during the described manipulations under high pressures, the following could be mentioned.

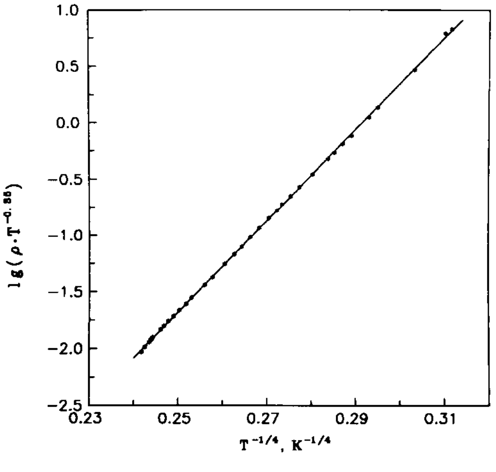

Fig. 4. Mott's plot for the data in Fig. 2, curve 3.

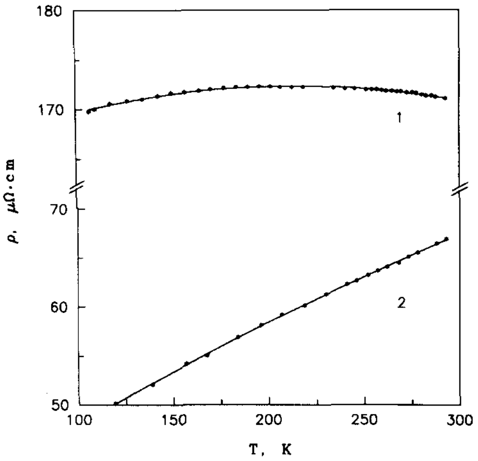

Fig. 5. Temperature dependences of electrical resistivity ρ at $P=70$ kbar for an amorphous $Zn_{41}Sb_{59}$ sample obtained by annealing of the δ-phase at 293 K for 24 h (curve 1) and for the same sample transformed into the δ-state by heating to 623 K without changing the pressure (curve 2).

The samples released from pressure at room temperature after completion of the experiments were X-rayed and found to be wholly amorphous. This proved that none of the samples underwent, even partly, a transition into either a crystalline mixture (ZnSb + Sb) or the δ-phase, in thermodynamic equilibrium at the lower and higher pressures respectively. As a matter of fact, the mixture (ZnSb + Sb), once formed and being thermodynamically stable under normal conditions, would not transform back into a non-equilibrium amorphous state. As for the δ-phase, additional experiments have shown that, upon decreasing pressure at room temperature, δ-$Zn_{41}Sb_{59}$ transformed directly into the mixture of crystalline ZnSb and antimony, missing out the stage of amorphization. Note also, that the ρ magnitudes and $\rho(T)$ dependences at $P=70$ kbar were shown to be essentially different for the initially amorphous $Zn_{41}Sb_{59}$ and δ-$Zn_{41}Sb_{59}$, see Fig. 5.

A few amorphous $Zn_{41}Sb_{59}$ samples were exposed to several given pressures from 28 to 70 kbar at room temperature during 24 h and then either quenched or slowly cooled down to 100 K. The chosen temperature of 100 K was low enough to fix any crystalline high-pressure phase known in the Zn–Sb and many other systems [8]. All the obtained samples proved amorphous by X-ray examination at atmospheric pressure and 100 K.

3.3. *Piezometry*

The behaviour of the volume V at room temperature and pressures to 28 kbar was studied on two amorphous $Zn_{41}Sb_{59}$ samples prepared by heating the δ-phase to 293 and 413 K respectively. The results were qualitatively the same. Figure 6 presents the $V(P)$ dependences for the second sample with a maximum initial specific volume featuring most clearly the observed irreversible effects. The dependences were taken at a step-wise increase and decrease in pressure with exposure of the sample to every given pressure until its volume stopped changing with time, the final value of volume being plotted.

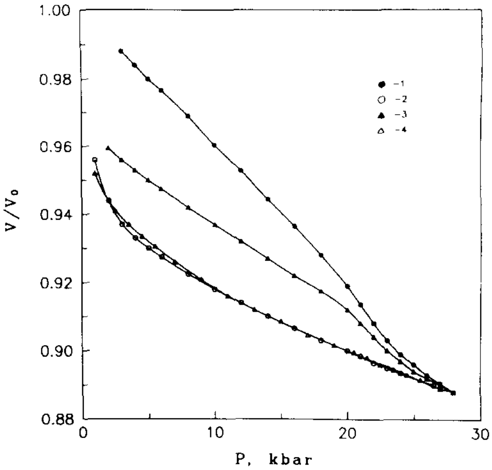

Fig. 6. Relative volume V/V_0 as a function of pressure at room temperature for an amorphous $Zn_{41}Sb_{59}$ sample obtained by heating of the δ-phase at atmospheric pressure from 100 to 413 K at a rate of 5 K min^{-1}: curves 1, 2, first run, increasing and decreasing pressure respectively; curves 3, 4, fifth run. V_0 is the volume of the initial sample at atmospheric pressure (see the text).

In the first run, a steady decrease in the sample volume with increasing pressure changed to a much steeper increase in the interval 20–24 kbar (Fig. 6, curve 1). Any increase in the pressure gave rise to a temporal drift of V, this process taking 5–10 min to complete at $P<18$ kbar and $P>25$ kbar, and 25–30 min at $20<P<24$ kbar.

One could see that the behaviour of the sample volume was similar to that of the electrical resistance (Fig. 3), the longer duration of the temporal drift of ρ being obviously due to the better relative accuracy of the ρ measurement. The similarity allows us to conclude that the observed peculiarities in the behaviour of ρ and V are related to the same processes; namely, to a gradual irreversible relaxation of the amorphous state occurring over the whole pressure interval and to an $a \rightarrow a'$ phase transition at $P \approx 20$ kbar. The decrease in the sample volume at $P>20$ kbar confirmed that the transition was of the first order.

The $V(P^{\downarrow})$ dependence (Fig. 6, curve 2) showed that this $a \rightarrow a'$ transition was characterized by a large hysteresis, since an increase in volume which could be ascribed to the reverse $a' \rightarrow a$ transition took place only at $P<4$ kbar. Just as in the case of the $\rho(P^{\downarrow})$ measurement, no temporal drift of V occurred upon decreasing pressure.

The behaviour of the sample volume in the second and subsequent runs of increase and decrease in pressure was well reproduced in all details. Prior to each run, the piezometer was completely unloaded and the sample was exposed to a residual (due to friction inside the high-pressure cell) pressure of about 0.3–0.5 kbar during a time varying from 10 min to 10 days. The reproducibility of the $V(P)$ dependences in the following runs implied that a stable state of amorphous $Zn_{41}Sb_{59}$ sample was reached under this pressure in less than 10 min.

In the fifth cycle of loading (curve 3), the sample volume steadily decreased at pressures up to approximately 18 kbar with a slightly decreasing slope (which is typical of single-phase materials) and displayed no temporal drift. At $P > 20$ kbar, an $a \rightarrow a'$ phase transition causing a much steeper fall in V accompanied by a drift of approximately 5 min at every fixed pressure was observed. The $V(P^{\downarrow})$ dependence obtained upon the following decrease in pressure (curve 4) was nearly the same as that in the first run (curve 2).

Coincidence of these $V(P^{\downarrow})$ curves demonstrates the absence of irreversible relaxation phenomena in the course of both the first decrease in pressure and subsequent runs. That is, in these runs, we dealt with a sample whose degree of relaxation corresponded to 28 kbar, a maximum pressure applied during its first increase. An extrapolation of the $V(P^{\downarrow})$ dependences 1 and 3 to atmospheric pressure shows that this degree of relaxation is characterized by an irreversible decrease in the initial sample volume by approximately 3.5%.

As is seen from Fig. 6, the pressure of the $a \rightarrow a'$ phase transition (conventionally defined as the point where the steepness of the $V(P^{\uparrow})$ dependences is maximum) was the same in the first and fifth runs and was approximately 22 kbar. The ΔV value for this transition (estimated as the distance at 22 kbar between the straight lines tangential to the portions of the $V(P^{\uparrow})$ curves adjacent to the region of the transition) was also the same, approximately 0.8%. The latter fact could be considered as strong evidence that, in spite of a large hysteresis, the $a \rightarrow a'$ phase transition was nearly completely reversible. It seems worth mentioning also, that a noticeable inflection was once observed in the $\rho(P^{\downarrow})$ curve near to 8 kbar (see the inset to Fig. 3), so the hysteresis could be much smaller in some of the amorphous $Zn_{41}Sb_{59}$ samples.

The above numerical estimates of the volume effects, unfortunately, could only be considered as semiquantitative. The reason is that, in the first run, we needed to apply about 3 kbar for the pressure transmitting medium (lead) to fill up the dead space in the high-pressure cell. The $V(P^{\uparrow})$ dependence was measured beginning from 3 kbar, and the initial sample volume V_0 was estimated by a linear extrapolation of this dependence to atmospheric pressure. Taking into account the large relaxation effects observed, one cannot exclude, however, that the dependence was much steeper at $P \ll 3$ kbar.

Keeping in mind the above, we nevertheless dare produce another two numbers. Namely, in the fifth run, the compressibilities, $(1/V_0)(\partial V/\partial P)$, of the amorphous $Zn_{41}Sb_{59}$ in the a- and a′-states were of the order of 2.6×10^{-3} and 1.6×10^{-3} $kbar^{-1}$ respectively (the former was estimated by the average slope of the $V(P^{\uparrow})$ dependence at $P < 18$ kbar, the latter by that of the $V(P^{\downarrow})$ dependence at $15 < P < 28$ kbar).

4. Summary

At atmospheric pressure, the amorphous state of the $Zn_{41}Sb_{59}$ alloy obtained by solid state amorphization of the high-pressure δ-phase is kinetically stable at room temperature, but changes irreversibly if the sample is heated to a higher temperature. The heating rate being kept constant, judging by the temperature dependences of the released heat and sample length at 300–425 K (Fig. 1), this relaxation process is spasmodic.

Upon application of increasing pressure up to 70 kbar, the room temperature resistivity of the amorphous $Zn_{41}Sb_{59}$ decreases by approximately five orders of magnitude from its atmospheric value. An activation character of electrical conduction of the initial amorphous alloys at atmospheric pressure (Fig. 2, curves 1 and 2) changes to that typical of conduction by variable-range hopping at $P = 35$ kbar (Fig. 4) and then to semimetallic at $P = 70$ kbar (Fig. 5, curve 1).

Two first-order phase transitions accompanied by a fall in resistivity occur in the amorphous $Zn_{41}Sb_{59}$ at room temperature and pressures varying, for different samples, from 16 to 23 kbar and from 43 to 53 kbar respectively; both transitions display a large hysteresis (Fig. 3).

The transition occurring at approximately 20 kbar is reversible and characterized by an approximately 0.8% decrease in sample volume, this value being well reproduced in many cycles of increasing and decreasing pressure (Fig. 6). The larger slope of the $V(P^{\uparrow})$ dependence in the first run is due to a gradual relaxation of the initial amorphous state of the sample.

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