

# Metallization in the molten and solid state and phase diagrams of the GeSe<sub>2</sub> and GeS<sub>2</sub> under high pressure

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We found that under high pressure, the GeSe<sub>2</sub> and GeS<sub>2</sub> melts pass into the metallic state. In the vicinity of the melting curves, their metallization begins at 3.5 and 7 GPa, respectively. The position of the semiconductor – metal transition line on the phase diagram for GeSe<sub>2</sub> liquid is established. The GeSe<sub>2</sub>-II and GeSe<sub>2</sub>-III high-pressure crystalline modifications are semiconductors, whereas the GeSe<sub>2</sub>-III modification at pressures exceeding 3.5–4 GPa is a metal ( $\sigma \approx 10^3 \Omega^{-1} \cdot \text{cm}^{-1}$ ). The  $P, T$  phase diagrams for these compounds are constructed in the pressure range up to 10 GPa. Metallization during the GeSe<sub>2</sub>-II–GeSe<sub>2</sub>-III transition is evidently responsible for the small jump of entropy and the corresponding almost vertical slope of the transition line.

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1. Dichalcogenides of germanium GeSe(S)<sub>2</sub> possess unique electron and physical properties. Recently, these compounds have been studied rather intensely under high-pressure conditions in the crystalline, glassy and liquid states [1–7]. However, there are many questions concerning insulator-metal transitions under compression in the liquid and solid states of these compounds, and concerning  $P, T$  phase diagrams of GeS<sub>2</sub> and GeSe<sub>2</sub>. Phase transitions in these substances at pressures up to 9 GPa were studied previously in works [1–7]. Glasses of the corresponding composition crystallize at  $T = (675–875)$  K and a pressure increase leads to the appearance of new phases: I→II→III, where phase I is the phase existing under normal conditions, phase II is formed in the pressure interval  $P = (0–5)$  GPa, and phase III, at  $P > 6$  GPa. All high-pressure modifications for each compound can be conserved in a metastable form under normal conditions.

The GeS<sub>2</sub>-II and GeSe<sub>2</sub>-II high-pressure phases are isostructural and belong to the  $\alpha$ -ZnCl<sub>2</sub> structural type ( $I - 42d$ ;  $Z = 4$ ,  $X$ -ray densities are  $D_x = 3.30$  and  $4.84 \text{ g} \cdot \text{cm}^{-3}$ , respectively) [6]. In contrast to the normal-pressure modifications, where 50% of GeX<sub>4</sub> tetrahedrons are bound by their corners and 50%, by their edges, high-pressure phases II are constructed from tetrahedrons jointed only by their corners. During the I→II phase transition, interatomic distances in the tetrahedron do not change, and the densities of GeS<sub>2</sub>-II and GeSe<sub>2</sub>-II increase during the transition by 10.3

and 9.6%, respectively, due to densification in the second coordination sphere. The GeS<sub>2</sub>-III phase synthesized through the crystallization of glass at  $P = 7$  GPa and  $T = 800$  K [1] was assigned to the HgI<sub>2</sub> structural type ( $P4_2/nmc$ ;  $Z = 2$ ;  $D_x = 3.49 \text{ g} \cdot \text{cm}^{-3}$ ), and the GeSe<sub>2</sub>-III phase, which was also obtained by the crystallization of glass in the interval  $P = (7–8)$  GPa,  $T = (700–800)$  K, was assigned to the CdI<sub>2</sub> structural type ( $P3m1$ ;  $Z = 1$ ;  $D_x = 4.62 \text{ g} \cdot \text{cm}^{-3}$ ). Recent investigations with the use of large crystals of high-pressure phases have made it possible to determine more exactly the structures of these modifications [8]. The GeS<sub>2</sub>-III phase in fact crystallizes into the structure with the symmetry group  $P4_2/nmc$ ; however, parameters of the unit cell ( $a = 3.46906 \text{ \AA}$ ,  $c = 10.9745 \text{ \AA}$ ) and density ( $3.44 \text{ g} \cdot \text{cm}^{-3}$ ) differ from those determined previously. The symmetry group for the GeSe<sub>2</sub>-III phase structure is unknown yet; parameters of the corresponding hexagonal unit cell are as follows:  $a = 6.468 \text{ \AA}$ ,  $c = 24.49 \text{ \AA}$ ,  $D_x = 5.18 \text{ g} \cdot \text{cm}^{-3}$ .

The GeSe<sub>2</sub> melt structure was studied as a function of pressure [7]. A sharp decrease in intermediate-order correlations within the melt structure and a certain modification of the short-range order structure at pressures of 2–3 GPa were detected.

The high pressure influence on electron properties of the compounds under consideration was investigated insufficiently. Metallization of GeSe<sub>2</sub> glasses at pressures above 7 GPa was observed in work [9]; however, the metallic phase structure was not studied. It was predicted in work [10], on the basis of calculations, that

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GeSe<sub>2</sub> crystalline modifications with the HgI<sub>2</sub> and GdI<sub>2</sub> structural types should be metals, although the calculated pressure of transitions noticeably differed from experimental values. Metallization of the GeS<sub>2</sub> and GeSe<sub>2</sub> melts under high pressures has not been studied previously. At the same time, it was established in works [11–15] that structural changes accompanied by metallization in melts of selenium and such chalcogenides, as As<sub>2</sub>S<sub>3</sub> and AsS, take place at pressures, which are substantially lower than the pressures of metallization in the crystalline state. Data on the melting lines of GeS<sub>2</sub> and GeSe<sub>2</sub> under pressure and the lines of phase transformations between various crystalline modifications were also rather scanty.

The purpose of this work was to establish the  $P$ ,  $T$  parameters of metallization of GeS<sub>2</sub> and GeSe<sub>2</sub> in the liquid and crystalline states, as well as to refine the  $P$ ,  $T$  phase diagrams of these compounds, including the determination of melting line positions.

2. The Toroid-type high-pressure device [16] allowing the generation of pressure up to 10 GPa and temperature up to 1700 °C was used in the work. The powder of the GeSe<sub>2</sub> and GeS<sub>2</sub> crystals of 99.9% chemical purity (Alfa Aesar) was used as a starting material. The metallization in the solid and liquid states was checked from the voltage-current ratio of the “sample plus graphite container” assembly. The change in the electric resistance of the sample upon heating was estimated from voltage-current dependencies. Both crystalline GeSe(S)<sub>2</sub> phases are insulators at low pressures, making no contribution to the electrical conductivity of the “heater plus sample” assembly. If the conductivity of the samples exceeds  $10 \Omega^{-1} \cdot \text{cm}^{-1}$ , accounting to 1% of the graphite heater conductivity, it may be detected from the change in the voltage-current dependence at the corresponding temperature. The value of the melt conductivity has been estimated from the data of current-voltage changes taking into account the value of the graphite container resistivity. The melting was recorded using the data of quenching experiments and morphology of samples *ex situ* or *in situ* by the onset of metallic conductivity, when the crystal is a semiconductor and the corresponding melt is a metal. Approximate lines of equilibrium between crystalline modifications were determined on the basis of quenching experiments. Electrical resistance of the GeSe<sub>2</sub>-III modification under pressure at room temperature was measured with the use of the Van-der-Pau four-probe method.

3. It was established during the recording of voltage-current characteristics at the heating of samples that the GeSe<sub>2</sub> melt becomes metallic ( $\sigma \approx 10^3 \Omega^{-1} \cdot \text{cm}^{-1}$ ) at pressures above 3.5 GPa, whereas the GeS<sub>2</sub> melt

becomes semimetallic ( $\sigma \approx 200 \Omega^{-1} \cdot \text{cm}^{-1}$ ) at pressures exceeding 7 GPa. Metallization of GeSe<sub>2</sub> in the liquid state at pressures below 3.5 GPa was observed somewhat above the melting temperature (see Fig. 1); therefore, the position of the semiconductor-metal transition

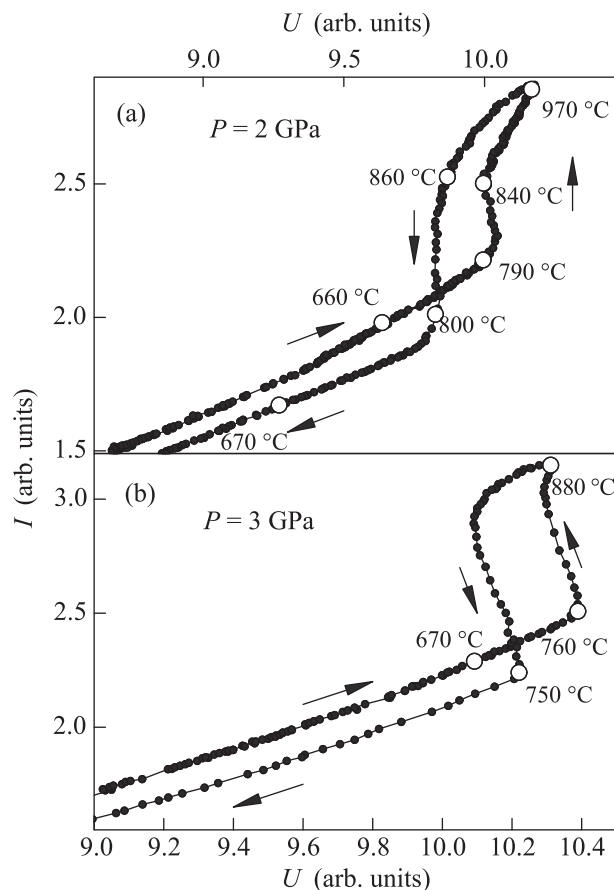


Fig. 1. Example of electric voltage-current dependencies for the experimental assemblies with GeSe<sub>2</sub> recorded during heating-cooling cycles at 2 and 3 GPa. The metallization of the melt occurs above the melting temperature

sition line was established for the melt on the phase diagram. Note that quenching from the melt under high pressures (above 1 GPa) leads to the crystallization of both GeSe<sub>2</sub> and GeS<sub>2</sub>, whereas at normal pressure, both substances readily form the glassy state. Evidently, similar to the previously investigated Se, AsS, As<sub>2</sub>S<sub>3</sub> [11–15], the viscosity of the GeSe<sub>2</sub> and GeS<sub>2</sub> melts sharply drops under pressure.

At higher pressures, metallization can be used for melting recording (see Fig. 2a). However, at pressures above 5.5 GPa, GeSe<sub>2</sub> metallizes at temperatures that are substantially lower its melting temperature, which is caused by the transition to the GeSe<sub>2</sub>-III phase. The metallic level of conductivity of this modification is re-

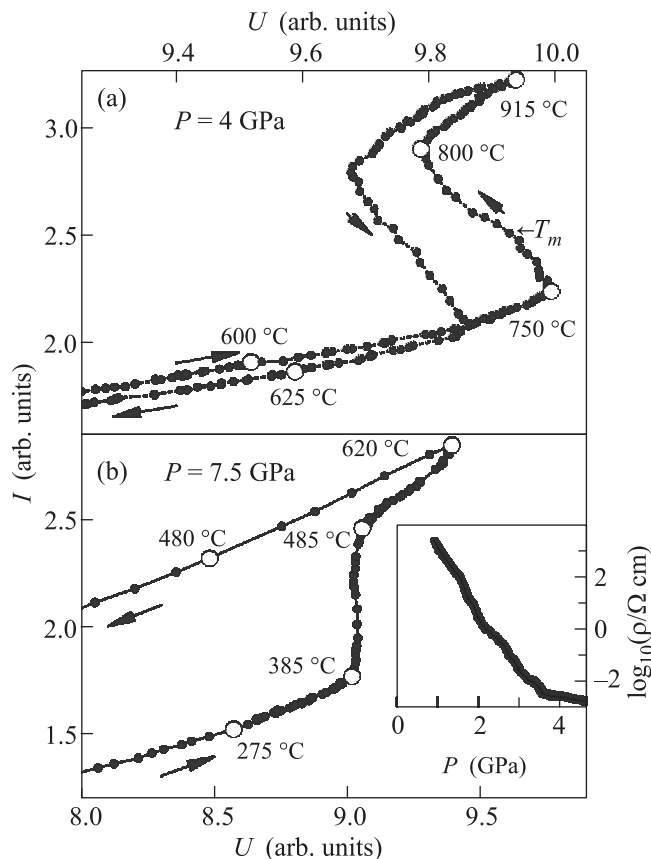


Fig. 2. Example of electric voltage-current dependencies for the experimental assemblies with GeSe<sub>2</sub> recorded during heating-cooling cycles at 4 GPa (a) and 7.5 GPa (b). The metallization during melting takes place at 4 GPa, whereas at 7.5 GPa the metallization occurs in the solid state during the transition to GeSe<sub>2</sub>-III modification. The inset shows the pressure dependence of the electric resistivity of GeSe<sub>2</sub>-III modification at room temperature

tained during the temperature decrease; however, upon the pressure decrease, the GeSe<sub>2</sub>-III phase becomes insulator. The electrical resistance versus pressure at room temperature for the GeSe<sub>2</sub>-III modification, quenched to the normal conditions, is presented in the inset of Fig. 2b. The sample of GeSe<sub>2</sub>-III modification for this study has been fabricated at 7 GPa and 700 °C and then has been quenched to the room conditions.

It can be concluded from these data that the semiconductor-metal transition in the GeSe<sub>2</sub>-III phase proceeds smoothly, without the phase transformation at pressures of 3.5–4 GPa. In this case, the electric resistance starts being measurable at the pressure 0.5 GPa and drops by seven orders of magnitude during further compression. No noticeable conductivity of other high-pressure modifications (GeSe<sub>2</sub>-II, GeS<sub>2</sub>-II, GeS<sub>2</sub>-III) is observed in the entire region of temperatures and

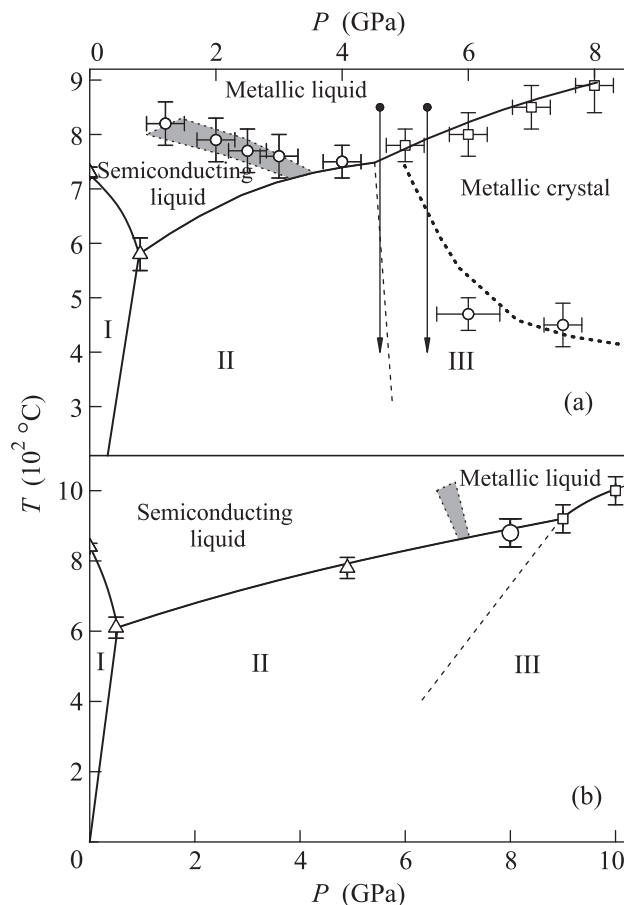


Fig. 3. Experimental pressure-temperature phase diagrams of GeSe<sub>2</sub> (a) and GeS<sub>2</sub> (b). The triangles show literature data from [1–7]. The metallization points during transformations in liquid state, solid state and melting during heating, observed in present work, are presented by open circles. The lines of metallization in the liquid and solid state are shown by dotted lines (in solid state it corresponds to the direct transition to GeSe<sub>2</sub>-III modification). The open squares correspond to the observation of the melting by *ex situ* quenching experiments. The approximate positions of the II–III equilibrium lines obtained by *ex situ* quenching experiments (both from [8] and present work) are shown by dashed lines. The vertical arrows in the panel (a) at 4.6 and 5.3 GPa show to the quenching from the melt with the formation of GeSe<sub>2</sub>-II modification and GeSe<sub>2</sub>-III modification correspondingly

pressures, where phases exist in stable or metastable states. Therefore, our experimental data support theoretical predictions [10] about the metallic state of the GeSe<sub>2</sub> modification with the CdI<sub>2</sub> structural type; however, they contradict the prediction about the metallic state of this modification with the HgI<sub>2</sub> structural type.

The data obtained, together with the data available in the literature, made it possible to construct schematic phase diagrams for both compounds (Fig. 3). It is nec-

essary to note that  $P$ ,  $T$  parameters characterizing substantial changes in the GeSe<sub>2</sub> melt structure established in work [7] correlate well with the position of the line of metallization in the melt. It can be suggested that the short-range order structure should substantially change under compression in the melts of both compounds (the fraction of 5th.- and 6th.-coordinated atoms of Ge increases). In spite of a doubtless similarity in the behavior of phase diagrams of the GeS<sub>2</sub> and GeSe<sub>2</sub> compounds at moderate pressures (up to 5 GPa), their phase diagrams differ drastically at higher pressures. On the  $P$ ,  $T$  diagram, the line of phase equilibrium GeS<sub>2</sub>-II-GeS<sub>2</sub>-III has definitely positive slope, whereas the line of phase equilibrium GeSe<sub>2</sub>-II-GeSe<sub>2</sub>-III has almost vertical (possibly negative) slope. The cooling of the melt of GeSe<sub>2</sub> at 4.6 GPa leads to the crystallization of GeSe<sub>2</sub>-II modification whereas the cooling at 5.3 GPa leads to the formation of GeSe<sub>2</sub>-III modification. GeS<sub>2</sub>-III and GeSe<sub>2</sub> III phases have, as above, different structures. Moreover, in the region of its thermodynamical stability the GeSe<sub>2</sub>-III compound is a metal, whereas the GeS<sub>2</sub>-III compound is a semiconductor. Metallization during the GeSe<sub>2</sub>-II-GeSe<sub>2</sub>-III transition is possibly responsible for the nearly zero or possibly small positive jump of entropy and the corresponding slope of the line of transformation taking into account the Clausius-Clapeyron equation.

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