

Glassy selenium at high pressure: Le Chatelier's principle still works

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(Received 31 July 2017; revised manuscript received 3 October 2017; published 17 October 2017)

Selenium is the only easily vitrified elementary substance. Numerous experimental studies of glassy Se (*g*-Se) at high pressures show a large spread in the data on the compressibility and electrical resistivity of *g*-Se. Furthermore, H. Liu *et al.* [*Proc. Natl. Acad. Sci. USA* **105**, 13229 (2008)] have arrived at the surprising conclusion that the volume of glass increases during pressure-induced crystallization. We have performed high-precision measurements of the specific volume and electrical resistivity of glassy selenium (*g*-Se) at high hydrostatic pressures up to 9 GPa. The measured bulk modulus at normal pressure is $B = (9.05 \pm 0.15)$ GPa and its pressure derivative is $B'_p = 6.4 \pm 0.2$. In the pressure range $P < 3$ GPa, glassy selenium has an anomalously large negative second derivative of the bulk modulus. The electrical resistivity of *g*-Se decreases almost exponentially with increasing pressure and reaches $20 \Omega \text{ cm}$ at a pressure of 8.75 GPa. The inelastic behavior and weak relaxation of the volume for *g*-Se begin at pressures above 3.5 GPa; the volume and logarithm of the electrical resistivity relax significantly (logarithmically with the time) at pressures above 8 GPa. Bulk measurements certainly indicate that the volume of *g*-Se glass in the crystallization pressure range is larger than the volumes of both appearing crystalline phases (by 2% and 4%). Therefore, the “volume expansion phenomenon” suggested in [H. Liu *et al.*, *Proc. Natl. Acad. Sci. USA* **105**, 13229 (2008)] is not observed, and the pressure-induced crystallization of glassy selenium is consistent with the laws of thermodynamics.

DOI: [10.1103/PhysRevB.96.134111](https://doi.org/10.1103/PhysRevB.96.134111)**I. INTRODUCTION**

Selenium is the only easily vitrified elementary substance (the critical melt cooling rate is 20 K/min) [1]. Amorphous selenium has been actively used in various copying technologies since the 1930s [1]. Amorphous and glassy selenium are widely applied in electronics and optoelectronics. The structure of liquid and glassy selenium is based on long curved pieces of quasi-one-dimensional chains of two-coordinated selenium atoms. The behavior of glassy selenium (*g*-Se) at high pressures was studied in many works. Already in 1985, review [2] summarized the results of ten studies of the compressibility of *g*-Se and eleven studies of the electrical resistivity and pressure-induced crystallization of *g*-Se. These works provided strongly different results. In particular, different groups gave values from 6.7 to 10.5 GPa for the bulk modulus and values from 3.2 to 10.5 for its pressure derivative [2]. The electrical resistivities of *g*-Se obtained in different works at the same pressures differ by several orders of magnitude, and the crystallization pressure is in the range from 6 to 14 GPa according to different studies. Such a large difference in the experimental data was due to several reasons including non-hydrostatic conditions, different phase and chemical purities of initial glasses, and methodical problems. Since the time of review [2], the situation has changed but only partially. It has been established that the processes of crystallization of *g*-Se strongly depend on the observation time and on the level of hydrostaticity of a pressure-transmitting medium, and the most reliable crystallization pressures lie in the range of 9–11 GPa. The authors of [3] explained an anomalous decrease

in the electrical resistivity of *g*-Se in the initial stage of crystallization: crystallization appeared to lead to a metastable metallic monoclinic phase, which is gradually transformed to a stable phase that is a semiconductor trigonal phase under these conditions. At the same time, data on the behavior of the volume of *g*-Se under pressure remain contradictory primarily because the accuracy of measurements of the volume of glasses at pressures above 5 GPa within the methods used in all works was no more than 1%–3%. Among measurements of the volume of *g*-Se at superhigh pressures, we emphasize work [4] where the volume was measured by an optical method at five pressures up to 10.3 GPa. In [3], the volume of the *g*-Se sample was measured by the microtomography method at three pressures up to 10.7 GPa. The authors of [4] and [3] stated that the volume was measured with an accuracy of 5% and 0.45%, respectively (the pressure was measured in both works with an accuracy of 0.2–0.3 GPa). Structural studies under pressure were also performed in both works. The conclusion that the pressure-induced crystallization of *g*-Se to the equilibrium trigonal modification is accompanied by an increase in the volume is the most surprising conclusion made in [3]. At the same time, all known cases of an increase in the volume of a system under pressure occurred with changes in the chemical composition or an irreversible decay into several phases. The expansion of a single-component monatomic system under pressure contradicts Le Chatelier's principle and violates the first law of thermodynamics. The metastable and nonequilibrium of the initial state of *g*-Se weakens this paradox but only at first glance.

The aim of this work is to perform high-precision measurements of the compressibility, electrical resistivity, and relaxation processes in *g*-Se at high pressures up to 9 GPa under purely hydrostatic conditions.

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II. EXPERIMENTAL METHODS

Initial glasses were obtained from pure Se (99.999%) (Aldrich Chemical Ltd.). To fabricate a glass sample, the pristine Se substance was placed in a copper frame with Teflon chemical insulation. Quenching from a melt in the frame was performed from 270 to 0 °C with an initial cooling rate of 50 K/s. The resulting glass samples had a density of 4.28 g/cm³ and were free of pores and impurity of the crystalline phase. The absence of traces of a crystalline phase was tested by the x-ray diffraction method. High-pressure experiments were performed in a toroid apparatus [5]. The volume of amorphous samples under hydrostatic pressure was measured at room temperature (294 K) by the strain gauge technique [6]. The method is based on usage of hand-made tiny strain gauges of original design. The sensor element of the gauge is made of single straight constantan wire with spot-welded potential contacts made of the same wire. It is the exact balance of pressure dependencies of volume and resistivity of constantan that make it possible to measure large deformations under high pressure with indistinguishable transition from elastic to plastic regimes. The nearly zero temperature coefficient of resistivity is also very helpful. The high accuracy of this method is attainable only at truly hydrostatic conditions with zero shear stresses in the sample. This technique was successfully applied to study both oxide and chalcogenide glasses (see, e.g., [7–10]). The absolute error of measurement of the volume in this method is 0.15% and the sensitivity of measurements is 10⁻⁵. The compressibility was measured for 3 × 2 × 1.5 mm samples. In order to avoid the formation of nuclei of the crystalline phase, strain gauges were attached to a sample by an epoxy glue at room temperature. This increases a possible systematic error of measurement of the volume to 0.2% at the maximum pressure. A methanol-ethanol (4:1) mixture with a hydrostatic limit of about 10 GPa was used as a pressure-transmitting medium. The pressure was measured by a calibrated manganin gauge. The reproducibility of the pressure scale was better than 0.01 GPa. The volume was measured under the continuous variation of the pressure at a rate of 0.08–0.12 and 0.03–0.05 GPa/min under compression and decompression, respectively. The electrical resistivity of the glasses was measured both by the two-probe method in silicon (quasihydrostatic) media and by the four-probe method under hydrostatic conditions. In the former case, because of the shunting of a sample by a gasket, the range of measurements of the electrical resistivity was limited from above by 10⁶ and 10⁸ Ω cm under compression and decompression, respectively. In the latter case, the conductivity of alcohols provided the upper limit of measurements of 10⁵ Ω cm. The silicon medium (the 1:1 mixture of acetate silicone sealant and polysiloxane fluid PES-5), being a good insulator, created some problems with measurements of the pressure. To solve these problems, in addition to the manganin pressure gauge, a Bi reference was placed in the high-pressure cell, which allowed the correction of the data from the manganin pressure gauge under both compression and decompression. For qualitative measurements, we used contacts glued by a silver paste and a condenser-like shape of the 1 × 2 × 2 mm sample. For high-precision quantitative measurements, we used solder contacts [eutectic In-Bi-Sn (3:1:1 atomic) solder]

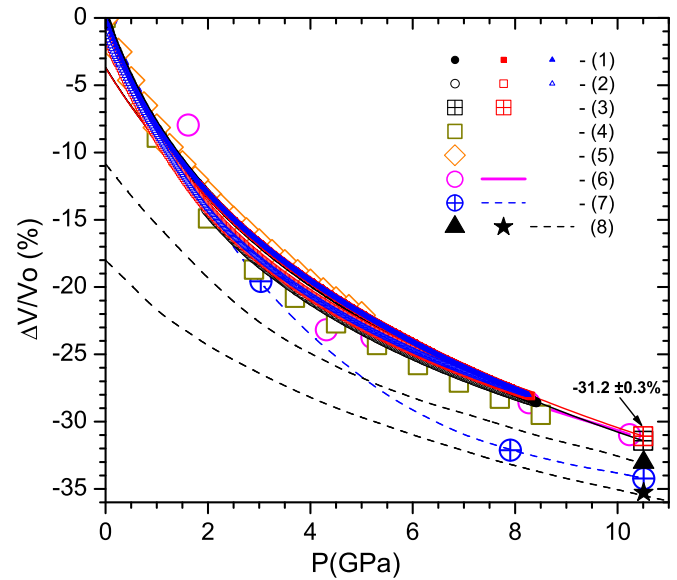


FIG. 1. Pressure dependencies of the volume of glassy selenium in three experiments under compression (1), decompression (2), and extrapolation to 10.5 GPa (3) in comparison with the data from [11] (4) with the pressure scale corrected above 2.5 GPa, [12] (5), [4] (6), and [3] (7). Symbols (8) denote the volumes of two crystalline phases after crystallization at high pressure and subsequent decompression [3].

to the 2.5 × 1 × 1 mm sample. In this case, the possible error of data on the absolute value of the electrical resistivity (determined by the errors of evaluation of the geometric factor of the samples) was estimated as 10%. Soldering was performed at a soldering tip temperature of (64 ± 0.5) °C. The absence of traces of a crystalline phase after soldering was tested by the x-ray diffraction method on a similar sample at a temperature increased by 4 °C and at the doubled soldering time. After high-pressure measurements, all samples were also preserved in a glassy state (it was also checked by x-ray diffraction).

III. RESULTS AND DISCUSSION

The results of the measurement of the volume under pressure are shown in Fig. 1. The data for three different samples under both compression and decompression coincide within an accuracy of 0.2%. The measurements were performed with a pressure step of 0.02–0.03 GPa, which allowed obtaining an almost continuous curve that does not require interpolation. The final part of the compression curve between 8.5 GPa and 10.5 GPa has been obtained using the extrapolation by Murnaghan's equation of state. For comparison, Fig. 1 also presents the experimental points from [3,4], as well as the most accurate early measurements performed for large samples in piston-cylinder chambers [11,12] (Bridgman's data are reduced to the current pressure scale). The main result of these measurements is the conclusion that the volume of *g*-Se at crystallization pressures is larger than the volumes of both crystalline phases, equilibrium trigonal and metastable monoclinic, by 2% and 4%, respectively. Although the measurements were performed up to a pressure

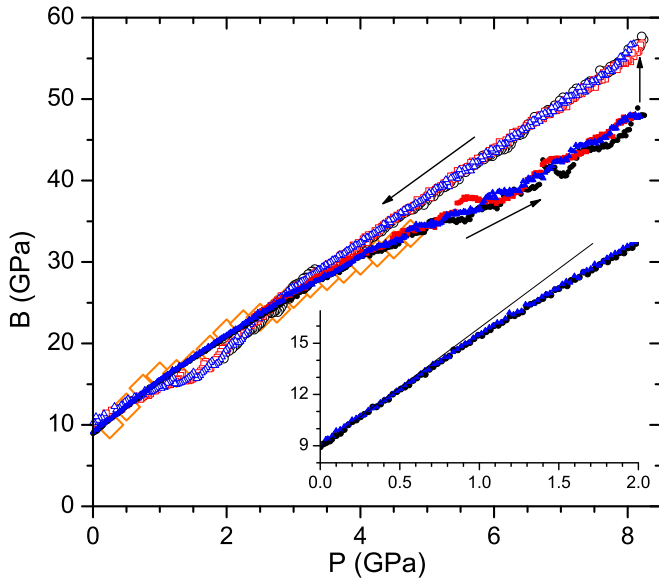


FIG. 2. Apparent bulk moduli of glassy selenium obtained from the initial $V(P)$ data by the formula $B = -VdP/dV$ under compression (closed symbols) and decompression (open symbols). Large open symbols are the data from [12]. The inset shows a magnified low-pressure region, the straight line highlighting the nonlinearity of bulk modulus and negative B'_p value. Colors and symbols representing results of various experiments correspond to the notation in Fig. 1.

of 8.5 GPa, they allowed estimating the densification degree in the crystallization region with the absolute accuracy of no worse than 0.3% [$(31.2 \pm 0.3)\%$]. Hysteresis in the behavior of the volume under compression and decompression is small; the residual densification is smaller than 1%.

A high sensitivity of the strain-gauge method allows determining the effective bulk moduli of glasses by direct differentiation over points without additional processing and without fitting by any equation of state. The pressure dependence of the effective bulk moduli for three glassy g -Se samples is shown in Fig. 2, where our experimental data are presented along with the results taken from [12]. The measured bulk modulus at atmospheric pressure is $B = (9.05 \pm 0.15)$ GPa and its pressure derivative is $B'_p = 6.4 \pm 0.2$, which are close to the data of early ultrasonic measurements (see [2]). In contrast to most of the glasses, the first pressure derivative of the bulk modulus of g -Se B'_p decreases strongly with increasing pressure, and the second pressure derivative of the bulk modulus determined in the range of 0–3 GPa is negative and quite large in absolute value: $B''_p = -(0.45 \pm 0.15)$ GPa $^{-1}$. Although the pressure dependence of the modulus is strongly nonlinear, the behavior of g -Se glasses is elastic (without relaxation processes) up to a pressure of 3.5 GPa. Weak relaxation processes begin at higher pressures; the additional “softening” of the effective relaxing modulus begins at these pressures, and the effective moduli under compression and decompression become different. Under decompression, the elastic behavior is observed to 3 GPa, and the pressure derivative of the relaxed modulus is $B'_p = 5.8 \pm 0.15$.

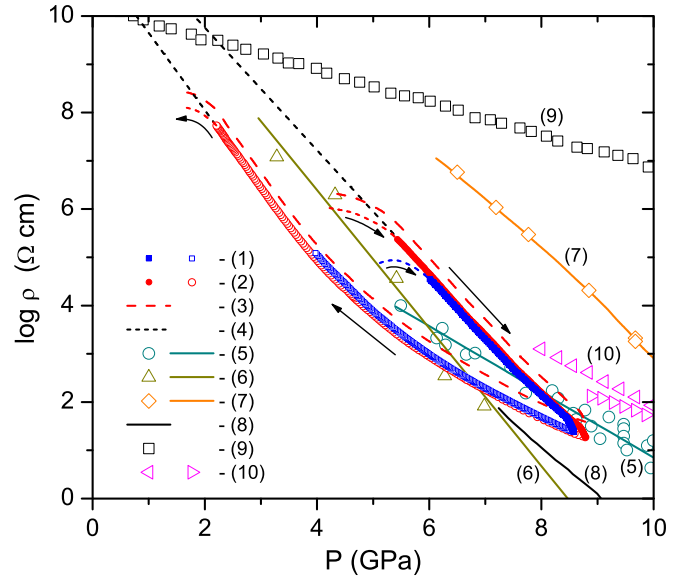


FIG. 3. Electrical resistivity of glassy selenium in two experiments under compression (small solid symbols) and decompression (small open symbols) for (1) four-probe soldered contacts under hydrostatic conditions; (2) two-probe silver paste glued contacts in silicon media, corrected (see main text); (3) the same data, as measured; and (4) linear extrapolation to the high-resistivity region. The previous data are taken from [13] (5), [14] (6), [15] (7), [16] (8), [3] (9), and [17] (10). Resistivity values (5–7) were recovered from $R(P)$ data assuming an estimate $(50\text{--}100) \times 10^{-6}$ Ω cm for the resistivity of metallic selenium from [13], resistivity (10) is taken from Fig. 26 in [17], and the geometrical factor is estimated by comparing Figs. 26 and 4 in [17].

Figure 3 shows the results of measurements of the electrical resistivity. Our measurements by the two-probe method provide a qualitatively correct dependence under both compression and decompression, but differ in absolute value by about a factor of 2 from quantitative measurements by the four-probe method on solder contacts under purely hydrostatic conditions. Both dependencies can be matched with a high accuracy by only one multiplier (see Fig. 3). It is seen that the electrical resistivity under pressure depends almost exponentially on the pressure in agreement with the hypothesis of an almost linear decrease in the gap with increasing pressure. The minimum electrical resistivity reached in our experiments is 20 Ω cm. For comparison, Fig. 3 shows the results of several early studies of the electrical resistivity [2,13–17]. It is seen that all preceding data are strongly (by orders of magnitude) different from each other and from correct values. This difference is mainly due to nonhydrostatic conditions of the previous experiments and to the absence of previous measurements by the four-probe method with solder contacts.

The electrical resistivity, as well as the volume, varies upon isobaric aging at high pressures. The relaxation rate increases monotonically with the pressure. Figure 4 shows examples of relaxation changes in the volume and electrical resistivity at pressures above 8 GPa. Similar to all glasses, changes in the volume and logarithm of the electrical resistivity are proportional to the logarithm of the time (logarithmic relaxation) [7–10]. The rate of volume relaxation in g -Se is

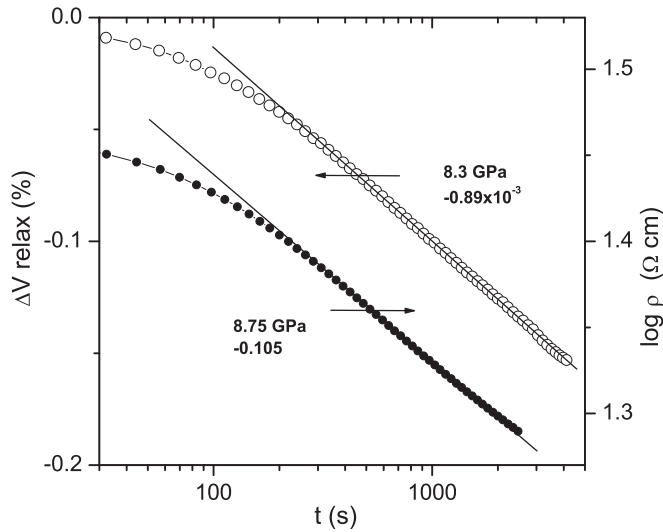


FIG. 4. Relaxation of the volume (open symbols, left scale) and electrical resistivity (solid symbols, right scale) of glassy selenium at the end of compression. The numbers beside the lines denote the pressures of expositions and the slopes of linear parts of the graphs.

comparable with the values for glassy germanium selenides and arsenic telluride at the same pressures [9,10]. At the same time, the relaxation rate of the electrical resistivity of *g*-Se is significantly higher than that for *g*-As₂Te₃ at the same pressures because *g*-As₂Te₃ under these conditions is already in a metallic state [10], whereas *g*-Se is in a narrow-gap semiconductor state.

The high-precision measurements of the bulk modulus and its derivative for *g*-Se together with the previous high-precision measurements of the bulk moduli for glassy germanium selenides [9] allow the analysis of the dependence of these quantities on the concentration of germanium atoms. The corresponding data are shown in Fig. 5. It is seen that the concentration dependencies of both the bulk modulus and its derivative are strongly nonmonotonic near a concentration of germanium atoms of 20 at. %. It was previously mentioned in [1] that many properties of glassy germanium selenides are nonmonotonic near this concentration. This anomalous concentration dependence is possibly due to the existence of a “reversibility window” [18].

As was mentioned above, during the experiment (several hours), the crystallization of *g*-Se glasses was not observed. In special experiments, the samples were aged at a pressure of 8.5 GPa for a day. After decompression, an insignificant (1%–2%) fraction of a nanocrystalline phase was detected in the sample. This confirms that the pressure-induced crystallization of *g*-Se glasses has sluggish kinetics and can occur in the wide pressure range from 8 to 12 GPa, depending on the conditions of the experiment.

IV. CONCLUSIONS

Thus, the behavior of glassy selenium compressed to crystallization exhibits two intervals: an elastic behavior up to 3.5 GPa with a strongly varying pressure derivative of the bulk modulus and an inelastic behavior with weak relaxation

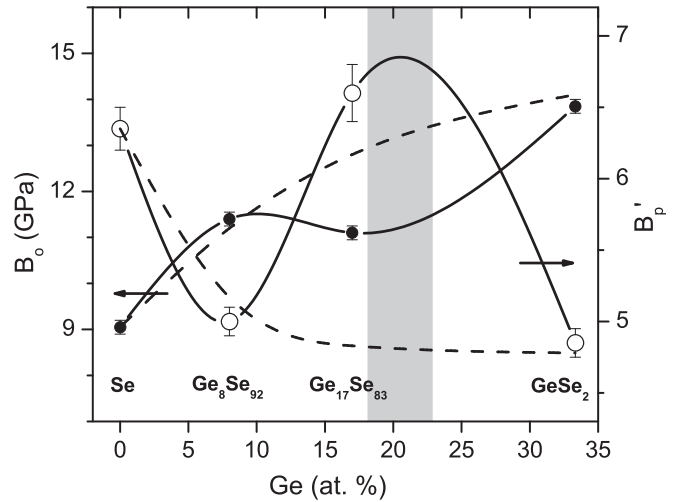


FIG. 5. Bulk modulus (solid symbols, left scale) and its pressure derivative (open symbols, right scale) versus the Ge concentration in the Se-Ge system. The gray region corresponds to the so-called “reversibility window” (see main text). The dashed lines represent an assuming regular behavior in the absence of this anomalous region of concentrations.

processes at higher pressures. The anomalous behavior of the derivatives of the bulk modulus in the elastic interval is obviously due to the specificity of the structure of *g*-Se (long curved quasi-one-dimensional chains) and to the fast variation of the effective interparticle interaction parameters. Relaxation processes are apparently associated with partially reversible changes in the structure of the intermediate-range order. The most important result obtained in this work is that the volume of *g*-Se glasses at crystallization pressures is larger than the volumes of both appearing crystalline phases (by 2% and 4%). The measured density of *g*-Se glasses at high pressures in [3] was overestimated by 3%, although the stated accuracy was 0.45%. It is noteworthy that the systematic overestimation of the density in [3] was observed at all three pressures at which the measurements were performed. It is remarkable that, on the contrary, despite a significant spread of points and a measurement accuracy of 5%, the averaged compression curve obtained in [4] is close to the correct one (the difference at maximum pressures is only 0.7%). The error of piezometric measurements of the volume in [11,12] was also no more than 1%.

It can be concluded that the behavior of glassy selenium under pressure is consistent with the laws of thermodynamics. According to Le Chatelier’s principle, the volume of an equilibrium system with an unchanged composition and a constant number of particles under isothermal compression can only decrease. The opposite behavior would mean that the compressibility is negative and contradict with the first law of thermodynamics. An increase in the volume under pressure can be possible either with the variation of the chemical composition and number of particles or with the irreversible decay of a metastable compound into several new phases (e.g., in the case of the explosion of an explosive). Such a possibility is absent for a single-component monatomic system. At the same time, glassy selenium is not an equilibrium phase and the above reasons seem at first glance not strict for it. Indeed,

a dense metastable phase under pressure at heating [or with time under constant (P , T) conditions] can be transformed to a less dense phase (e.g., diamond to graphite at temperatures above 1000°C and pressures below 5 GPa). However, the energy barriers (and, correspondingly, temperature) for such a transformation should increase with the pressure, and the segment with a negative compressibility under isothermal compression is impossible even for the metastable phase. A similar consideration is also valid for *g*-Se: crystallization should be accompanied by a decrease in the volume, and the “volume expansion phenomenon” for this glass is forbidden by the laws of thermodynamics. It should be noted that the second “volume expansion phenomenon” that is observed in [3] and

is associated with the transition of a metastable monoclinic phase to a stable tetragonal phase does not contradict the laws of thermodynamics because this metastable phase is first formed by kinetic reasons from “more metastable” glass with a significant decrease in the volume.

ACKNOWLEDGMENTS

We are grateful to N. F. Borovikov and I. P. Zibrov for assistance in the chemical and phase analysis of the samples. This work was supported by the Russian Science Foundation (Project No. 14-22-00093).

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