AsS Melt Under Pressure: One Substance, Three Liquids

V. V. Brazhkin,[1,*] Y. Katayama,[2] M. V. Kondrin,[1] T. Hattori,[2] A. G. Lyapin,[1] and H. Saitoh[2]

[1]*Institute for High Pressure Physics, Russian Academy of Sciences, 142190, Troitsk Moscow region, Russia*
[2]*Japan Atomic Energy Agency (JAEA), SPring-8, 1-1-1 Kuoto, Sayo-cho, Sayo-gun, Hyogo, 679-5143, Japan*
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An *in situ* high-temperature—high-pressure study of liquid chalcogenide AsS by x-ray diffraction, resistivity measurements, and quenching from melt is presented. The obtained data provide direct evidence for the existence in the melt under compression of two transformations: one is from a moderate-viscosity molecular liquid to a high-viscosity nonmetallic polymerized liquid at $P \sim 1.6$–2.2 GPa; the other is from the latter to a low-viscosity metallic liquid at $P \sim 4.6$–4.8 GPa. Upon rapid cooling, molecular and metallic liquids crystallize to normal and high-pressure phases, respectively, while a polymerized liquid is easily quenched to a new AsS glass. General aspects of multiple phase transitions in liquid AsS, including relations to the phase diagram of the respective crystalline, are discussed.

A decade or two ago, the phenomenon of phase transitions in simple isotropic liquids was not given worthy consideration in the scientific literature, except for a few theoretical works, for example, Ref. [1]. However, in recent years, these transformations have been found to occur under high pressures in the melts of elementary substances (P, Se, S, Bi, e.), oxides (H_2O, Y_2O_3-Al_2O_3, GeO_2, etc.), and halogenides ($AlCl_3$, $ZnCl_2$, AgI, etc.) [2–13]. Transformations in melts under pressure are accompanied by structural changes (both in the short-range and intermediate-range order structures) and variations in physical properties. Transformations in simple liquids can be both smooth and sharp. The analysis of the reasons for different transformation scenarios in disordered media [14] suggests that sharp transitions in liquids are realized for the substances that experience, in the crystalline state, substantial changes in the short-range order structure and type of bonding.

While the possibility of structural transformations under compression in some melts is beyond doubt, the question, raised in Refs. [8,9], of whether the phase diagram of the melt is a shifted reflection of the pressure-temperature phase diagram of the crystal, remains to be answered. Multiple phase transitions under pressure for one substance in the crystalline state are possible; whether multiple structural transformations can similarly be observed in the respective melts is a matter of debates.

This work reveals a striking example of the realization under compression of two phase transformations in the AsS chalcogenide melt, with both of them occurring in narrow pressure intervals and accompanied by a considerable change in the structure and properties.

Chalcogenide substances are attractive for research on phase transformations in solid and liquid states, since under changes of pressure and temperature, these systems feature a great number of structures and various types of bonding. Under compression, elementary substances Se and S show structural phase transformations followed by

insulator-metal transitions both in solid and liquid states [7–9]. The $GeSe_2$ compound displays a series of interesting phase transitions under compression in the crystalline state, as well as a significant modification of the intermediate-range order structure in the melt [15].

This work includes *in situ* high-temperature high-pressure studies of the structure and electrical conductivity of the AsS chalcogenide melt. The AsS system at various concentrations of components realizes (a) network covalent structures in solid and liquid states, revealing high melt viscosity and a tendency to the formation of the glass based on the As_2S_3 composition, and (b) pseudomolecular structures based on As_4S_5, As_4S_4, As_4S_3 pseudomolecules [16]. The As_4S_4 substance is based on As_4S_4 molecular groups both in crystalline and liquid states. Very few attempts to examine crystalline As_4S_4 under pressure have been made [17,18]; the properties and structure of the melt of the AsS composition under compression have not been studied. In this work, two fairly sharp transitions accompanied by a significant modification of the structure and properties in liquid AsS were found in the 1.6–2.2 GPa and 4.6–5 GPa ranges.

The As_4S_4 realgar of 99.7% chemical purity was used as a starting material. The *in situ* structural study of solid and liquid AsS was carried out by the energy-dispersive x-ray diffraction (EDXD) method using the SMAP 180 press machine at the SPring-8 synchrotron beam line BL14B1. The structures of the melts were examined at temperatures exceeding the melting points by 30–150 K. The AsS sample was placed in a container made from hexagonal BN or high-purity graphite. A cubic press was used for generating high pressure up to 8 GPa. Heating was produced by passing the alternating current through a graphite heater. The temperature was measured by using a chromel-alumel thermocouple. The cooling rate varied in the 1 K s^{-1}–500 K s^{-1} range and was measured by taking the thermocouple readings directly. The pressure was determined from the Decker equation of state of NaCl. The

0.2 mm thick tablet of a NaCl-BN mixture was placed near the sample. The metallization of the melt was observed from the voltage-current ratio of a "sample plus graphite container" assembly in the Toroid high-pressure device [19].

The AsS pressure-temperature phase diagram resulting from the *in situ* x-ray diffraction measurements is presented in Fig. 1. Most of the experiments can be defined as heating-cooling cycles at almost constant pressure. Under compression, crystalline As_4S_4 undergoes phase transformation into a high-pressure modification that can be retained in metastable form at normal conditions. We present the kinetic lines of the direct and reverse transitions. In the narrow pressure and temperature range of about 2.8 GPa and 800 K, another modification, similar to the one reported in Ref. [18], exists. In this range, the AsS I phase on heating directly transforms into the AsS III phase. Structural data on the AsS crystalline phases under compression will be presented elsewhere.

The principle result of this work is the discovery of a considerable change in the structure of the AsS melt under compression. The structural data obtained for liquid AsS under pressure are shown in Figs. 2 and 3. At small diffraction angles $2\theta = 3°$–$4°$, the EDXD technique adequately depicts the main characteristics of the structure factor (including peak positions and intensities) only for small wave vectors ($k = 1$–2 Å^{-1}). For examining the

structure factor in the 3–8 Å^{-1} region of the wave vectors, large diffraction angles $2\theta = 8°$–$14°$ are required. Intermediate values of the wave vectors ($k = 2$–3 Å^{-1}) should be investigated at the $2\theta = 5°$–$6°$ diffraction angles. Figures 2(a)–2(d) show the intensities of the scattering

FIG. 2 (color online). EDXD experimental spectra recorded at different scattering 2θ angles [(a) $2\theta = 3°$, (b) $2\theta = 4°$, (c) $2\theta = 6°$, and (d) $2\theta = 10°$] and normalized by the amplitudes 1st diffraction peak (a)–(c) and 2nd diffraction peak (d), respectively. The initial EDXD data, recorded with the ≈ 40 eV energy step, have been smoothed by the Fourier transformation filter and converted from the energy abscissa scale to the wave scattering vector Q. The asterisk on the plot (a) marks the peaks at $Q \approx 1.8$ Å^{-1}, appeared in the spectra due to contribution of the (002) reflections from the graphite heater. Double structure of the 2nd diffraction peak is due to instrumental factor. Plot (b) shows changes of the prepeak, while examples of the whole spectra are shown in the inset. The thin and thick lines correspond to different states of the AsS melt (see the text).
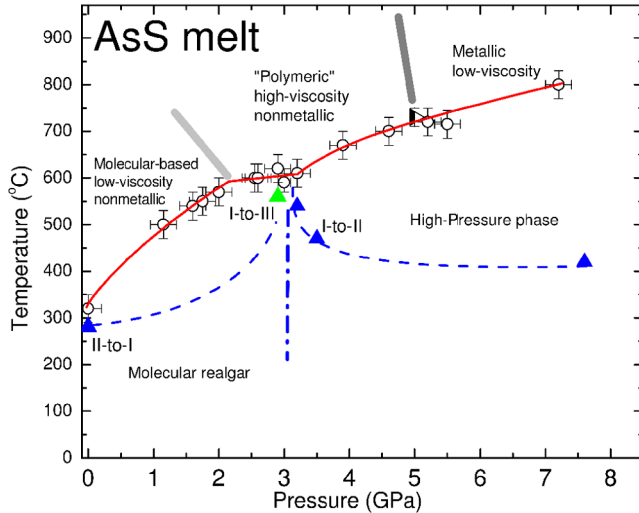

FIG. 1 (color online). Pressure-temperature phase diagram of AsS in crystalline and liquid states. Opened circles correspond to the experimental melting points of AsS crystal, while the thin line and thick lines are approximations of melting line and boundaries between liquid states, respectively. Solid triangles correspond to phase transitions between crystalline phases, determined at the near isobaric heating. Semisolid triangle corresponds to metallization of liquid AsS. Dashed lines are approximation of experimental transition lines (kinetically dependent) from AsS I (right line) and AsS II (left line) crystalline phases, while dashed-dotted line is approximation of I-II equilibrium line.
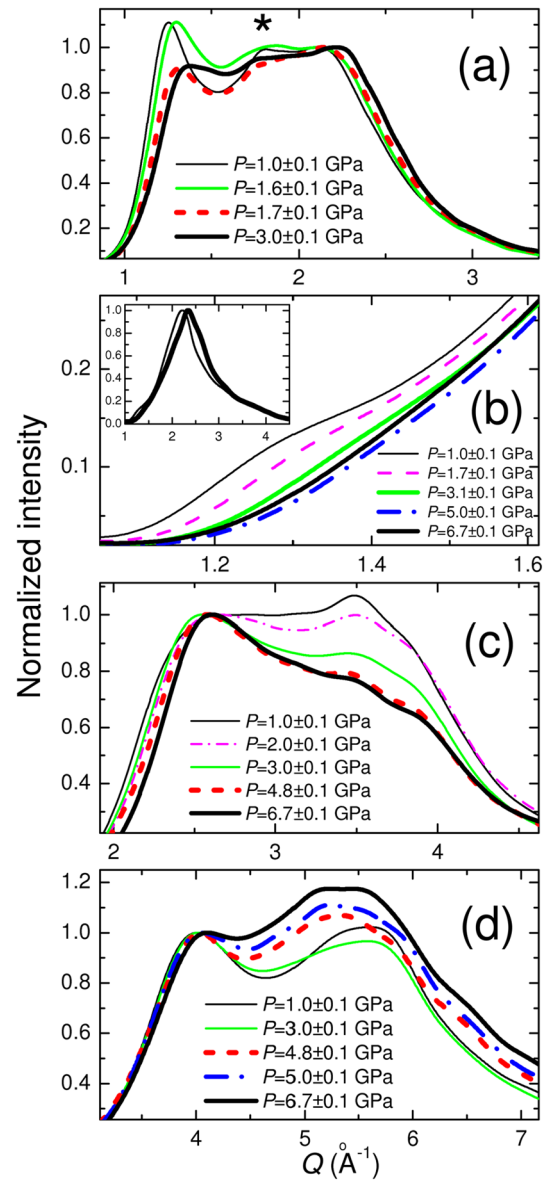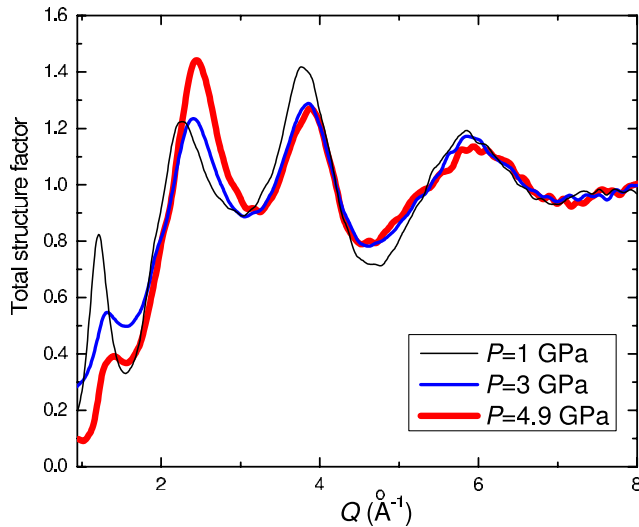
FIG. 3 (color online). Typical structure factors for different states of the AsS melt, including the molecular liquid at 1 GPa (thin line), polymeric liquid at 3 GPa (intermediate-thickness line), and metallic liquid at 4.9 GPa (thick line). All structure factors are obtained for the experimental sets of spectra recorded at temperatures exceeding the melting point by 70 K.

for different diffraction angles; Fig. 3 presents the structure factors calculated on the basis of the raw intensity data.

When compressing liquid As_4S_4, one can observe a significant decrease of the prepeak of the structure factor at $k = 1.2–1.4$ Å^{-1} [Figs. 2(a) and 2(b)]. This decrease corresponds to the breakdown of the intermediate-range order in the liquid under compression, which is a fairly common phenomenon.

At $P \approx 1.6–2.2$ GPa pressure, a change in the short-range order structure of the AsS melt is observed: the relative intensity of the second maximum of the structure factor at $k \sim 3.5–3.8$ Å^{-1} is considerably reduced in comparison with the first maximum at $k \sim 2.2–2.5$ Å^{-1} [see Figs. 2(c) and 3]. In the 2.2–3.5 GPa pressure range, the structure factor of liquid AsS is quite similar to that of the network covalent melt As_2S_3 at normal pressure. On the melting curve at $P \approx 2$ GPa, the change of the slope, implying a notable densification of the melt, is observed. It can be assumed that at $P \approx 2$ GPa in liquid AsS, a transition from the quasimolecular to covalent polymerized As_2S_3-like melt takes place. A complimentary argument in favor of this assumption is provided for by glass formation of the AsS melt at cooling in the 2–4 GPa range (which was discovered in the course of this work), while at $P < 1.5$ GPa, the AsS melt crystallizes, even at a high cooling rate of 100 K s^{-1}, to β-realgar. At 1.5 GPa $< P <$ 2 GPa and at 3.8 GPa $< P <$ 4.3 GPa on cooling, a submicron crystals plus glass mixture is formed. Hence, in the 2–4 GPa pressure range, the AsS melt has high viscosity, which is bound to be observed for the polymerized melt.

Another qualitative change in the melt structure is observed at $P \sim 4.6–4.8$ GPa. This change represents a com-
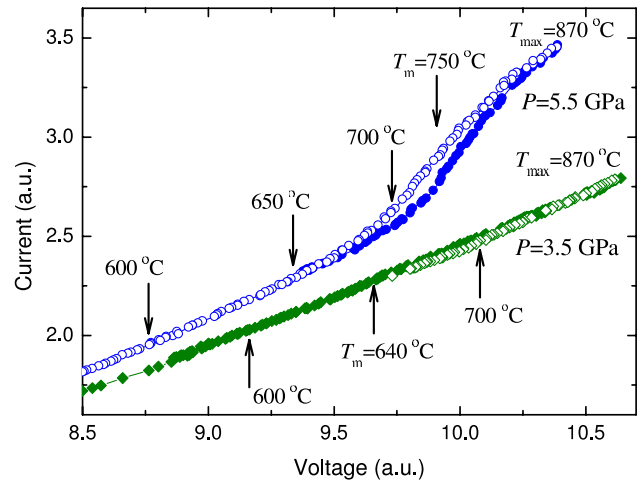

FIG. 4 (color online). Example of electric voltage-current dependencies recorded at 3.5 GPa (diamonds) and 5.5 GPa (circles) for the "graphite ampoule plus AsS sample" assemblies. The close and open symbols correspond to the temperature increase and decrease, respectively. At pressures $P > 4.8$ GPa, a significant current increase was observed at the melting temperature, suggesting the metallic state ($\sigma \sim 10^3$ Ω^{-1} cm^{-1}) of the liquid at these pressures. The width of the voltage-current dependency anomaly, corresponding to the melting, is associated with the temperature hysteresis on the sample. Sample temperatures at increasing current are indicated on the diagram.

plementary decrease in the intensity of the second peak of the structure factor as compared to the first and third (at $k \sim 5.2–6$ Å^{-1}) peaks [Figs. 2(c), 2(d), and 3]. The electric conductivity data obtained for liquid AsS under pressure revealed that metallization of the melt occurs exactly within this pressure range (Fig. 4). A rapid cooling of the AsS melt with the cooling rate of 100 K s^{-1} at $P >$ 4.5 GPa does not lead to glass transition of the melt. Instead, the crystallization to the high-pressure phase with large (50–100 μm) grain size is observed. Hence, the viscosity of the AsS metallic melt is obviously low.

Thus, the AsS melt under compression gives the example of the existence in one substance of three liquid states with different structures and properties: a molecular-based liquid at $P < 1.6$ GPa, polymerized viscous liquid at $2.2 < P < 4.5$ GPa, and metallic liquid at $P > 4.8$ GPa (Fig. 1).

From the data on the critical cooling rate required for glass formation and from the grain size of a solidified phase, we can conclude, like it was done in Ref. [12], that the melt has moderate viscosity at low pressures, low viscosity at high pressures, and very high viscosity at intermediate pressures. The direct measurements of the viscosity are urgently needed to collect quantitative data.

The change in the electric resistance of the sample on heating was estimated from voltage-current dependencies. The crystalline AsS phases are insulators, making no contribution to electrical conductivity of the "heater plus sample" assembly. If the AsS conductivity after melting

becomes higher than 10 $\Omega^{-1}\,cm^{-1}$, making up 1% of the graphite heater conductivity, it may be detected through the change in the voltage-current dependence at the melting temperature. From the voltage-current dependences obtained at $P > 4.8$ GPa (Fig. 4), we can assess that the electro conductivity of the sample after melting becomes comparable with the graphite heater conductivity, i.e., $\sim 10^3\ \Omega^{-1}\,cm^{-1}$. At $P < 4.5$ GPa, the AsS melting is not accompanied by the change in the voltage-current dependencies (Fig. 4); hence, the conductivity of the sample still remains lower than 10 $\Omega^{-1}\,cm^{-1}$. That is, at the melt metallization at 4.5–4.8 GPa, the conductivity rises by more than two orders.

Semiconductor-metal transitions have been previously observed for the Se, S, I_2, P melts [9], with the last one showing transformation between the molecular (insulator) and polymeric (metallic) states. In the $ZnCl_2$ and $AlCl_3$ liquids, a transition from the molecular-network state to the ionic melt is observed [12]. The AsS melt, however, experiences two transformations. It can be expected that this behavior is not unique and will be observed for many liquids, including many other chalcogenide melts. In this connection, a recent study on liquid ZnTe reports an interesting and uncommon behavior of structural characteristics of the substance under pressure [20]. Unfortunately, it is not yet possible to be certain about whether rather sharp transformations in the AsS melt are in reality continuous or first order. The observation of the crystals trapped into glassy phase in the samples quenched around 2 and 4 GPa provides the indirect evidence of the sharpness of the transitions, although the gradual rapid structural and viscosity changes still cannot be excluded.

The structural changes in melts are bound to be reflected in the behavior of the respective glasses and amorphous solids; i.e., both can undergo more than one transformation too. Indeed, in glassy SiO_2 and amorphous H_2O ice, two regions of transformations are observed under compression [21,22]. Worthy of mention also is the recent Letter [23], reporting a transition from the molecular to polymeric state for glassy chalcogenide $As_{51.5}S_{46.25}Ce_{2.5}$, a substance similar in many respects to the As_4S_4 chalcogenide.

Thus, multiple phase transformations in melts and crystals are equally possible. It may be supposed that the occurrence of multiple phase transitions in melts under compression is a feature common to a wide class of substances with a molecular-based structure at normal pressure. The pressure-temperature diagrams of such melts can be regarded in some respects as shifted reflections of the phase diagram of their respective crystalline states. The existence of several phase transformations in simple isotropic liquids and the corresponding presence of more than two critical points in a substance remain a challenge for various theoretical models of simple melts.

*brazhkin@hppi.troitsk.ru
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