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Structural transformation yielding an unusual metallic state in liquid As_2S_3 under high pressure

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The As_2S_3 melt at room pressure represents a liquid having a three-dimensional network structure, semiconducting properties, and a huge viscosity. We have found that under high pressure a considerable change in the medium and short-range structure of this liquid is observed. Intermediate-range order correlations in the atomic arrangement almost disappear under pressure and an increase in the coordination number is observed. This increase is evidently associated with the formation of a significant fraction of the wrong neighbors As-As. At pressures above 6 GPa, the As_2S_3 melt has a conductivity close to the minimum conductivity value of $\sim 100\ \text{Ohm}^{-1}\ \text{cm}^{-1}$ and a moderate viscosity of $\sim 0.5-1$ Pa s. Obviously, the transition under high pressures to such "strange metallic" liquids are bound to be seen in many other chalcogenide melts with network structure.

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Phase transformations in liquids and a change in the structure and properties of liquids under pressure are one of the hottest topics of condensed-matter physics.[1,2] The As_2S_3 melt is one of the most important archetypical strong glass-forming liquids, whose viscosity of 8000 Pa s near the melting temperature at normal pressure is record high for chalcogenide melts,[3] making the crystallization of As_2S_3 almost impossible.[4] The As_2S_3 substance ranks first among chalcogeniges from the viewpoint of the production of amorphous and glasslike industrial materials. The crystalline phase of As_2S_3 is a semiconductor (orpiment) with a layer structure, each As atom is surrounded by three S atoms and each S atom by two As atoms. The liquid and glassy states of As_2S_3 largely preserve the short-range order (SRO) and medium-range order (MRO) of the crystalline counterpart and have a similar electronic structure.[5] However, the layer structure in the melt is partially disrupted and the liquid network contains some amount of broken bonds or "wrong" As-As (S-S) bonds.[6]

Interest in liquid arsenide chalcogenides, such as As_2S_3, As_2Se_3, and As_2Te_3, as well as in elementary liquid Se, S, and Te, is also aroused by the fact that the transition from a semiconductor to a metallic state occurs in these melts at high temperatures and moderate pressures in the supercritical region[7–12] and (or) under high pressures in the vicinity of the melting curve.[13–17] Similarly, the glassy states of these materials undergo a semiconductor-metal transition under compression at room temperature.[18] The mechanism of the semiconductor-metal transition in these substances has not yet been fully clarified;[7] at any case, it is not the classical Mott-type transition.[5] The best theoretically and experimentally studied semiconductor-metal transition is the one occurring in liquid chalcogenides As_2Se_3, As_2S_3, and As_2Te_3, and liquid Se at high temperatures and moderate pressures. This transition is accompanied by significant structural and thermodynamic changes.[7–12] It has been found that with an increase in temperature, the three-dimensional network structure is transformed into a twofold chainlike structure. An important feature of the electronic structure of these chalcogeniges is the existence of lone-pair electron states; these states do not participate in chemical bonding and are located on S (Se) atoms. At high temperatures, a charge transfer from S (Se) to As atoms leads to metallization.[7–11] At the same time, some peculiarities of this semiconductor-metal transition, particularly, a volume contraction upon metallization of liquid Se and As_2Se_3, remain unexplained.[7] Apparently, a very important aspect of the structural transformations in liquid As_2Se_3 and As_2S_3 is the formation of new As-As bonds in the metallization region.[7,10,11]

The melts of the given chalcogenides have virtually been unstudied experimentally at very high pressures in the vicinity of the melting curve. The intermediate-range order in liquid and glassy As_2S_3 under pressure has been investigated by *ab initio* molecular-dynamics simulation.[17] It has been revealed that the three-dimensional network structure is evidently largely disrupted under pressure and the As-As coordination number substantially increases. Some experimental data on the SRO, MRO, and optical properties of glassy As_2S_3, As_2Se_3 under pressure at room temperature have been obtained.[5,19] The conclusion about the change in the SRO, MRO, and delocalization of lone-pair electron states under pressure has been drawn.

The metallization of liquid Se under pressure has been studied more thoroughly.[13–16] Note that the Se melt, unlike As_2S_3 and As_2Se_3, is not a three-dimensional network but a set of long chains of two-coordinated Se atoms. It is found that near the melting curve, the metallization occurs in a narrow pressure range around 4 GPa and is accompanied by considerable structural changes and a volume contraction by 4–5 %.[13–16] The structural changes involve the break in the chains and the formation of a significant fraction of three-coordinated Se atoms.[14,15] The structure of the Se melt under high pressures becomes similar to that of liquid Te at normal pressure. In doing so, the viscosity of liquid Se drops from moderate values of 0.1–1 Pa s to typical metallic values of 0.005–0.01 Pa s (Ref. 20) and the electrical conductivity increases to sufficiently high values of $3-5 \times 10^3\ \text{Ohm}^{-1}\ \text{cm}^{-1}$.[13] There is the continuous line of metallization of liquid Se onto P,T plane. Nevertheless the mechanisms of metallization of liquid Se at low-pressure-high-temperature region and under high pressures near melting curve are quite different from each other.[16]

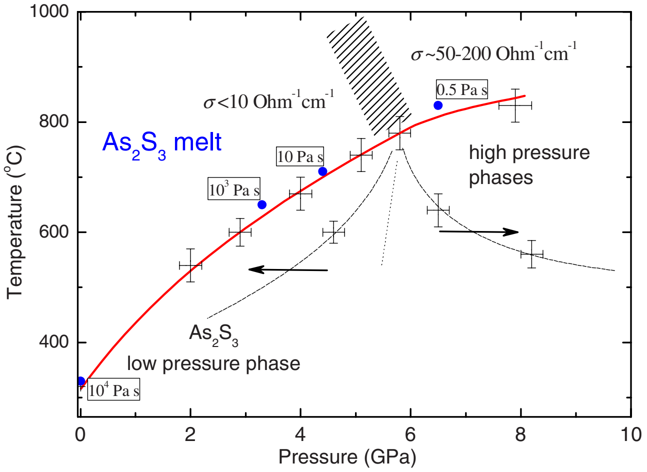

FIG. 1. (Color online) Experimental pressure-temperature phase diagram of As_2S_3. Crosses show points and their uncertainties for the experimentally observed phase transitions. Solid line is an approximation of the melting curve and dashed lines are approximations for the experimental kinetic curves of the solid-solid phase transitions. The points of viscosity measurements are shown by solid circles and marked by measured values of viscosity. Shaded region selects a boundary between the melting states with low and high conductivities.

We have very recently investigated the structural changes and metallization in the realgar melt AsS.[21,22] It has been revealed that the structure of the AsS melt under pressure changes from a molecular structure to covalent and then to a liquid metallic structure. It has been found that at $P > 5$ GPa, liquid AsS has a metallic conductivity level of $0.5-1 \times 10^3$ $\text{Ohm}^{-1}\ \text{cm}^{-1}$ and a sufficiently low viscosity of 0.02 Pa s.

One might expect that the metallization and structural changes in liquid As_2S_3 under high pressure will have their own peculiar features. How similar the mechanism of the metallization of liquid As_2S_3 under high pressures near the melting curve to that of the metallization of liquid As_2S_3 at high temperatures and moderate pressures is also unclear. The purpose of this work was to examine the structure of liquid As_2S_3 at pressure up to 8 GPa and study possible melt metallization in this pressure range.

The powder of the As_2S_3 glass of 99.9% chemical purity (Alfa Aesar) was used as a starting material. The *in situ* structural study of solid and liquid As_2S_3 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 As_2S_3 sample was placed in a container made from hexagonal boron nitride (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 pressure was determined from the Decker equation of state of NaCl. A 0.2-mm-thick tablet of the NaCl-BN mixture was placed near the sample. The structures of the melt were examined at temperatures exceeding the melting points by 30–100 K. The spectra were registered at different diffraction angles 2θ from 3° to 18°, which made possible the restoration of the liquid structural factor and the respective radial distribution function with high accuracy. The radial distribution function $4\pi r^2 \rho(r)$ was calculated from the structural factor $S(Q)$ with damping factor diminishing from 1 down to 0 in the interval $8-12$ Å^{-1} of the scattering wave vector. The metallization of the melt was observed from the voltage-current ratio of a "sample plus graphite container" assembly in a Toroid-type high-pressure device.[23]

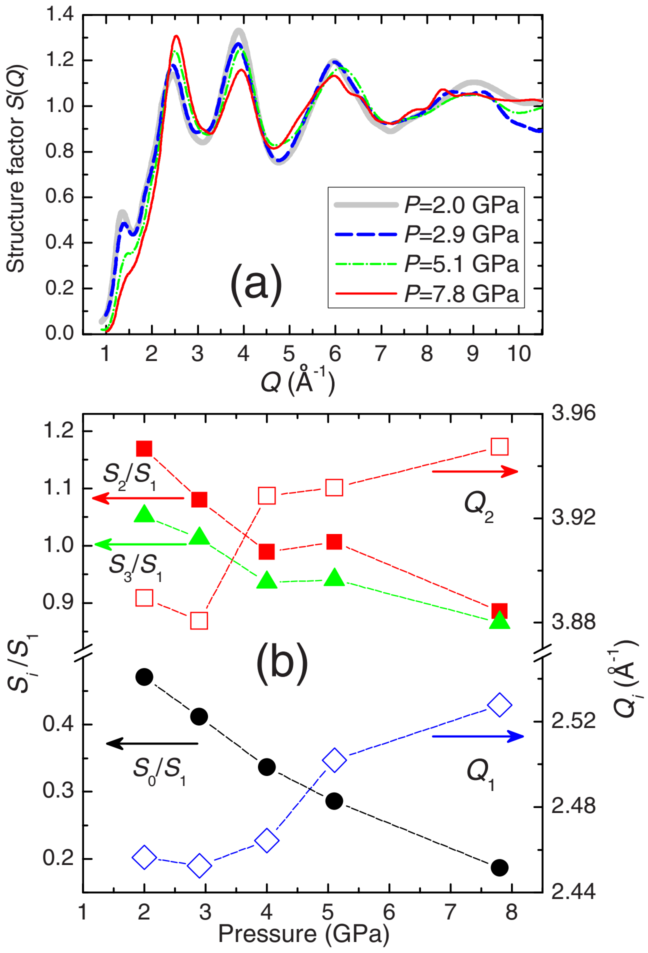

FIG. 2. (Color online) (a) Calculated from the experimental EDXD data and smoothed total interference functions (structure factors) of the As_2S_3 melt at different pressures near melting curve and (b) Q positions of the first and second main peaks of the structure factor $S(Q)$, as well as amplitudes of the prepeak, second and third peaks of $S(Q)$ scaled by the amplitude of the first main peak. Dashed lined on the panel (b) are guides for eyes.

The As_2S_3 pressure-temperature phase diagram resulting drawn the *in situ* x-ray diffraction measurements is presented in Fig. 1. Most of our experiments can be described as heating-cooling cycles at almost constant pressure. Under compression, crystalline As_2S_3 undergoes a phase transformation into high-pressure modifications which can be retained in a metastable form with red color at normal conditions. Previously the synthesis of such forms has been reported in Ref. 24 although it has been questioned in Ref. 4. We present the kinetic lines of the direct and reverse transitions. Structural data on the high-pressure crystalline phases will be presented elsewhere.

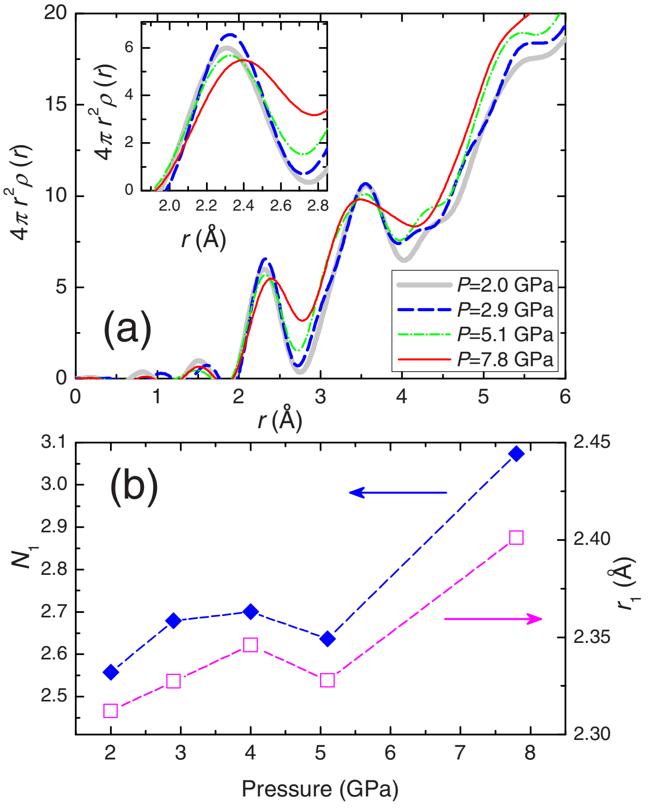

FIG. 3. (Color online) (a) Radial distribution functions of the As_2S_3 melt, where the inset shows the same for the first coordination sphere and (b) pressure dependence of the radius r_1 and area under the radial distribution curve N_1 for the first coordination sphere. Dashed lined on the panel (b) are guides for eyes.

The principle result of this work is the discovery of a considerable change in the structure of the As_2S_3 melt under compression. The structural data obtained for liquid As_2S_3 under pressure are shown in Figs. 2 and 3. When compressing liquid As_2S_3, one can observe a significant decrease in the prepeak of the structure factor at $k=1.3-1.4$ 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. Furthermore, under pressure, the relative heights of the first and second structure factor peaks change so that the first peak becomes more intensive then the second one [Figs. 2(a) and 2(b)]. Whereas the amplitude of the prepeak in the structure factor shows monotonic behavior (decrease) with pressure increase [Fig. 2(b)], other quantitative characteristics determined from the structure factors or radial-distribution functions (RDF) [Figs. 2 and 3(b)] demonstrate clear anomalies in the pressure dependences between 4 and 5 GPa. Starting from 5 GPa, a significant increase in the first coordination number N_1 and the radius of the first coordination sphere r_1 occurs (see Fig. 3). Thus the intermediate-range order of the melt is strongly modified up to 5 GPa whereas the short-range order begins to change intensively starting from 4 to 5 GPa. The presented experimental pressure evolution of the As_2S_3 melt structure [particularly, the reduction in the $S(Q)$ prepeak amplitude and an increase in N_1] is in good agreement with the *ab initio* molecular-dynamics simulation of the As_2S_3 melt.[17] Based on the results reported in Ref. 17, one can relate the increase in N_1 under pressure to the appearance of a significant fraction of As-As bonds in the liquid. The first peak of the experimental RDF at high pressures has a shoulder at 2.6–2.7 Å which coincides with the position of the As-As subpeak observed for the simulated partial pair distribution functions in Ref. 17. At pressure 7.2 GPa, the structure factor of the melt becomes similar to that of liquid chalcogenides with metallic conductivity. In a certain sense, the transformation of the structure factor of liquid As_2S_3 is akin to the behavior of the structure factor of liquid AsS under pressure, beginning from 2 to 2.5 GPa pressures,[21] when the molecular structure of the AsS melt had already changed to the covalent one.

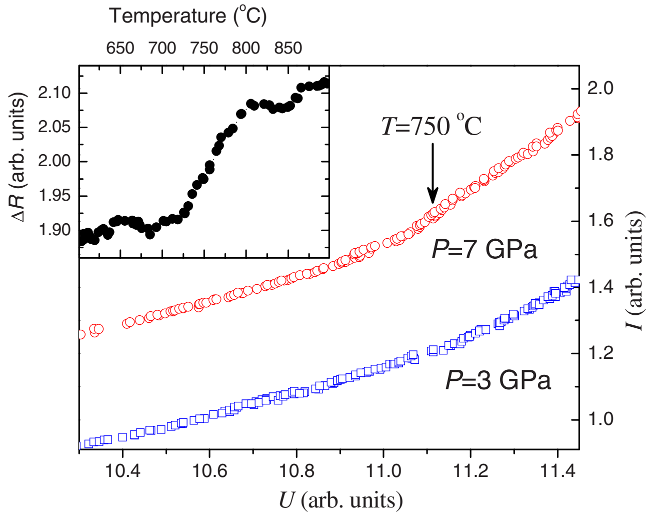

FIG. 4. (Color online) Example of electric voltage-current dependencies for the experimental assemblies with As_2S_3 recorded during heating at 3 and 7 GPa. The inset shows a fragment of the temperature dependence of resistance difference $\Delta R(T)=R(T,P=3\ \text{GPa})-R(T,P=7\ \text{GPa})$, which illustrates anomaly related to the melting of As_2S_3 to a conductive liquid at 7 GPa.

Rapid cooling of the As_2S_3 melt with the cooling rate of 10–100 K s^{-1} at $P>6$ GPa does not lead to the glass transition of the melt. Instead, the crystallization to the high-pressure phases with a large 10–50μ grain size is observed. This is in agreement with the fact that the viscosity of the As_2S_3 melt in the 5–6 GPa pressure range drops to values below 1 Pa s.[22]

The change in the electric resistance of the sample on heating was estimated from voltage-current dependencies. Both crystalline As_2S_3 phases are insulators, making no contribution to the electrical conductivity of the "heater plus sample" assembly. If the As_2S_3 conductivity after melting becomes higher than 10 Ohm^{-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 $P>6$ GPa (Fig. 4), we can estimate that the electrical conductivity of the sample after melting is 5–20 % of that of the graphite heater, i.e., 50–200 Ohm^{-1} cm^{-1}. At $P<5$ GPa, the melting of As_2S_3 is not accompanied by a change in the voltage-current dependencies (Fig. 4), hence, the conductivity of the sample in liquid state still remains lower than 10 $\mathrm{Ohm}^{-1}\,\mathrm{cm}^{-1}$. Thus, resistivity values for the "metallic" state of the As_2S_3 melt are three to ten times larger than those for the metallic state of AsS and 20–50 times large than those for the metallic state of Se. The same ratios are observed for the viscosities of the given metallic states of the melt. As a result, the As_2S_3 melt at pressures above 6 GPa represents a rather "strange" liquid, whose electrical conductivity is close to the minimum metallic conductivity values and whose viscosity is 100 times higher than the values typical for ordinary liquid metals. It can be assumed that this sufficiently high viscosity is associated with a partially retained three-dimensional network structure of the liquid, possibly sulfur-enriched (e.g., AsS_2-based) while the near-metallic conductivity is due to the appearance in the melt of a noticeable fraction of near neighbors As-As and to the delocalization of the lone-pair electron states (see Ref. 17).

Thus, the As_2S_3 melt under high pressures is subject to a significant modification of its structure and properties. Of course, similar to Se and other chalcogenides, there should be the continuous line of metallization of liquid As_2S_3 onto P,T plane starting from low-pressure-high-temperature (~1400 °C) region. However, unlike the metallization of the As_2S_3 and As_2Se_3 melts at high temperatures, the key factor in the metallization at high pressures is not the emergence of a twofold chainlike structure but the increase in the coordination number, which is largely due to the appearance of a significant fraction of the wrong neighbors As-As. It might be expected that the melts of many similar chalcogenide compounds under high pressures transform to strange metallic liquids with relatively high viscosity values, typical rather for covalent melts.

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[1] V. V. Brazhkin and A. G. Lyapin, J. Phys.: Condens. Matter **15**, 6059 (2003).

[2] P. F. McMillan, J. Mater. Chem. **14**, 1506 (2004).

[3] A. Feltz, *Amorphe und Glasartige Anorganische Festkörper* (Academic-Verlag, Berlin, 1983).

[4] P. Espeau *et al.*, Chem. Mater. **18**, 3821 (2006).

[5] V. V. Struzhkin, A. F. Goncharov, R. Caracas, H.-K. Mao, and R. J. Hemley, Phys. Rev. B **77**, 165133 (2008).

[6] O. Uemura *et al.*, J. Non-Cryst. Solids **30**, 155 (1978).

[7] S. Hosokawa and K. Tamura, J. Phys.: Condens. Matter **16**, R1465 (2004).

[8] Y. Kajihara *et al.*, J. Non-Cryst. Solids **353**, 1985 (2007).

[9] S. Hosokawa, Y. Sakaguchi, H. Hiasa, and K. Tamura, J. Phys.: Condens. Matter **3**, 6673 (1991).

[10] F. Shimojo, K. Hoshino, and Y. Zempo, J. Phys. Soc. Jpn. **74**, 621 (2005).

[11] F. Shimojo, S. Munejiri, K. Hoshino, and Y. Zempo, J. Phys.: Condens. Matter **12**, 6161 (2000).

[12] Y. Tsuchiya, J. Phys. Soc. Jpn. **60**, 960 (1991).

[13] V. V. Brazhkin, R. N. Voloshin, and S. V. Popova, JETP Lett. **50**, 424 (1990).

[14] J. Y. Raty *et al.*, J. Phys.: Condens. Matter **11**, 10243 (1999).

[15] Y. Katayama *et al.*, Phys. Status Solidi B **223**, 401 (2001)

[16] A. A. Likal'ter, Sov. Phys. JETP **93**, 379 (2001).

[17] F. Shimojo, K. Hoshino, and Y. Zempo, J. Non-Cryst. Solids **312-314**, 388 (2002).

[18] N. Sakai and H. Fritzsche, Phys. Rev. B **15**, 973 (1977).

[19] M. Vaccari *et al.*, J. Chem. Phys. **131**, 224502 (2009).

[20] V. V. Brazhkin, K. Funakoshi, M. Kanzaki, and Y. Katayama, Phys. Rev. Lett. **99**, 245901 (2007).

[21] V. V. Brazhkin, Y. Katayama, M. V. Kondrin, T. Hattori, A. G. Lyapin, and H. Saitoh, Phys. Rev. Lett. **100**, 145701 (2008).

[22] V. V. Brazhkin, M. Kanzaki, K. I. Funakoshi, and Y. Katayama, Phys. Rev. Lett. **102**, 115901 (2009).

[23] L. G. Khvostantsev, V. N. Slesarev, and V. V. Brazhkin, High Press. Res. **24**, 371 (2004).

[24] V. A. Kirkinskii, A. P. Ryaposov, and V. G. Yakushev, Izv. Akad. Nauk SSSR, Neorg. Mater. **3**, 1931 (1967).