Chain breakage in liquid sulfur at high pressures and high temperatures

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High-energy synchrotron x-ray diffraction was utilized to study the local order of liquid sulfur at high-pressure and high-temperature conditions. A temperature driven structure change in liquid sulfur was observed, signified by an order of magnitude reduction in lengths of sulfur chains. The large change in chain length implies that this is a liquid-liquid phase transition in sulfur. The chain breakage may strongly influence the physical properties, such as the semiconductor-metal transition and a drastic decrease in viscosity across the transition.

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I. INTRODUCTION

The nature of phase transitions in liquids is of great interest in condensed matter physics. However, compared to crystalline materials, our knowledge of phase transitions in liquids and amorphous materials in general is exceedingly limited, largely due to experimental and computational challenges [1,2]. The discovery of allotropes in phosphorus above its melting curve [3], regarded as the first observation of a first-order phase transition in an elemental liquid, prompted extensive studies in liquid-liquid phase transitions (LLPTs) in recent years [4–11]. Later studies on phosphorus indicated that the transition is from a molecular fluid to a polymeric liquid, because the phase transition boundary lies above the liquid-gas critical point of molecular phosphorus [4]. Support for an unambiguous LLPT in an elemental liquid in a stable liquid regime, as evidenced by direct structure determination, is scarce to date [10,11].

Sulfur, next to phosphorus in the periodic table, also displays LLPT [12,13]. At ambient pressure and high temperatures, a so-called λ transition in liquid sulfur, linked to the breakdown of molecular S_8 rings and polymerization into long chains, has been reported, accompanied by viscosity, density, and heat capacity anomalies at 432 K [14–19]. The length of the sulfur chains reaches a maximum at 460 K and then decreases at higher temperatures, as does the viscosity. The viscosity of liquid sulfur across the λ transition strongly correlates to the length of the chains [16,17]. The λ-transition temperature decreases with increasing pressure and intersects the melting curve at 0.13 GPa [20].

In the low-pressure range of 0–2 GPa, five liquid phases were reported by differential thermal analysis and quenched samples analysis [12]. At higher pressures of 4–12 GPa, Brazhkin *et al.* [13] proposed two phase boundaries with negative slopes for liquid sulfur from thermobaric analysis and resistance measurements. One boundary corresponds to the semiconductor-metal transition, and transitions across both boundaries are accompanied by volume reductions. However, the nature of liquid transitions in sulfur at high pressures is still poorly understood because of the lack of critical structure information of liquids, and uncertainty as to whether the transitions are continuous.

In this study, *in situ* energy dispersive x-ray diffraction (EDXRD) experiments were performed to study the evolution of the structure of liquid sulfur with varying temperature at high pressures. We found that the sulfur chains abruptly broke at high temperatures. This chain breakage was found to be mainly temperature driven.

II. EXPERIMENTAL METHODS

The *in situ* EDXRD experiments were performed using a VX-3 Paris-Edinburgh press at the white x-ray beamline 16-BM-B, High Pressure Collaborative Access Team (HPCAT) at the Advanced Photon Source, Argonne National Laboratory. The sample-cell assemblages, which are optimized to prevent the extrusion of cell materials so as to maintain sufficient vertical access for the x-ray beam, are illustrated in Fig. 1. The sulfur sample (Alfa Aesar, 99.999%) was contained in a capsule, which is surrounded by a cylindrical graphite heater. Different capsule materials [*h*-BN (Run A), sapphire single crystal (Run B), and NaCl (Run C)] were used to clarify if there was any chemical contamination of the sulfur by capsule materials. The pressure was determined from the thermal equation of state of the MgO pressure transmitting media [21], and the pressure difference between the MgO ring and the sample was taken into account [22]. The estimated errors in pressure were ±0.2 GPa. The temperature was determined using the power-temperature curves calibrated in an identical cell assembly [22]. Reproducibility of the temperature calibration has been investigated by the well known melting curves of NaCl and KCl, which show less than ±5% uncertainty in the temperature estimation in the range of 1323–2023 K [23]. The incident white x-ray beam was collimated to a size of 0.3 mm (vert.) × 0.1 mm (horiz.) using two sets of tungsten slits. The sample was first compressed to a desired pressure at room temperature and then increased to high temperature above the melting curve. The liquid state was assessed by monitoring the disappearance of the crystalline

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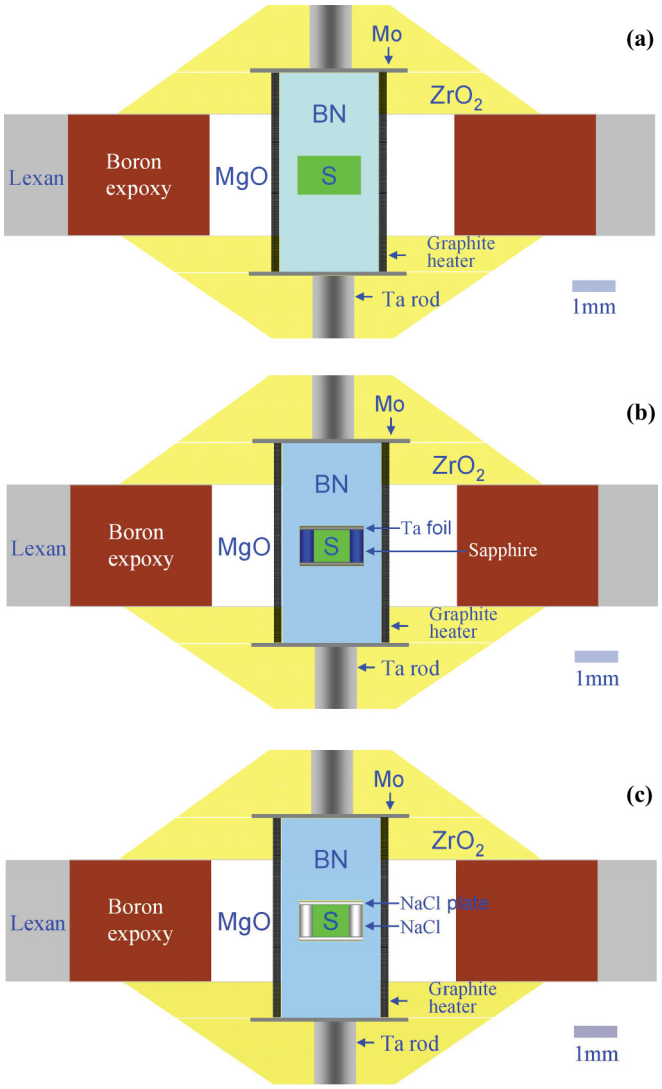

FIG. 1. (Color online) Cross sections of the sample cell with different capsule materials. (a) h-BN capsule, (b) sapphire capsule, and (c) NaCl capsule.

Bragg diffraction peaks and the coincident appearance of the diffuse scattering of the liquid. The x-ray diffraction patterns of the liquid sample were collected by a Ge solid-state detector at eight different 2θ angles (2.5°, 3.5°, 5°, 7°, 10°, 14°, 20°, and 25°), in order to cover a large range in Q space ($Q = 4\pi E\sin\theta/12.398$, where E is the x-ray energy up to 100 keV). The typical time for collecting one set of diffraction patterns of eight angles was ~2 h. Details of the EDXRD measurement and data analysis method are described elsewhere [22].

III. RESULTS AND DISCUSSION

Typical diffraction patterns of liquid sulfur collected at eight different 2θ angles are shown in Fig. 2(a). There was a discontinuity in the diffraction patterns at ~69 keV attributed to the tungsten absorption edge, probably coming from beamline components such as the tungsten slit blades. To avoid the influence of the tungsten edge on the results, only the data in the energy range up to 60 keV were used. The

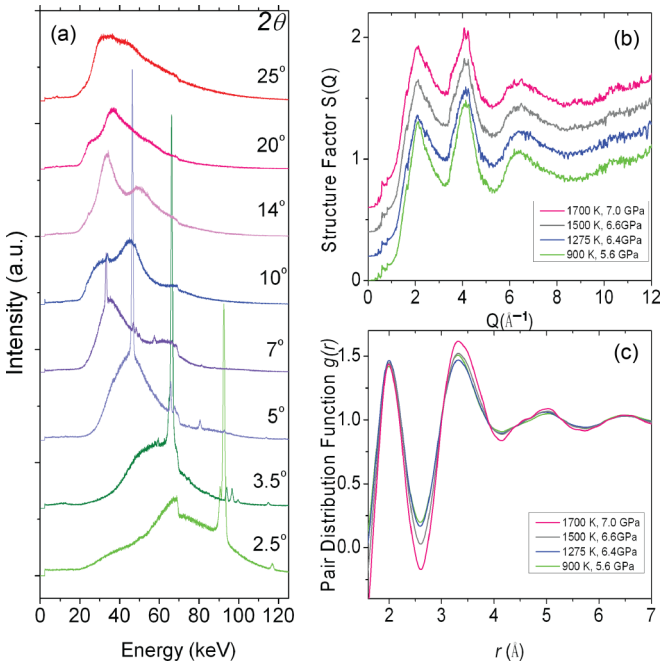

FIG. 2. (Color online) (a) Typical x-ray diffraction patterns collected at 5.6 GPa and 900 K. The strong, sharp peaks come from the capsule material h-BN. (b) Selected structure factor $S(Q)$ of liquid sulfur (Run A). (c) Selected pair distribution functions $g(r)$ of liquid sulfur (Run A). Pressure and temperature conditions are shown in the figures.

structure factors $S(Q)$ [Fig. 2(b), Run A] and pair distribution functions (PDFs) $g(r)$ [Fig. 2(c), Run A] of liquid sulfur are derived from the diffraction patterns using an algorithm described in Ref. [24]. In the calculation of the $g(r)$ from $S(Q)$, the density of liquid sulfur determined by the falling-sphere method [25] was used by extrapolating to high temperatures. Changes in overall shapes and peak positions of $S(Q)$ and $g(r)$ are found to be small at various temperatures, indicating that the liquid sulfur retains similar local structure and density in this pressure-temperature range. Details of the structure variations as a function of temperature are discussed below.

The scaled structure factor $S(Qr_1)$ (r_1 is the nearest-neighbor distance) of liquid sulfur at high pressure is compared to that of liquid selenium at ambient pressure in Fig. 3(a). The similarity between the scaled structure factors indicates that liquid sulfur at high pressure has a chain structure, as does liquid selenium at ambient pressure [28]. Our experimentally obtained $g(r)$ are also compared with those from the first-principle simulations [29] of the chain, S_6 ring, and S_8 ring structures [Fig. 3(b)]. The first and third peak positions of S_6 ring structure are consistent with our results. However, the second peak of S_6 ring structure, located at about 2.86 Å, is not consistent with our results. Additionally, the third peak position of S_8 ring structure is clearly different from the experimental data. Therefore, our structure data indicate a structure composed of chains for high-pressure liquid sulfur.

Detailed analysis of $S(Q)$ and $g(r)$ reveal structural changes at high temperatures. The areas under the first peaks scaled by r^2 in the PDF [$S = \int_{r_0}^{r_{\max}} r^2 g(r) dr$] display a kink at high temperature in all runs of the experiments [for example,

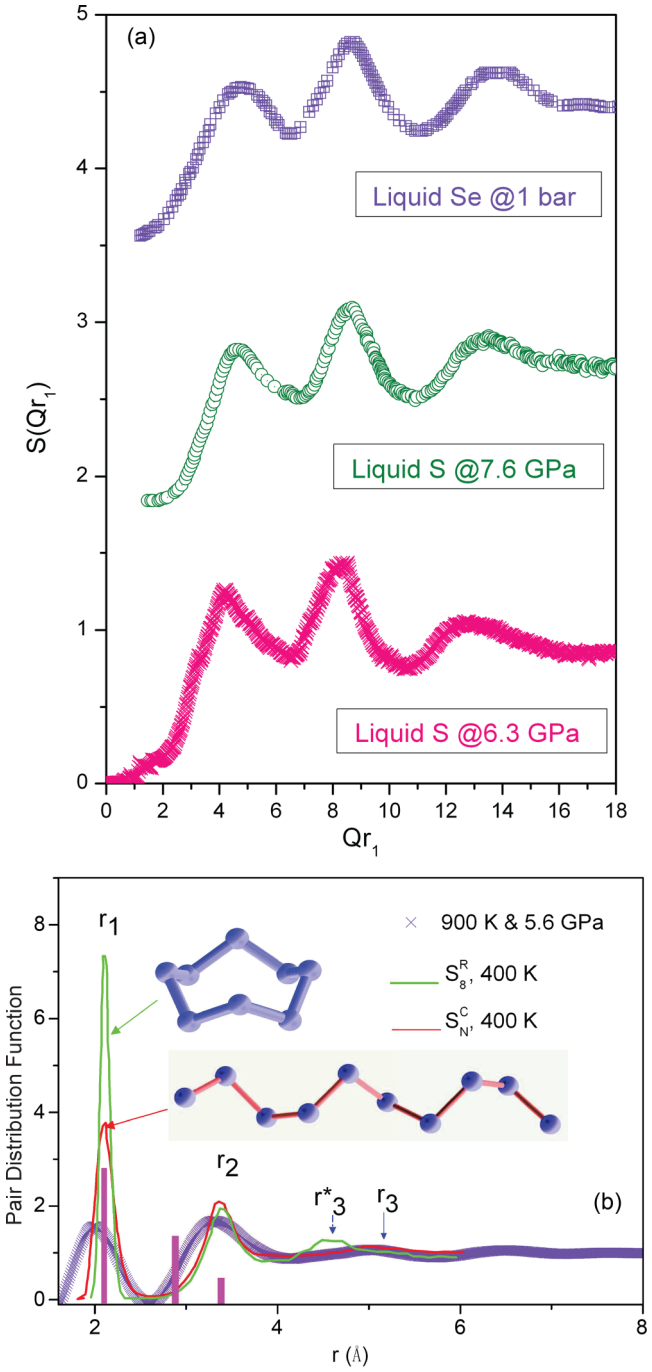

FIG. 3. (Color online) (a) The structure factor as a function of Q scaled to the nearest-neighbor distance r_1, which is estimated from the first peak position of pair distribution functions. Red crosses are our result of sulfur at 1200 K and 6.3 GPa. Green circles are Katayama's results of sulfur determined at about 1023 K and 7.6 GPa [26]. Blue squares are Waseda's result of Se at atmospheric pressure [27]. The resemblance between the structure factors of sulfur at high pressure and that of Se at atmospheric pressure indicates that liquid sulfur at high pressure has a chain structure similar to that of liquid Se at ambient pressure. (b) Experimental and simulated pair distribution functions of liquid sulfur. The cross data are the present results at 900 K and 5.6 GPa. The green and red lines are simulated results from random S_8 rings and random length atomic chains, respectively [29]. Pink bars indicate the positions of the $g(r)$ peaks of liquid sulfur with S_6 ring structure [30].

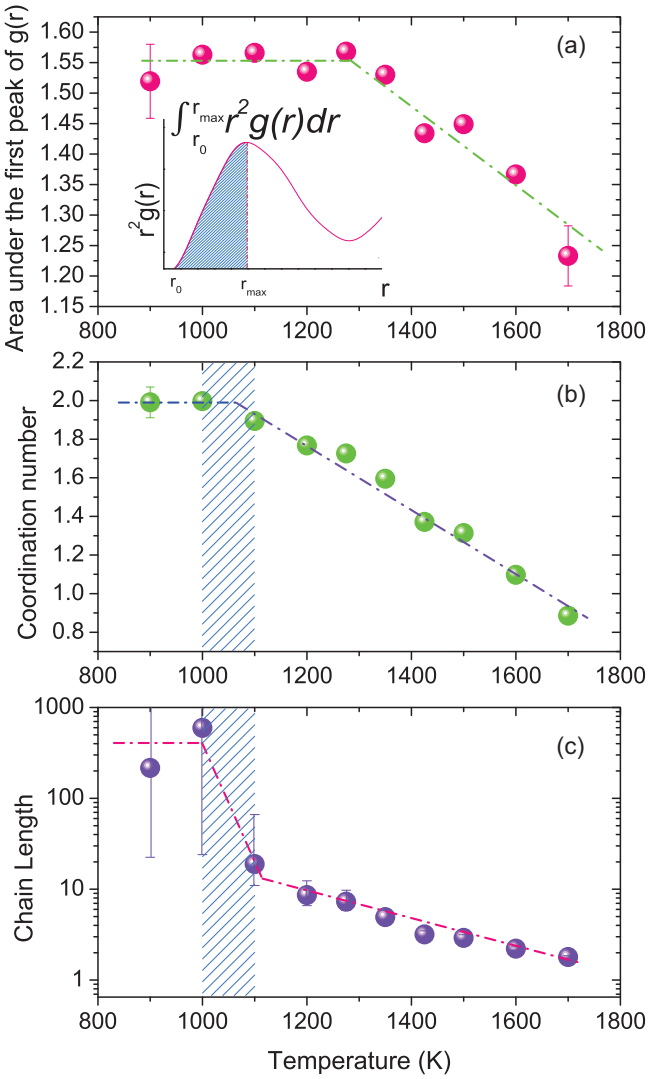

FIG. 4. (Color online) (a) The areas under the first peaks of $g(r)$ scaled by r^2 : $S = \int_{r_0}^{r_{\max}} r^2 g(r) dr$ of Run A. r_0 and $r_{\max}$ are the left-hand edge of the first peak and where $r^2 g(r)$ at the maximum of the first peak, respectively, as illustrated in the inset. (b) The coordination number is estimated from $2 \int_{r_0}^{r_{\max}} 4\pi\rho_0 r^2 g(r) dr$; ρ_0 is the number density of atoms. The error bars in (a) and (b) are provided by the highest and lowest temperature points. (c) The chain length as a function of temperature. For high-temperature (>1300 K) data points, the error bars are smaller than the symbol size. Dash-dot lines are guides for the eye.

Fig. 4(a) presents the results in Run A]. The errors of the integrated S, which result mainly from uncertainties in the density ρ_0, are reflected in Fig. 4(a) by the lowest and highest temperature points. The first-neighbor coordination numbers (CN) can be estimated from $\mathrm{CN} = 8\pi\rho_0 S$, where ρ_0 is the number density of atoms. We used the density of liquid sulfur determined by a previous study [25]. The CN as a function of temperature is illustrated in Fig. 4(b). The coordination numbers remain almost constant below 1100 K, and decrease quickly above 1100 K. At the highest temperature of 1700 K, the CN is smaller than 1, implying the existence of monatomic sulfur in the liquid. Based on a simple chain model, the average

first-neighbor CN of a chain structure is $2–2/N$, where N is the length of the chain. The average chain lengths are calculated and shown in Fig. 4(c) as a function of temperature. The average chain length undergoes an abrupt reduction between 1000 and 1100 K: from ~600 atoms at 6 GPa and 1000 K, to ~19 atoms at 6.2 GPa and 1100 K, a reduction by more than one order of magnitude [Fig. 4(c)]. The breakage of sulfur-sulfur bonds may result from electron excitation from the bonding state to the antibonding state [31,32]. This large chain length reduction may be considered as a LLPT for liquid sulfur at high-pressure and high-temperature conditions. However, we were not able to experimentally determine the reversibility and hysteresis through the structural measurements, because all experiments ended when the sample leaked out of the containment, most likely due to the significant decrease in viscosity resulting from the chain breakage. The measured temperature dependence of the chain length provides a clue to the kinetics of the LLPT. It can be seen from Fig. 4(c) that the transitions took place abruptly in the temperature range of ~100 K. In other words, as the chain breakage happens, the average chain length is abruptly reduced across a narrow temperature range (~100 K) as temperatures increases. At higher temperatures (>1100 K) in our experiments, the CN keeps gradually decreasing, implying that the transition is progressively continuous.

The results from all experimental runs are summarized in the pressure-temperature phase diagram in Fig. 5. The solid balls indicate the conditions where chain breakages occurred. It is important to note that the chain breakage occurs below the

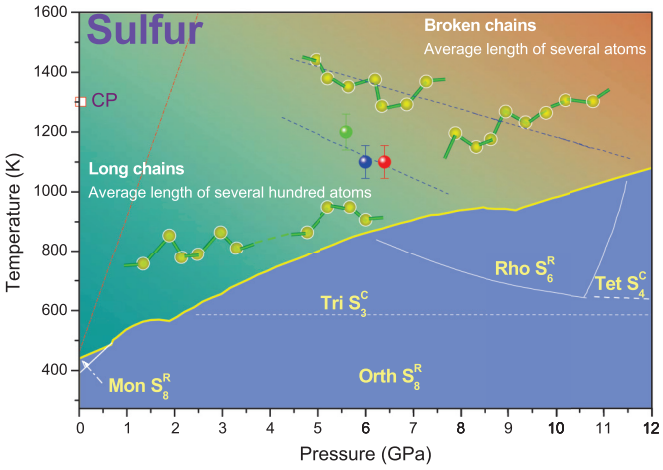

FIG. 5. (Color online) Pressure-temperature phase diagram of sulfur. The red, blue, and green balls correspond to the results obtained using h-BN, sapphire single crystal, and NaCl capsules, respectively. The white square is the liquid-gas critical point (CP, 1314 K and 20 MPa).The liquid phase boundaries proposed by Brazhkin *et al.* [13] are presented by blue dot lines. The red dash-dot line is the depolymerization boundary of the λ transition replotted after Ref. [12] and extrapolated to high pressure. The melting curve is taken from Ref. [33], and the phase diagram of solid phases is replotted after Ref. [34]. The superscripts R and C denote ring and chain structures, respectively. Mon, Orth, Tri, Rho, and Tet are the abbreviations for monoclinic, orthorhombic, triclinic, rhombohedral, and tetragonal structures, respectively.

liquid-gas critical point of sulfur. Thus, this abrupt change in chain length is a structural change in a stable liquid regime. Our observed LLPT points are generally consistent with Brazhkin's results [13], taking temperature uncertainties (less than ±5%) into account. However, Brazhkin's results contain two boundaries, while only one abrupt change is observed as a function of temperature in our experiments [Figs. 4(a)–4(c)]. Another known liquid transition is the λ transition, which is also linked to the breakage of sulfur bonding. The λ-transition temperature decreases with increasing pressure and intersects the melting curve at 0.13 GPa [20]. The depolymerization temperature of the λ transition increases with increasing pressure with a slope of ~475 K/GPa [12]. If we linearly extrapolate the depolymerization boundary to higher pressures (red dash-dot line in Fig. 5), it reaches ~3547 K at 6.5 GPa, almost three times above the highest transition temperature (1100 K) in this study. However, the depolymerization boundary was determined at low pressures, and has not been explored in the pressure range we investigated. Further investigations in a wide pressure and temperature range are necessary to clarify the relationship between the depolymerization of liquid sulfur [12], and our observed high-temperature chain breakage.

For liquids consisting of chains, viscosity is proportional to the length of the chains (N) and the concentration of chain atoms (ρ) in the form of $N^3\rho^3$ [35]. The decreases in the chain length should result in drastic decreases in viscosity for liquid sulfur, which may explain why the samples leaked after the chains were broken in our experimental trials. Terasaki *et al.* [36] have investigated the pressure dependence of the viscosity of liquid sulfur along melting curves across the phase transition boundary of Brazhkin *et al.* [13], and they found no drastic decrease of viscosity at high pressures. This fact may imply that the chain breakage is mainly temperature driven and has weak pressure dependence. The considerable reduction in the length of sulfur chains at higher temperature would cause a drastic decrease in viscosity, which may reach values of only a few mPas.

In discussions of the semiconductor-metal transition in liquid Se [37], it has been proposed that the ending Se atoms of the chains have eigenenergies around the Fermi level, thus filling the energy gap in liquid Se. Similarly in liquid sulfur at high temperatures, the breakage of long chains leads to an increase in the number of ending sulfur atoms (from ~1.0% at 1000 K and 6 GPa to ~10% at 1100 K and 6.2 GPa). In analogy to liquid Se, the increase in ending atoms may imply that the high-temperature phase of liquid sulfur is a metallic phase. This conclusion is consistent with the observation of a metallic phase by Brazhkin *et al.* [13] using resistance measurements. The viscosity of metallic liquid sulfur is predicted to be much smaller than that of nonmetal liquid sulfur [37], which is also consistent with the chain breakage mechanism discussed above.

IV. CONCLUSIONS

In summary, *in situ* high-pressure EDXRD experiments indicate a LLPT in liquid sulfur at high pressures and high temperatures, structurally signified by the breakage of long sulfur chains into short chains and even monatomic form. The observed liquid-liquid transition is mainly temperature

induced and involves little density change. The observed chain breakage supports the idea that the high-temperature phase of liquid sulfur is a metallic liquid of low viscosity.

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