Structural Transition in Compressed Amorphous Sulfur

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(Received 14 November 2007; revised manuscript received 13 December 2007; published 20 February 2008)

Properties of amorphous sulfur (*a*-S) were investigated by synchrotron x-ray diffraction up to 100 GPa between 40 and 175 K. Measurements of the structure factor yielded the radial distribution function and the densities of two amorphous forms. *a*-S undergoes a structural transition above 65 GPa, accompanied by density discontinuity of 7%. These results indicate the amorphous-amorphous transition, from a low-density to a high-density form, and open up the possibility for the direct measurements of density of liquid-amorphous materials at extreme conditions.

DOI: 10.1103/PhysRevLett.100.075701 PACS numbers: 64.70.−p, 61.05.C−, 61.43.Er, 62.50.−p

Polyamorphism between low- and high-density amorphous (LDA/HDA) forms has been extensively studied in archetypal compounds such as silica [1], ice [2], and GeO_2 [3]. Among the elements, Si [4,5] and Ge [4,6] are known to exhibit pressure-induced polyamorphism which, as in the case of SiO_2 and H_2O, is characterized by transformation within the tetrahedral framework, the HDA form having a higher coordination number [7]. Polyamorphism has also attracted attention due to the controversies on the nature of the transition, i.e., first vs second order. This has been illustrated by the cases of amorphous water [8–10] and silica [11–13]. To resolve these issues, density measurements are the most complementary method to the observation of structural changes as a first-order transition can be detected by a density change across the transition. In the case of simple liquids, density can be indirectly extracted from structure factor measurements, either using a hard-sphere model or empirical relationships [14]. Nevertheless, direct density measurements on noncrystalline samples under static high-pressure conditions still present a technical challenge, limiting the accessible pressure range to ~10 GPa [2,15–18]. With the arrival of the third generation synchrotron sources and better detector techniques, it became possible to observe very weak diffraction signals from amorphous and liquid states in diamond-anvil cells (DACs) at pressures up to 100 GPa [18–20]. Quantitatively accurate structure factors, allowing diffraction-based determination of the density, were first measured in a DAC on liquid argon and liquid water [18]. Although the pressure in these experiments was limited to 1.1 GPa, this pioneer work demonstrated the feasibility of density measurements in DAC experiments, even on low Z materials.

Recently, pressure-induced amorphization (PIA) of sulfur was observed at low temperatures, and the P-T field of the existence of *a*-S was mapped out [21]. In this Letter, we report *in situ* x-ray diffraction data on *a*-S between 50 and 100 GPa and between 40 and 175 K, and an implemented method to extract the information at such extreme conditions. Diffraction-based direct density measurements yield the structure factor, $S(Q)$, the radial distribution functions, $g(r)$, and density data up to 100 GPa, extending the pressure range of such direct measurements in the DACs by a factor of 100 [18]. Our measurements show that two regions of different structures and densities exist within the field of *a*-S.

The method to extract the density of noncrystalline materials from diffraction data was first derived for liquids at ambient pressure [22] and later adapted to DACs [18]. In the latter case, the diffraction signal needs to be corrected for the background signal from the anvils, and for the limited angular transmission by the cell. The method used here for the data analysis is an adaptation of this method to much weaker signals due to the higher pressure conditions. In the diffraction-based method, density is extracted by minimizing the oscillations on $g(r)$ for r lower than the first interatomic distance. These oscillations are due to errors in processing the scattered intensity into $S(Q)$. Termination effects due to the limited experimental Q range might also generate artificial ripples on $g(r)$ but at larger r (~2–5 Å range [22]) and are therefore less critical for density measurements than for precise structural interpretations. In this work, a crystalline sample reference spectrum was taken from the closest P-T point at which *a*-S was observed. It should be noted that the spectra observed upon recrystallization of *a*-S were single-crystal-like [21]. This reference spectrum was substracted from the amorphous spectrum after removal of the solid diffraction peaks. Although this procedure correctly removes the incoherent scattering from the sample and greatly reduces the background, some difference [$\Delta I_{bkgd}(Q)$] exists due to slight changes of geometry and/or pressure conditions between the amorphous and the crystalline sample reference spectra (Fig. 1). At extreme conditions, the background signal dominates the signal diffracted by the sample by an order of magnitude (Fig. 1). Therefore, at such conditions, a fully consistent iterative method [18] is not sufficiently well behaved to allow the determination of both the density and any remaining $\Delta I_{bkgd}(Q)$. Instead, the method is modified by introducing an *a minima* assumption, i.e., $S(0) \sim 0$, making use of the fact that

$$\lim_{Q\to 0} S(Q) = \frac{nk_BT}{K_T}, \tag{1}$$

where n is the density, K_T is the isothermal bulk modulus, and k_B is the Boltzmann constant. Extrapolation of the equation of state S-I [23] gives a bulk modulus exceeding 500 GPa at 70 GPa, roughly the same value found using the equation of state S-III [24]. Although the bulk modulus of a-S is *a priori* unknown and different from that of the crystalline phases, it could not be lower than by a factor of 2. This implies $\lim_{Q\to 0} S(Q) \sim 3 \times 10^{-4}$, i.e., a value undistinguishable from zero given the experimental noise on $S(Q)$ of ± 0.02 at low Q.

P-T conditions were generated by using membrane DACs in a l-He cooled cryostat at the European Synchrotron Radiation Facility (beam line ID09A). Boron nitride seats were used to increase the angular access to the sample and consequent Q range; using such semitransparent material does introduce an additional correction function to account for absorption by those seats. However, the angular access in this work was limited to 46° by the cryostat windows, implying a maximum of 2% absorption variation at the cutting angle. This effect has therefore been neglected. Sulfur powder was loaded along with helium gas as the pressure transmitting medium in the sample chamber of the rhenium gasket. Pressure was monitored by *in situ* fluorescence measurements of SrB_4O_7: Sm^{2+} [25,26]. The temperatures were measured to within ±5 K by two Si diodes placed next to the sample chamber and on the body of the cell. The energy of the monochromatic x-ray beam was $E = 30$ keV; data were recorded on 2D image plates and angularly integrated with FIT2D software [27].

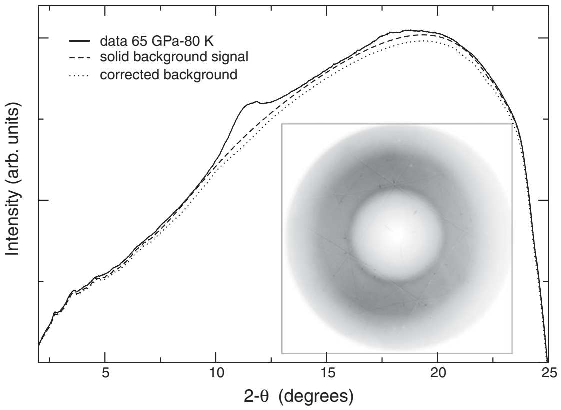

FIG. 1. Representative x-ray diffraction spectrum of a-S at 65 GPa and 80 K. The solid line is the raw integrated intensity, the dashed curve is the solid background signal at 41 GPa (80 K), and the dotted curve is the corrected background. Inset: corresponding image plate.

a-S was synthesized along three *P-T* paths, as shown in Fig. 2, by pressurizing S-I at 175 K and at 80 K [21]. At 175 K, the sample recrystallized into phase S-III at 59 GPa. In one of the two 80 K runs, the sample was cooled down at 65 GPa to $T = 40$ K and further compressed up to 99 GPa; at this pressure, temperature was increased to 50 K and the sample recrystallized into the incommensurately modulated phase S-IV within 5 minutes. Cooling down the cell from 80 to 40 K resulted in a pressure increase from 65 to 70 GPa. Drastic changes are observed in $S(Q)$ upon this step [Fig. 3(a)]. The first peak is shifted to higher Q, and, more markedly, the second peak is much wider and weaker. These results indicate an abrupt transition between two different amorphous forms of sulfur. These structural changes are translated into $g(r)$ [Fig. 3(b)] with a marked discontinuous decrease of the mean first distance (Fig. 4 inset). In terms of density, the transition is accompanied by a volume reduction of about 7% (Fig. 4), indicating the first-order-like nature of this transition between a low-density and a high-density amorphous form. However, because no data point was recorded over the 5 GPa interval between 65 and 70 GPa, the possibility of having a second-order transition cannot be ruled out. Below 65 GPa, the density closely follows the equation of state of phase S-III [24] within the error bars, while at 70 GPa and above, it is similar to the density of phase S-IV [30]. The coordination number, calculated as $\int_0^{r_{\min}} 4\pi g(r) r^2$, dr also changes abruptly from 16.1 ± 0.1 to 15.0 ± 0.4 upon transition. A

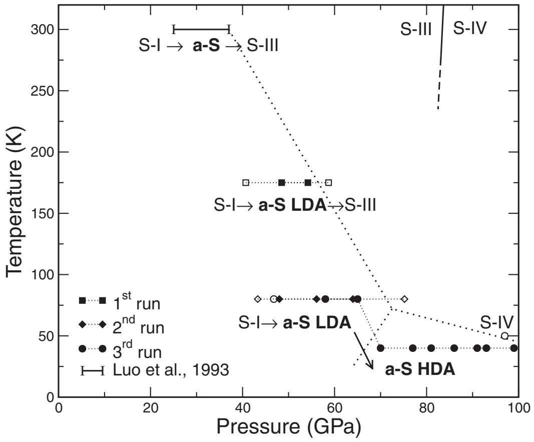

FIG. 2. Experimental *P-T* paths and the observed phases of sulfur. Open symbols: crystalline phases; full symbols: a-S.

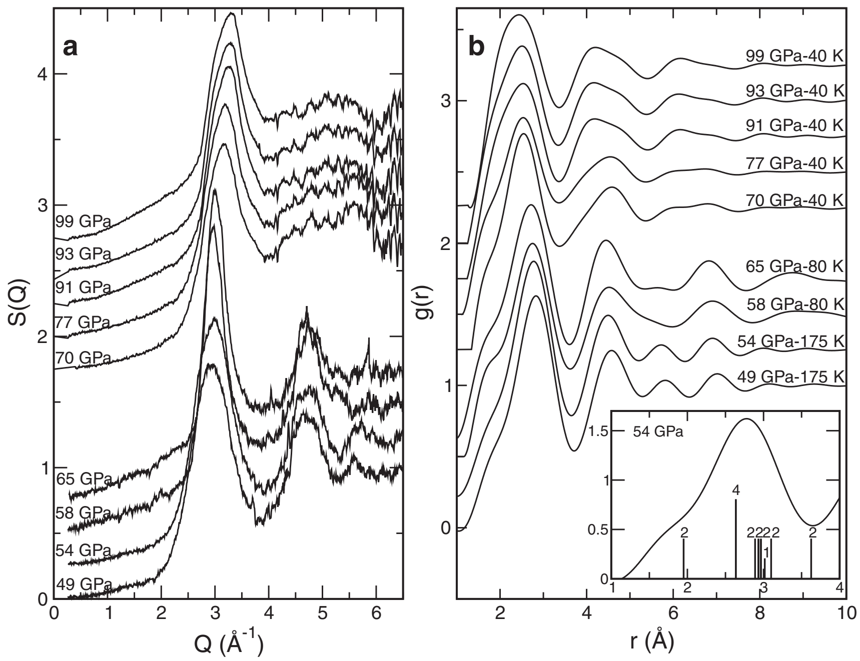

FIG. 3. (a) Structure factors. (b) Radial distribution functions; inset: zoom on the first set of coordination shells and comparison with the structure of S-III at 54 GPa.

value of 16.1 is acceptable if the low pressure *a*-S is structurally related to S-III as expected from its density; 17 atoms are indeed in this structure below r_{min} according to the refined structure of S-III [24,28] [Fig. 3(b) inset]; comparatively, the S-IV structure has one atom less in this range [29,30]. The coordination number therefore decreases upon the LDA/HDA transition in sulfur, unlike those reported for the transitions observed in 4-coordinated species [7]. This decrease of the mean coordination number partly compensates the important decrease of the mean first distance, from 2.667 Å at 65 GPa (80 K) to 2.554 Å at 70 GPa (40 K). Both effects combined imply a density increase of 7%, in agreement with the density measurements. A catch, however, is the concomitant variation of P from 65 to 70 GPa and T from 80 to 40 K. Taking as a proxy the thermal expansion coefficient of phase S-I at 80 K [31], a thermal contraction of 0.5% results from a 40 K decrease at ambient P, and consequently less in the 50–100 GPa range. The temperature contribution to the observed density increase is therefore negligible. Along the extrapolated equation of state of LDA sulfur taken as that of S-III, a compaction of only 2% is expected going from 65 to 70 GPa. The 7% density increase can thus not be related to the normal compression of *a*-S, even when considering the experimental error bar of 2%, but involves a transition to a different and denser form as first indicated by changes in $S(Q)$.

Our study shows that pressure-induced *a*-S undergoes a LDA/HDA transition above 65 GPa, and that this transition could be of first order as shown by the density measurements. The slope of the S-III/S-IV boundary is not known, but if the transition P at ambient T is linked to our 80–40 K/65–70 GPa transition range, it implies a very steep negative slope for the LDA/HDA boundary. Pressure is therefore the most important thermodynamic variable in bringing the phase transformation. The analysis of the P-T paths taken here poses interesting questions. First, PIA of sulfur has been reported at 300 K and 25 GPa on the basis of energy-dispersive diffraction [23], followed by a crystallization at 37 GPa [32] to what is now known as phase S-III [24,28]. At 300 K, *a*-S is obtained in coexistence with

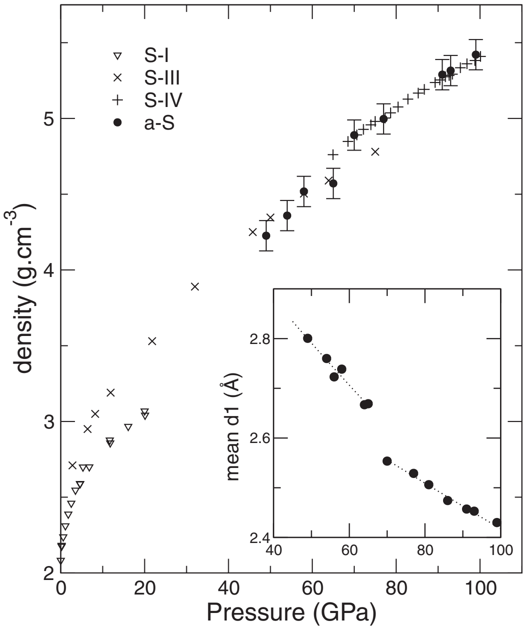

FIG. 4. Density of *a*-S compared to crystalline phases vs P; up to 65 GPa, data were obtained at 80 K, and at 40 K at higher P. Data for S-III are from [24], data for S-IV are from [30]. Inset: mean first distance in $g(r)$ as a function of pressure; d_1 is determined from the position of the midpoint at $g(r) = 1$.

a crystalline sulfur in the present work; these data taken together with those presented here and in Ref. [21] suggest a change of slope in the amorphous-crystallization line (Fig. 2) at the LDA/HDA transition. Second, LDA/HDA transitions have been related to molecular to network transitions, as is the case for liquid phosphorous and supercooled water [33,34]. It does not seem to be the case here, as LDA/HDA sulfur phases have physical properties close to those of S-III/S-IV phases, respectively, both being nonmolecular [24,28–30].

The similarities between not only the local structures but also the densities of LDA and HDA sulfur with those of phases S-III and S-IV, respectively, are striking, implying very similar equation of states. This would not be expected for a truly amorphous material, even if its local structure is closely related to the crystalline phase, as a disordered material has more freedom in its compressibility mechanisms than do corresponding crystals. Instead, the synthesized high-pressure amorphous forms of sulfur might be nanocrystalline structures. From an x-ray diffraction point of view, one cannot distinguish an amorphous from a nanocrystalline material if the crystallite's size is of the order of a few interatomic distances, i.e., too small to be coherent to the x-ray radiation and the sample can then be described as x-ray amorphous. As observed in this study, the transition from molecular S-I to higher pressure polymeric crystalline phases is kinetically hindered at low T, as it takes considerable energy to open the 8-membered rings. The subsequent occurrence of PIA could correspond to the conversion of the metastable and defect-rich S-I phase into the nanocrystalline S-III phase. Above 25 GPa, the structural fit to S-I became indeed increasingly worse, indicating a high number of defects in the structure. Those defects such as vacancies could condense to free surfaces, forming nanocrystalline material [35]. More generally, x-ray PIA can be explained as the nucleation of a high P phase from an unstable crystalline lower P phase if the thermal energy is not kinetically high enough to provide large crystallite size [36]. This phenomenon is especially predicted to happen when a large energy barrier exists for the transformation of the low P phase to the high P phase [37], as is the case here from S-I to S-III. Consequently, HDA sulfur would be nanocrystalline S-IV as a result of the crossing of the S-III → S-IV phase boundary, which is effectively a first-order transition. The case of sulfur might not be representative of all reported cases of PIA. Nonetheless, these results bring a new argument to the long-standing debate on the possibility of having first-order transitions in compressed amorphous materials and help in understanding the appearance of single-crystal-like diffraction patterns upon further compression with the amorphous-crystalline transition reflecting crystal growth. They also open new synthesis paths of nanocrystalline materials. Recovery of a-S at ambient conditions was not attempted in this study; however, this recovery might not be possible if the nanocrystalline x-ray amorphous material transforms to a truly amorphous form upon decompression [37].

The x-ray diffraction-based method provides a unique way to extract both structural and density data on noncrystalline materials in the megabar range; it is also promising for measuring transport properties such as the electrical resistivity [14] simultaneously at the same conditions.

We acknowledge the ESRF for provision of synchrotron radiation facilities on ID09A and the anonymous referees for their helpful comments.

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