

Incommensurate sulfur above 100 GPa

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S-III, the high-pressure phase of sulfur stable above 80 GPa, is found to have the same incommensurately modulated monoclinic crystal structure as Te-III and Se-IV and is the first element observed to have a modulated structure above 100 GPa. A previously unreported phase is found between S-II and S-III on pressure decrease, and there is also evidence that the same phase exists on pressure increase. This phase has the same triclinic structure as Te-II and Se-III.

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Sulfur is a member of the group VIa elements and exists in a large number of complex allotropic forms at ambient conditions.^{1,2} Numerous high-pressure forms have also been reported, and it is only recently that this extremely complex behavior has begun to be simplified.³ The stable crystal structure at ambient conditions comprises covalently-bonded S_8 rings arranged in an orthorhombic structure.^{1,4} On compression at room temperature, this orthorhombic form is reported to undergo a gradual transition to an amorphous form, such that above 26.5 GPa no diffraction peaks are observed.⁵⁻⁷ Further compression results in recrystallisation, with diffraction peaks first reappearing at 37 GPa,⁶ and complete recrystallization occurring at 54.5 GPa (Ref. 7) or 75 GPa.⁶ The structure of this recrystallized form, named S-II, has long been uncertain, but recently it has been shown to have a body-centered tetragonal structure comprising parallel chains of atoms with 4_1 and 4_3 symmetry running along the c axis.^{8,9} A further phase transition, to S-III, occurs on further compression to 83–86 GPa,^{6,7,9} although peaks from S-II are observed at pressures up to ~ 100 GPa.⁶ S-III is reported to have the same base-centered orthorhombic (bco) structure as Te-III and Se-IV (Refs. 6, 7, and 10) and is both a metal¹¹ and a superconductor,¹²⁻¹⁴ with a superconducting temperature that increases from $T_c=10$ to 14 K over the pressure range 90–160 GPa. On further pressure increase Luo *et al.* observed a transition to the rhombohedral β -Po structure at 162 GPa, and this phase is stable to at least 212 GPa.⁶ The β -Po phase is also a superconductor, with a maximum T_c of 17.3(5) K at 200 GPa.¹⁴

Recently, we have shown that the phases of Te and Se previously reported as having the bco structure, Te-III and Se-IV, are in fact monoclinic, with incommensurately modulated atomic coordinates.^{15,16} In McMahon *et al.*¹⁶ we commented that the bco structure of S-III might have the same incommensurate structure, but that the earlier S-III diffraction data of Akahama *et al.*⁷ and Luo *et al.*⁶ were of insufficient quality to observe any of the satellite diffraction peaks arising from the modulation. A recent reinvestigation of S-III has reported that the structure is indeed incommensurately modulated.¹⁷ To investigate the structure of S-III further, we have performed diffraction studies of sulfur to 100.5 GPa. We show that it does indeed have the same incommensu-

rately modulated structure as Te-III and Se-IV, with an incommensurate q vector and modulation amplitudes similar to those seen in these other group VIa elements. We also find a previously unreported high-pressure phase of sulfur between S-II and S-III, the triclinic structure of which is the same as that of Te-II and Se-III.¹⁸

Powder diffraction data were collected on station ID09a at the European Synchrotron Radiation Facility (ESRF), Grenoble, using an incident x-ray wavelength of 0.41756 Å and a beamsize of $10 \mu\text{m} \times 10 \mu\text{m}$. The powdered sample of orthorhombic S_8 was provided by Mezouar (ESRF)¹⁹ and was loaded into a diamond-anvil cell with He as a pressure transmitting medium. The pressure was measured using both the fluorescence from a small grain of $\text{SrB}_4\text{O}_7:\text{Sm}^{2+}$ placed within the gasket hole,²⁰ and from the lattice parameters of the helium within the irradiated part of the sample via its equation of state (EOS).²¹ At pressures above ~ 35 GPa, the principal fluorescence peak from the $\text{SrB}_4\text{O}_7:\text{Sm}^{2+}$ was observed to broaden, and the pressure determined from the $\text{SrB}_4\text{O}_7:\text{Sm}^{2+}$ and the He-EOS differed, suggesting a pressure gradient across the gasket hole. The maximum pressure gradient of 6 GPa was observed at a pressure of 70 GPa, and at pressures above this the pressure gradient decreased. At all pressures above 35 GPa, therefore, the sample pressure was determined from the EOS of the helium as this gave a better estimate of the true sample pressure. At the highest pressure reached in this study, 100.5 GPa, the pressures determined by the $\text{SrB}_4\text{O}_7:\text{Sm}^{2+}$ (102 GPa) and He-EOS (100.5 GPa) differed by only 1.5 GPa. The diffraction data were collected on an image-plate detector placed approximately 365 mm from the sample. To improve powder averaging, the sample was oscillated by $\pm 3^\circ$ during the 40 s exposures. The resulting two-dimensional diffraction images were integrated using FIT2D (Ref. 22) to give standard diffraction profiles. Rietveld refinement of these profiles was performed using the JANA2000 software package.²³

On pressure increase, we observe S-I to transform directly to tetragonal S-II at 37.5(1.5) GPa, with no evidence of any intermediate amorphous form. We suggest that the previous reports of such a phase arose because of the absence of any hydrostatic medium in those studies.^{6,7} The transition from S-II to S-III was observed to start at 75 GPa, and two phase

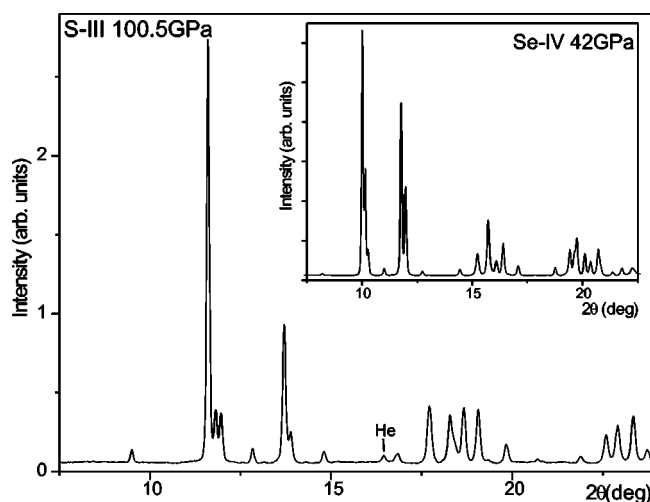


FIG. 1. Powder diffraction profile of S-III at 100.5 GPa. The strongest peak from the He pressure medium is identified. For comparison with the S-III profile, the inset shows a diffraction profile from incommensurate Se-IV at 42 GPa.

S-II/S-III mixtures were observed up to 95 GPa. The single-phase diffraction profile of S-III observed at 100.5 GPa, the highest pressure reached in this study, is shown in Fig. 1 and is clearly similar to those from Se-IV,¹⁶ a diffraction profile from which is shown in the inset to Fig. 1 for comparison. All the diffraction peaks from S-III can be indexed on the same $I'2/m(0q0)s0$ super spacegroup as Se-IV,¹⁶ with $a = 2.805(2)$ Å, $b = 3.457(2)$ Å, $c = 2.210(2)$ Å, $\beta = 113.1(2)^\circ$, and $q = 0.279(3)$ at 100.5 GPa.²⁴

Although all the peak positions in S-III can be accounted for by an incommensurate Se-IV-like structure, the relative peak intensities in S-III and Se-IV are different (see Fig. 1) as a result of preferred orientation (PO) in the S-III sample. The best Rietveld fit to the S-III diffraction profile at 100.5 GPa, which included the refinement of a correction for preferred orientation and the refinement of the amplitudes of the atomic modulations B_{1x} and B_{1z} ,²⁵ is shown in Fig. 2. The refined structural parameters are $a = 2.802(1)$ Å, $b = 3.455(1)$ Å, $c = 2.208(1)$ Å, $\beta = 113.15(1)^\circ$, and $q = 0.281(1)$, with $B_{1x} = 0.028(1)$, $B_{1z} = 0.118(1)$, and a single atom at $(0, 0, 0)$. Tests to determine the effect of different PO corrections on the modulation amplitudes at 100.5 GPa revealed that the refined value of B_{1z} was almost independent of the choice of PO model, but that the value of B_{1x} varied in the range 0.002–0.028. However, the overall fit to the S-III profiles was very poor for many of these PO models, and the values for B_{1x} and B_{1z} given above are those from the best-fitting model.

The modulation amplitudes in S-III at 100.5 GPa are similar to those observed in Te-III at 8.5 GPa, where $B_{1x} = 0.0215(9)$ and $B_{1z} = 0.0925(7)$,¹⁵ and in Se-IV at 42 GPa, where $B_{1x} = 0.0236(11)$ and $B_{1z} = 0.0900(8)$.¹⁶ In the unmodulated S-III structure, which has spacegroup $I2/m$, each sulfur atom is six-fold coordinated with two nearest neighbors at a distance of 2.208(1) Å and four further atoms at a distance of 2.225(2) Å. The nearest-neighbor distance is equal to the c -axis lattice parameter and is thus unaffected by the modu-

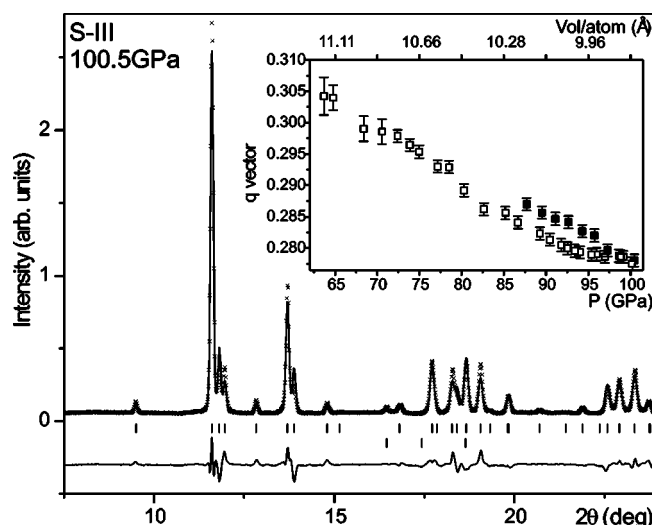


FIG. 2. Rietveld refinement of incommensurate S-III at 100.5 GPa. The upper tick marks below the profile show the calculated peak positions from the main and modulation peaks, while the lower tick marks show the calculated peak positions from the He pressure transmitting medium. The difference between the observed and calculated profiles is shown below the tick marks. The inset shows the pressure dependence of the incommensurate wave vector q both as a function of pressure and volume per atom. Filled (unfilled) symbols denote data collected on pressure increase (decrease).

lation. However, the next-nearest-neighbor contact distance varies from 2.082(2) Å to 2.441(2) Å as a result of the modulation, with an average distance of 2.243(1) Å.²⁶ The closest approach distance at 100.5 GPa is similar to the average S—S bondlength of 2.060(3) Å found within the S_8 molecules at ambient conditions,¹ and with the S—S bondlengths of 2.070(4) Å and 2.096(7) Å found within the chains of the polymeric form of sulfur recently reported to exist at 3 GPa and 400 °C,³ but is slightly longer than the S—S intrachain distance of 1.96(1) Å we find in S-II at 85.4 GPa—the highest pressure at which we could refine the detailed structure of S-II.

On pressure decrease, the sample was found to remain single-phase S-III down to 90 GPa. Although additional diffraction peaks appeared at this pressure, and they increased in intensity on further pressure decrease, as illustrated in Fig. 3, diffraction peaks from S-III were visible at all pressures down to 63.7 GPa. The pressure dependence of the incommensurate q vector was obtained by least-squares fitting to the positions of the S-III diffraction peaks and is shown in the insert to Fig. 2. As in Te-III and Se-IV,^{15,16} q varies strongly with volume, and, over the pressure range 64–100 GPa, decreases approximately linearly with volume at the rate $2.11(5) \times 10^{-2} \text{ \AA}^{-3}$. This is only $\sim 20\%$ less than the linear pressure dependence of $2.7(1) \times 10^{-2} \text{ \AA}^{-3}$ observed in Se-IV between 34 and 42 GPa (Ref. 16) and is considerably larger than the pressure dependence of $1.35(6) \times 10^{-2} \text{ \AA}^{-3}$ observed in Te-III between 5.0 and 8.5 GPa.¹⁵ Although the pressure dependence of q is initially linear in both Te-III and Se-IV, at higher pressures the pressure dependence becomes strongly nonlinear.^{15,16} Further data over an

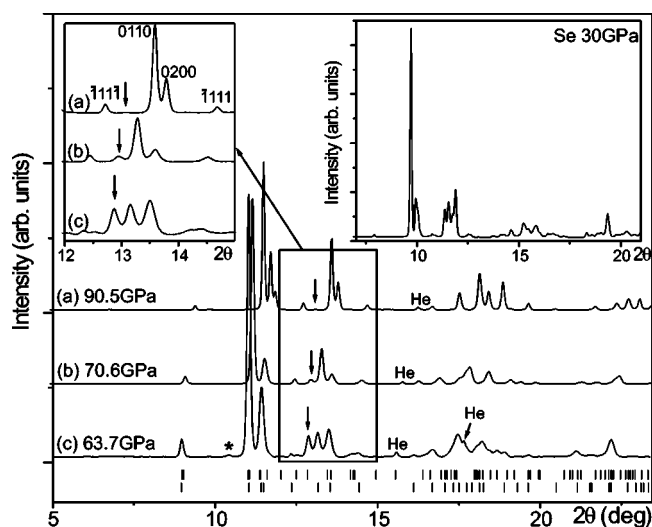


FIG. 3. Diffraction profiles collected from sulfur on pressure decrease. Diffraction peaks from the He pressure medium are labeled. The most intense sulfur-V peak first appears at 90 GPa, as identified by the arrow in profile (a), and it increases in intensity as the pressure is decreased, as identified in profiles (b) and (c), and enlarged in the left-hand inset. The mixed-phase profile at 63.7 GPa is very similar in appearance to the diffraction profile from a mixture of Se-III/Se-IV at 30 GPa, as shown in the right-hand inset for comparison. The upper (lower) tickmarks beneath the 63.7 GPa profile show the calculated peak positions from S-V (S-III). The single peak in the 63.7 GPa profile not accounted for by either S-III or S-V is identified with an asterisk.

extended pressure range are necessary to determine whether similar behavior is observed in S-III.

The weak additional peaks that first appear in the S-III profiles at 90 GPa—see profile (a) of Fig. 3—are not from the tetragonal S-II phase. Rather, their positions relative to the S-III peaks are reminiscent of the positions of peaks from Te-II and Se-III relative to those from Te-III and Se-IV, respectively,¹⁸ as illustrated for Se in the inset to Fig. 3. Close examination of the mixed S-II/S-III patterns obtained between 75 and 95 GPa on pressure increase clearly shows that the most intense of these additional peaks (that indicated by the arrow in Fig. 3) is also visible in a profile collected at 91 GPa on compression. We call this new high-pressure phase of sulfur S-V. As with Te-II and Te-III,¹⁸ S-III and S-V form mixed-phase profiles, but attempts to obtain a single-phase profile of S-V at lower pressures were unsuccessful as both the gasket hole and diamonds failed on attempting to decrease the pressure below 63.7 GPa. Although the 63.7 GPa profile shown in Fig. 3 still contains many reflections from S-III, it is possible to index all but one of the remaining peaks on a triclinic body-centered Te-II-like structure¹⁸ with $a=2.966(8)$ Å, $b=10.666(3)$ Å, $c=2.284(2)$ Å, $\alpha=86.67(2)^\circ$, $\beta=111.89(1)^\circ$, and $\gamma=91.30(1)^\circ$ at 63.7 GPa. Although this cell is nonprimitive²⁷ and thus nonstandard, we chose it previously to describe Te-II and Se-III because it highlights the close relationship to the (commensurate) structures of Te-III and Se-IV when their q vectors are $(0, \frac{1}{3}, 0)$, and thus when their b axes are tripled in length.¹⁸ We have chosen to use the nonstandard space-

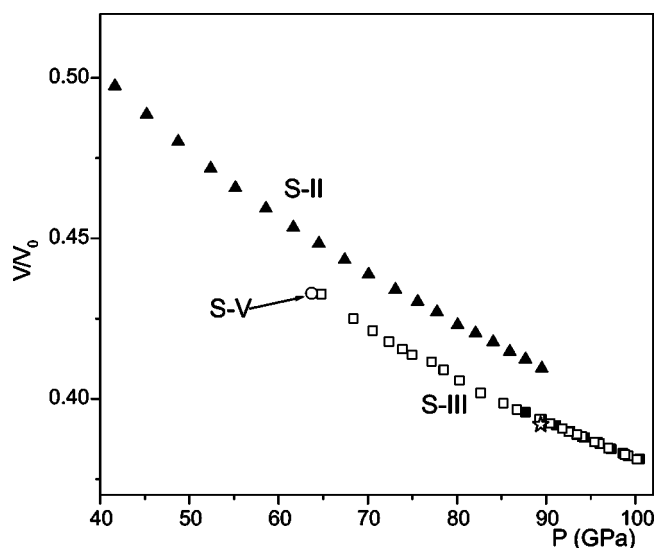


FIG. 4. The compressibility of sulfur from 40 to 101 GPa. Filled (unfilled) symbols denote data collected on pressure increase (decrease). The data point plotted as a star at 89.4 GPa, is from Ref. 7. The unfilled circle at 63.7 GPa is from triclinic sulfur-V.

group here as the same close structural relationship exists between S-III and S-V. The compressibility of sulfur from 40 to 101 GPa is shown in Fig. 4. The volume change ($\Delta V/V_0$) at the S-II \rightarrow S-III transition is 1.6(1)%, while no volume change, within error, is observed at the S-III \rightarrow S-V transition. The density of the bcc structure of S-III reported by Akahama *et al.*,⁷ reinterpreted using a Te-III-like monoclinic unit cell,²⁸ is in excellent agreement with our results.

Sulfur thus joins its group VIA neighbors Se and Te in having a phase with an incommensurately modulated crystal structure at high pressure, and is the first element observed to have such a structure above 100 GPa. The reasons why these elements should adopt such complex structures is still not completely clear. However, *ab initio* calculations of the Se-IV structure using commensurate approximants with $q = \frac{1}{4}$ and $q = \frac{2}{7}$ have indicated that the incommensurate modulation might arise via a Kohn anomaly that reduces the energy of a phonon mode at $q=2k_F$ to below zero. The resulting pseudogap at the Fermi energy reduces the overall energy of the structure.²⁹

In conclusion, we have shown that S-III is isostructural with Te-III and Se-IV, and has an incommensurately modulated crystal structure. Although the current study was limited to 100.5 GPa, the previous study of Luo *et al.* suggests that S-III is stable to 162 GPa,⁶ although the more recent study of Degtyareva *et al.* reports a transition pressure of 153 GPa.¹⁷ Triclinic S-V has not been observed in previous studies of sulfur, but the observation of this Te-II-like structure, the isostructural nature of S-III, Se-IV, and Te-III, and the recent observation of a S-II-like structure in selenium,^{8,9,17} reveals that the high-pressure behavior of S, Se, and Te is much more similar than previously believed.

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- ¹⁹The sample was prepared by Dr. H. Muller (ESRF) by first dissolving high purity sulfur in toluene or dichloromethane and then letting the solution cool slowly to 238 K. The pale yellow precipitate that formed was collected by filtration and dried in a vacuum.
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- ²⁴Super spacegroup $I'2/m(0q0)s0$ is a nonstandard setting of spacegroup $C2/m(0q0)s0$. We have chosen to use the nonstandard setting for consistency with our previous descriptions of Te-III (Ref. 15) and Se-IV (Ref. 16). In the $C2/m(0q0)s0$ setting the structural parameters of S-III at 100.5 GPa are $a=2.808 \text{ \AA}$, $b=3.457 \text{ \AA}$, $c=2.210 \text{ \AA}$, $\beta=113.27^\circ$, with $q=0.721$.
- ²⁵The modulation is modeled as a sum of Fourier amplitudes, as described in Ref. 15. For the refinement of only first-order Fourier components, the superspace symmetry of S-III reduces the number of refineable modulation parameters to 2, B_{1x} and B_{1z} .
- ²⁶Different models of preferred orientation have little effect on the variation in next-nearest-neighbor distance—all the models investigated resulted in a variation in the range $2.11(2)–2.42(3) \text{ \AA}$ at 100.5 GPa.
- ²⁷The equivalent primitive unit cell for S-IV at 63.7 GPa is $a=2.284 \text{ \AA}$, $b=2.966 \text{ \AA}$, $c=5.508 \text{ \AA}$, $\alpha=102.35^\circ$, $\beta=92.91^\circ$, and $\gamma=111.89^\circ$.
- ²⁸The relationship between the bco cell of Akahama *et al.* (Ref. 7) (A) and the present monoclinic cell (I), is $\vec{a}_A=-\vec{b}_I$, $\vec{b}_A=2\vec{a}_I+\vec{c}_I$ and $\vec{c}_A=\vec{c}_I$.
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