



	Experiment title: Incommensurate Sulfur at Pressures Above 100GPa	Experiment number: HS-2503
Beamline: ID09	Date of experiment: from: 15/09/2004 to: 19/09/2004	Date of report: 28/02/05
Shifts: 12	Local contact(s): M. Hanfland	<i>Received at ESRF:</i>
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Report: The high-pressure behaviour of the group VI elements (Te, Se and S) has long been the subject of interest and attention. Under compression, Te is reported to undergo a number of structural transitions to complex low-symmetry phases: Te-I (rhombohedral) \rightarrow Te-II (monoclinic) at 4GPa, Te-II \rightarrow Te-III (orthorhombic) at 7GPa, Te-III \rightarrow Te-IV (rhombohedral) at 10GPa, and Te-IV \rightarrow Te-V (cubic) at 27GPa [1]. The lighter members of the group, Se and S, are reported to have similar transition sequences and structures: Se-III, IV and V are reported to be isostructural with Te-II, III and IV, respectively [2], and S-III, stable between 83 and 162GPa, is also reported to be isostructural with Te-III [3,4].

Recently, using a combination of powder and quasi-single crystal techniques at SRS Daresbury, we have shown that Te-III has a body-centred monoclinic structure, but one which is *incommensurate* with structural modulations perpendicular to the *b* axis [5]. We have also studied Se-IV, stable above 28GPa and long reported to be isostructural with Te-III, and find that it has the same incommensurately modulated monoclinic structure, and the incommensurate wavevector is again strongly pressure dependent [6].

In this proposal we asked for 4 days of beamtime to determine whether S had the same incommensurate crystal structure. Data were collected from a sample of S₈ provided by Dr M Mezouar (ESRF) using helium as a hydrostatic medium. On pressure increase, we observed S-I to transform to tetragonal S-II at 37.5GPa, the transition from S-II to S-III was observed to start at 75GPa. Single phase profiles of S-III were observed above 95GPa, and the profile from S-III at 100.5GPa is shown in Figure 1. This diffraction pattern is clearly very similar to that from incommensurate Se-IV (shown in the inset to Fig. 1), and, indeed, all the diffraction peaks can be indexed on the incommensurate monoclinic structure as Se-IV and Te-III, with $a=2.802\text{\AA}$, $b=3.455\text{\AA}$, $c=2.208\text{\AA}$, $\beta=113.15^\circ$, and $q=0.281$ at 100.5GPa. The Rietveld refinement of the 100.5GPa profiles is shown in Figure 2.

The inset to Figure 2 shows the pressure dependence of the incommensurate wavevector, q . As in Se-IV and Te-III, q is strongly pressure dependent, varying from 0.281 at 100GPa to 0.304 at 63.7GPa, the lowest pressure at which it could be measured.

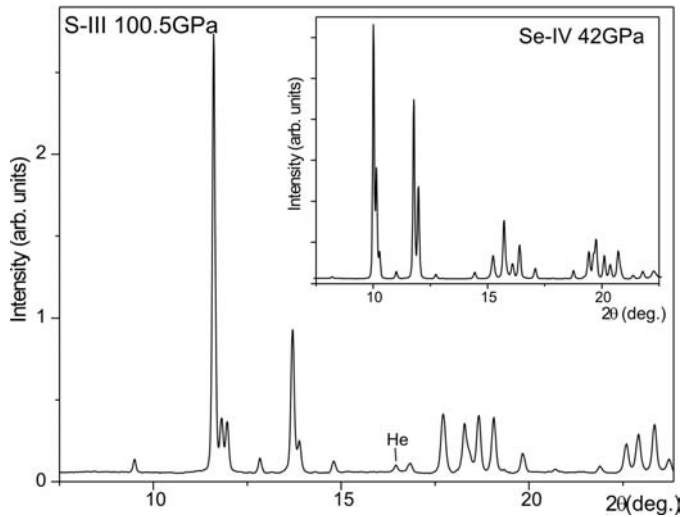


Fig 1: Diffraction profile from S-III at 100.5GPa. For comparison, the inset shows a diffraction profile from incommensurate Se-IV.

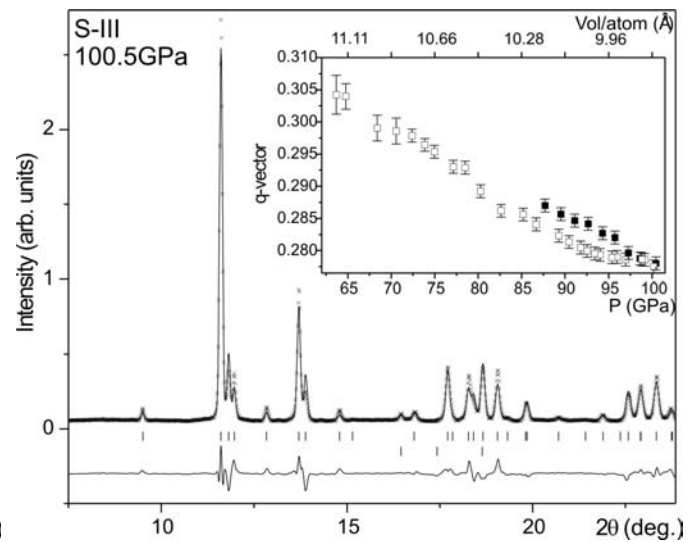


Fig 2: Rietveld refinement of S-III at 100.5GPa. The inset shows the pressure dependence of the incommensurate wave vector q .

Sulfur thus joins its group VIA neighbours 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 100GPa. 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 $q = 1/4$ and $q = 2/7$ 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 [7].

The results of this experiment were published in Physical Review B Rapid Communications in January 2005, as detailed below.

PHYSICAL REVIEW B 71, 020101(R) (2005)

Incommensurate sulfur above 100 GPa

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(Received 19 October 2004; published 21 January 2005)

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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