ESRF	**Experiment title:** Structural transformations in amorphous GeS_2 at high pressure	**Experiment number:** HD-361
Beamline: ID09A	**Date of experiment:** from: 15/04/2009 to: 18/04/2009	**Date of report:** July 3, 2009
Shifts: 9	**Local contact(s):** M. Hanfland	*Received at ESRF:*

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Report:

Both X-ray diffraction (XRD) and X-ray absorption fine structure (XAFS) spectroscopy results of experiment HD-361 have been submitted for publication to *Phys. Rev. B* [1].

The occurrence of amorphous-amorphous transformations (AATs) at high pressure represent a strongly debated issue in modern condensed matter physics. In recent times, there has been a renewed interest in the nature of high pressure polyamorphic transitions for a variety of tetrahedral systems such as amorphous silicon, germanium, carbon, silica and germania. On the other hand, high pressure AATs have been by far less studied in tetrahedral semiconducting chalcogenide glasses, although at least amorphous $GeSe_2$ received some attention: a conversion of edge-sharing to corner-sharing tetrahedra and the onset of a coordination increase have been detected below 10 GPa by high-energy X-ray diffraction and acoustic measurements. With increasing pressure, it has been shown from both Raman and EXAFS measurements that amorphous GeS_2 (a-GeS_2) undergoes a normal densification up to about 10 GPa. However, possible AATs in a-GeS_2 at higher pressures had never been experimentally investigated and were therefore the subject of the present study.

The X-ray diffraction experiment has been performed at the European Synchrotron Radiation Facility (ESRF) at beamline ID09A. High pressure up to 45 GPa was generated by a membrane Le Toullec-type diamond anvil cell (DAC) equipped with conical Boehler-Almax diamonds having a $250\mu m$ diameter flat culet. Amorphous GeS_2 was prepared as described in [1] and introduced into a glove box for the further manipulations. The sample was loaded in a stainless steel gasket with a hole of $120\mu m$ of diameter and an initial thickness of $40\mu m$. No pressure transmitting medium was used, thus sacrificing hydrostaticity in favor of the highest possible data quality. The pressure was determined through the ruby fluorescence technique. XRD patterns were recorded using a MAR555 image plate detector placed at about 34 cm from the sample. The wavelength was tuned to 0.4148 Å through a Si 111 monochromator. Two-dimensional image plate data were integrated with Fit2D to produce intensity patterns as a function of the wave-vector Q. The DAC angular opening limited the good Q-range of the diffractograms (Fig. 1) to about 7 Å^{-1}.

The XRD data evidence that the structural transformation in a-GeS_2 [1] has an amorphous-amorphous nature: intensity patterns as a function of the wave-vector Q show that no crystallization takes place. At

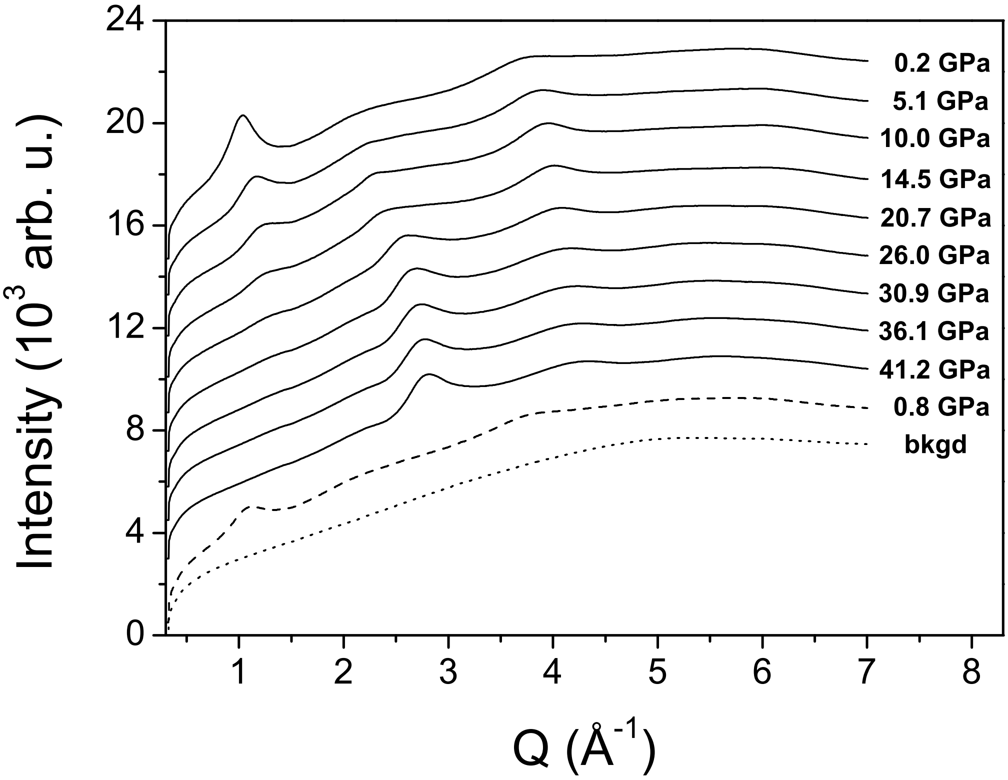

Figure 1: X-ray diffraction patterns of amorphous GeS_2 at selected increasing pressures from top to bottom (continuous lines), of the sample recovered at nearly ambient pressure (dashed line) and of the measured empty-cell background (dotted line).

ambient conditions, the first sharp diffraction peak (FSDP) is found at $Q = 1.02$ Å^{-1} and the following principal peak (PP) at $Q \sim 2.2$ Å^{-1}. With increasing pressure, the FSDP progressively loses intensity and shifts towards higher Q values. While the FSDP almost disappears above about 20 GPa, the PP gains intensity after a few GPa and upshifts over the entire pressure range of the study. Also in a-$GeSe_2$ a positive shift of both the FSDP and PP, as well as dramatic changes in their intensities, were found by high-energy diffraction up to 9.3 GPa.

The position of the FSDP and PP has been determined from the XRD pattern fitted by a gaussian curve after subtraction of a proper baseline. The quantitative results have been shown and critically discussed in [1].

References

[1] M. Vaccari, G. Garbarino, G. Aquilanti, M.-V. Coulet, A. Trapananti, S. Pascarelli, M. Hanfland, E. Stavrou, and C. Raptis, *Phys. Rev. B* (submitted).