ESRF	**Experiment title:** Structural transformations in amorphous GeS_2 at high pressure	**Experiment number:** HD-361
Beamline: ID24	**Date of experiment:** from: 13/05/2009 to: 19/05/2009	**Date of report:** July 3, 2009
Shifts: 18	**Local contact(s):** M. Vaccari	*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 XAFS experiment has been performed at the European Synchrotron Radiation Facility (ESRF) at beamline ID24. 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. Energy dispersive EXAFS data were recorded at the Ge K-edge using a two-dimensional FReLoN camera. The beam was focused horizontally by a curved polychromator Si 111 crystal in a Bragg geometry and vertically by two bent Rh and Pd mirrors with grazing incidence of 3 and 4 mrad, respectively.

X-ray absorption data have been analyzed through established procedures by using the IFEFFIT package. EXAFS signals have been interpreted in terms of a single Ge-S shell, by using theoretical amplitudes and phases calculated by FEFF6. The Bragg diffraction peaks arising from the diamond anvils limited the

exploitable k-range of the spectra to about 250 eV after the edge (Fig. 1); therefore the accuracy in interatomic distances was not better than 0.02 Å.

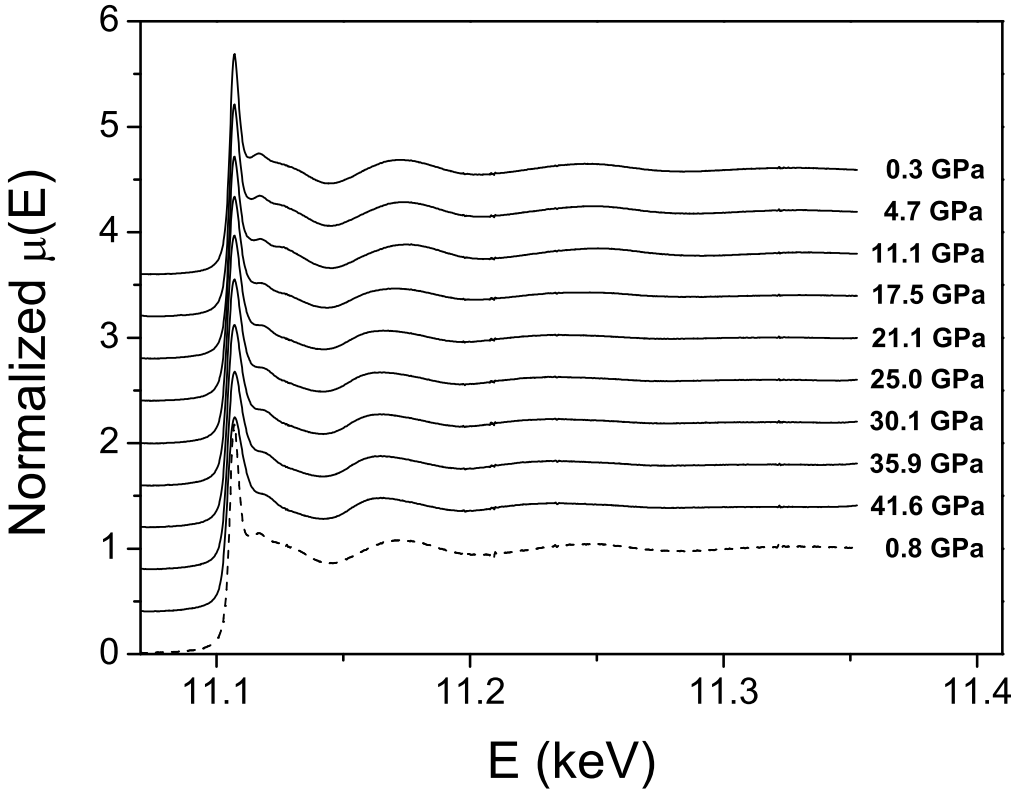

Figure 1: Normalized XAFS spectra at the Ge K-edge of amorphous GeS_2 at selected increasing pressures from top to bottom (continuous lines) and of the sample recovered at nearly ambient pressure (dashed line).

The quantitative evolution of the Ge-S bond length is shown in [1]. Below about 13 GPa there is a bond-compression of about 0.03 Å, in agreement with previous EXAFS findings and in consistence with relevant Raman data. Between 15 and 25 GPa, the average Ge-S distance in a-GeS_2 undergoes a gradual elongation of about 0.1 Å. This is interpreted as the signature of a fourfold to sixfold change, in close analogy with the same phenomenon well known in a-GeO_2 at lower pressures. The nearest-neighbors distance elongation is qualitatively evident also from raw data in Fig. 1 through an increase in the EXAFS oscillation frequency. After 25 GPa a post-transition compressional behavior is measured, with a slight Ge-S distance reduction up to the maximum pressure reached. The structural change observed in a-GeS_2 is reversible (Fig. 1), although with large hysteresis: when pressure is released, the Ge-S distance first slightly increases, then below 10 GPa suddenly decreases down to the original value of 2.22(1) Å [1].

The Ge K absorption edge position is found to shift towards lower energies by about -1.2 eV in the first 20 GPa [1]. This behavior is connected to the known pressure induced metallization of a-GeS_2, in agreement with the band gap closure measured by old optical experiments limited to lower pressures. As for the local structural changes, the semiconducting-metallic transformation of a-GeS_2 is fully reversible but with strong hysteresis.

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).