ESRF	**Experiment title:** Structure and bonding of liquid ZnSe under extreme conditions of P and T.	**Experiment number**: **HC-1608**
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Report:

The aim of this experiment is the investigation of the evolution of the local structure and the degree of chemical order in multicomponent covalent liquids under extreme conditions of pressure and temperature (P/T). ZnSe is a good candidate as a previous X-ray diffraction study showed that upon compression the local structure in the liquid of ZnSe changes from a 4-coordinated (zincblende-like, ZB) liquid structure to a 6-coordinated (rocksalt-like, RS) structure, as in the solid **[1]**.

We therefore performed a series of XAS experiments on ZnSe at the K-edge of Zn (9.66 keV) using the diamond anvil cell (DAC) technique coupled with laser heating. The samples were ZnSe foils sandwiched between two pellets of KCl and loaded together with a ruby pressure sensor in the DAC. Nano-crystalline diamonds with a culet size of 250 microns were employed in order to avoid glitches in the XAS spectra. We achieved high P/T conditions of up to 42 GPa and 2700 K **(Fig. 1)**.

We encountered some difficulties during laser heating, which prevented a smooth increase of the sample temperature at low P/T conditions due to relatively low coupling of the sample with the laser. At high temperatures when the sample transformed into the metallic liquid phase a (too) strong coupling with the laser led to an abrupt increase of the sample temperature and in some cases the sample was destroyed before data could be acquired. Typical normalized XAS spectra acquired during the experiment are shown in **Fig. 2**.

Data analysis is currently in progress. The XANES spectra were normalized and analysed qualitatively. In order to interpret the experimental results in terms of electronic configuration and atomic bonding behaviours *ab initio* simulations of ZnSe at high pressure were performed at the Zn- and Se-edge using instantaneous configurations as input for full multiple scattering calculations using the feff9 code. First results of the simulation show that the evolution of the XANES signal at the Zn K-edge in the liquid with pressure is weak, while the Se edge is more sensitive to the pressure than that at the Zn edge.

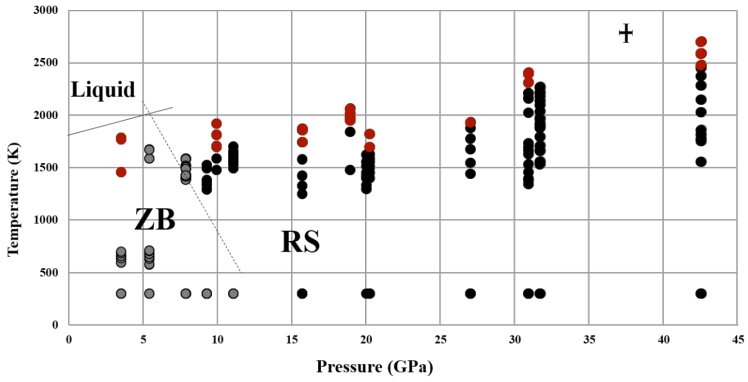

Fig.1. PT-points of the laser heating runs in the ZnSe system. Grey and black symbols indicate spectra corresponding to the ZB and RS structure, respectively. Red points indicate the temperature at which the second shoulder in the XANES spectra disappears (Fig. 2). This observation might either indicate the starting of melting or high disorder in the structure (hot solid). The black dotted line shows the phase boundary between the zinc blende (ZB) and rock salt (RS) structure polymorphs while the black solid line indicates the melting curve of the ZB polymorph obtained from a previous laser-heating study using X-ray diffraction [2]. The cross in the upper right corner gives an indication about the average errors on the pressure and temperature.

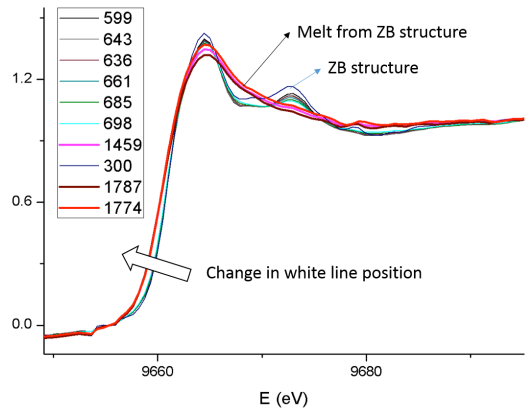

Fig. 2. Normalized spectra from run load7_P2.9 at 2.9 GPa. Numbers in the legend correspond to sample temperatures in K.

Data obtained at high P and ambient T have been reduced using the software Athena and further analysed using the software Arthemis in order to extract the Debye-Waller-factor and the half path length. From this data set the phase transition from ZB to the RS structure could be located between 14.6 and 14.9 GPa which is slightly higher than previous reported transition pressures of 13 GPa (Itkin *et al.*, 1991) **[5]**. We observed that this transition of the RS structure involves a shift of the edge energy position by +0.59 eV, compatible with the predicted semiconductor to metal transition. Different input models were used to test the potential appearance of an intermediate phase during the transition including the SC16 structure and Cmcm cinnabar structure following the observations of Qteish *et al.* **[3]** and Cote *et al.* (1997) **[4]**.

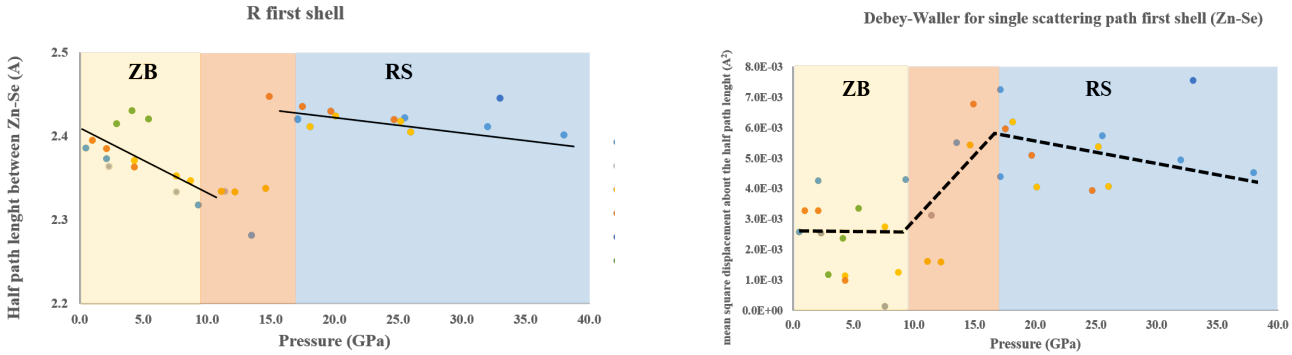

Fig. 3 Evolution of a) the half path length and b) the mean square displacement about the half path length (also called Debye-Waller factor) with pressure for the first shell around Zn (Zn-Se bonding). Note the intermediate region between 10 and 17 GPa highlighted in red, in which the Debye-Waller factor increases continuously.

We are currently working on the improvements on the heating techniques in order to acquire data at high temperature conditions. Unfortunately, we were not able to access the Se-edge with this setup. In a following proposal we propose to collect XAS data at high PT conditions at the Se-edge at ID24 as well as conducting laser-heating diffraction experiments on ID27, in order to obtain complementary results that will allow us to resolve the liquid-liquid transition at high-pressure and temperature conditions in ZnSe.

References:

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