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ESRF

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- fill in a separate form for each project or series of measurements.
- type your report, in English.
- include the reference number of the proposal to which the report refers.
- make sure that the text, tables and figures fit into the space available.
- if your work is published or is in press, you may prefer to paste in the abstract, and add full reference details. If the abstract is in a language other than English, please include an English translation.

ESRF	**Experiment title:** “High pressure XAS on GaSe single crystal at the Se K-edge”	**Experiment number**: HS-1191
Beamline: ID24	**Date of experiment**: from: 5-7-00 to: 10-7-00	**Date of report**: 5-2-01
Shifts: 17	**Local contact(s)**: Sakura Paskarelli	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

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Report:

Abstract

In this experiment we have carried out a high-pressure X-ray Absorption Spectroscopy (XAS) experience in GaSe at the Se K-edge, up to 35 GPa. Thanks to the new vertical focusing mirror introduced in beamline ID24 and to the horizontal dispersive optics, we have been able to focus the synchrotron radiation alternatively in the sample and next to it, inside the pressure chamber. With this achievement the quality of the normalization performed to obtain the XAS spectra is improved, and the distortion of the spectra is reduced. The Extended X-ray Absorption Fine Structure (EXAFS) fit shows clearly a high-pressure phase transition at 20±2 GPa. In the low-pressure phase, up to 15 GPa, the evolution of the Se-Ga distance is coherent with previous experiments carried out at the Ga K-edge. The distance evolution in the rocksalt high pressure phase agrees with recent angle dispersive x-ray diffraction experiments.

Experiment

High quality GaSe crystals were prepared by the Bridgman method. Samples were cleaved from the ingots with a razor blade and cut into parallelepipeds with typical dimensions of 150x150x30 μm^3. A wide-angle aperture membrane diamond anvil cell was used as pressure generator. The diamonds were of the Drukker standard type, with culet size of 0.48 mm. The single crystal sample was placed in a 260 μm diameter hole drilled in an Inconel gasket. A 4:1 methanol-ethanol mixture was used as pressure transmitting medium, and the pressure was measured in-situ using the linear ruby fluorescence scale.

The x-ray absorption experiments were carried out at the ID24 energy dispersive x-ray absorption station of the European Synchrotron Radiation Facility (Grenoble, France). The measurement was performed at the Se K-edge (12.6531 keV). A profiled curved Si (111) monochromator focused the beam to a spot of approximately 120 μm in the horizontal direction. In the vertical direction the beam was only 60 μm, thanks to the action of a vertical mirror. In this way both the direct beam and the signal coming from the sample could be taken inside the pressure chamber. An essential experimental aspect of XAS experiments at high pressure is the presence of glitches in the XAS spectra originated by X-Ray Diffraction (XRD) associated to the diamond single crystals. The pressure cell is oriented with respect to the polychromatic x-ray beam in order to remove these glitches from the widest spectral domain around the x-ray absorption edge. This operation takes advantage of the real time visualisation of the XAS spectra thanks to the x-ray parallel collection characteristic of the energy dispersive set-up. We found two orientations of the cell were the presence of glitches was minimised. In addition, the remaining (and relatively smooth) glitches do not appear in the XAS spectra after normalising with the direct beam. The quality of the resultant spectra (Fig.1) is improved and the spectra are not distorted. Given the geometry of the experiment the polarisation vector of the synchrotron radiation was always in the layer plane. The pressure was increased up to 34 GPa, the maximum pressure attainable with our diamond anvil cell.

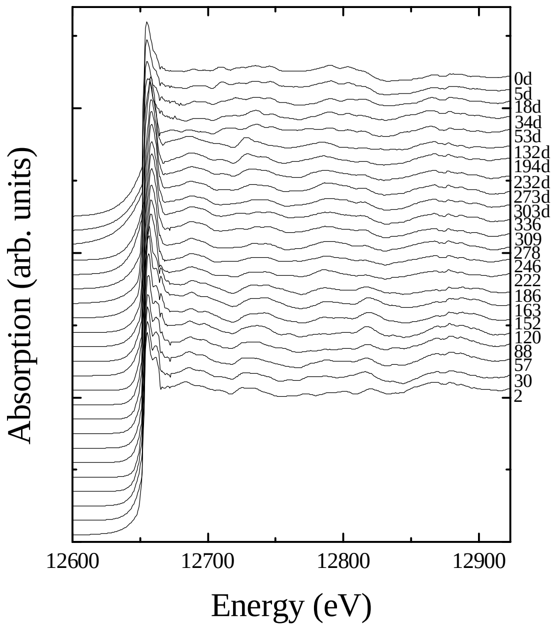

Fig.1. XAS spectra of GaSe at the Se K-edge. The numbers next to each spectrum refer to the pressure (in kbar) at with the spectrum was taken. The letter d indicates if the spectra was taken in the downstroke.

Results

The PPDF was obtained by Fourier transformation of the EXAFS signal in a k domain between 2.7 and 8 $Å^{-1}$, and using a Bessel based ($\tau = 4$) apodization window. The spectrum taken at ambient conditions was used to extract the phases and amplitudes corresponding to the Se-Ga backscattering process, using the known structural data. This allow to follow the pressure variation of the structural parameters of the first coordination shell. The evolution of the intralayer first neighbour Se-Ga distance obtained from the EXAFS fit is shown in Fig. 2.

We have fitted the monotonous decrease observed up to 15 GPa to a Murnaghan-type equation of state, resulting in a bulk modulus of B0 = 92±6 GPa, with B' fixed to 5. This value is slightly smaller that the ones found for InSe (116±20)[1] or GaTe (124±6GPa)[2] for the cation-anion distances.

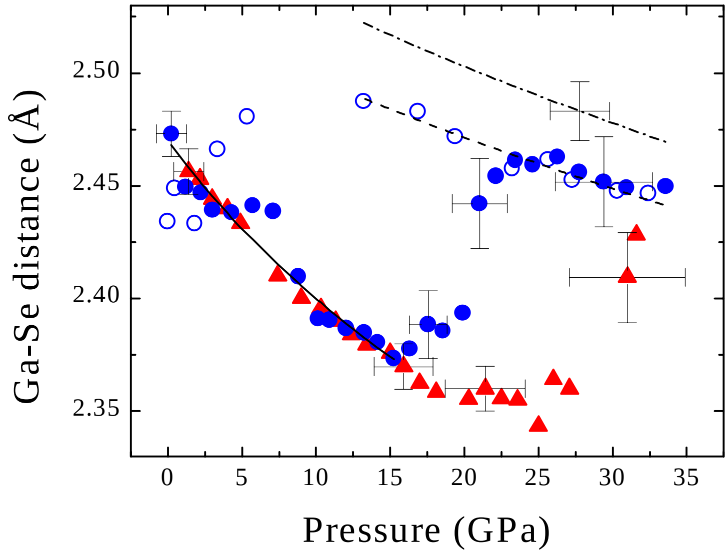

Fig.2. Ga-Se distance as obtained from the EXAFS fit. a) Solid triangles: Ga K-edge[3], upstroke; b) Solid circles: Se K-edge, upstroke; c) Hollow circles: Se K-edge: downstroke; d) Solid line: Murnaghan fit of a) and b) with d0=2.470±0.003 Å, B0 = 92±6 GPa and B0' fixed to 5; e) Dash line: Murnaghan fit of c) with d0=2.53±0.02 Å, B0 = 260±40 GPa and B0' fixed to 4.1; e) Dash-dot line: Murnaghan fit of data coming from XRD[4,5] with d0=2.56±0.01 Å, B0 = 230±10 GPa and B0' fixed to 4.1

The Ga-Se distance evolution up to 15 GPa agrees with a previous experiment carried out at the Ga K-edge[3].

The evolution of the Ga-Se distance in the downstroke (hollow circles in Fig. 2) is compatible with the XRD equation of state of the high pressure phase (dashed-dot line) down to around 13 GPa, if we take into account the error in the determination of distances both in EXAFS and in XRD. A Murnaghan fit (dashed line) to the downstroke points obtained by EXAFS results in d0=2.53±0.02 Å and B0 = 260±40 GPa with B0' fixed to 4.1. The same fit performed to the data obtained from XRD gives d0=2.56±0.01 Å and B0 = 230±10 GPa with B0' fixed to 4.1, in agreement with EXAFS results. Below 13 GPa in the downstroke a structural change takes place and the cation-anion distance obtained tends progressively to that of hexagonal GaSe.

References

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[3] J.P. Itié, A. Polian, M. Gauthier and A. San Miguel. ESRF Highlights 1996/1997.
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