EUROPEAN SYNCHROTRON RADIATION FACILITY

INSTALLATION EUROPEENNE DE RAYONNEMENT SYNCHROTRON

Experiment Report Form

	Experiment title: **Towards a better understanding of the unique ultra-low thermal conductivity in SnSe thermoelectric from constraints of its bond anharmonicity**	**Experiment number**: HC-5049
Beamline: BM23	**Date of experiment**: from: 13/09/2022 to: 19/09/2022	**Date of report**: 24/05/2023
Shifts: 18	**Local contact(s)**: Joao Elias FIGUEIREDO SOARES RODRIGUES	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

Joao Elias FIGUEIREDO SOARES RODRIGUES [1]

Javier Gainza [2]

Federico SERRANO-SANCHEZ [2]

[1] *European Synchrotron Radiation Facility (ESRF), 71 Avenue des Martyrs, 38000 Grenoble, France.*

[2] *Instituto de Ciencia de Materiales de Madrid (ICMM), CSIC, E-28049 Madrid, Spain.*

Report:

This project aimed to study the bond anharmonicity and anisotropy in binary compounds SnSe by employing high-quality EXAFS under isobaric condition in diamond anvil cell and cryostat, from 10 to 300 K at high pressures. The use of high-pressure and low-temperature is more than essential to provide a more complete thermodynamics scenario in SnSe.

We have asked for this project 6 fresh nanopolycristalline diamonds (NPDs) with Boehler-Almax design and height 1.6 mm and cullet sizes of 250 μm from a collaboration with Ehime University (Japan). Initially, we intended to perform *quasi*-hydrostatic EXAFS measurements using Ne as pressure transmitting medium; however, we faced difficulties for obtaining bottles of Ne which had become rare and expensive due to the Ukrainian War. Therefore, we have changed the experimental condition by considering solid loading, in which the gasket hole is filled entirely by fine powders of SnSe. For this purpose, we requested three pairs of already used 300 μm cullet size NPDs to be mounted in three CuBe diamond anvil cells (DACs) for low-temperature. These additional diamonds were obtained from the BM23/ID24 stock.

We performed EXAFS measurements at Sn *K*-edge (29.2 keV) under isothermal compression in the range 0–25 GPa at three different temperatures: 65 (run1), 100 (run2), and 200 (run3) K. The ruby was employed as pressure gauge. We used a He-flow cryostat for diamond anvil cells developed in collaboration with and at the HP-ESRF sample environment. The temperature was then monitored from a thermocouple mounted near the DAC. The

different isothermal conditions were considered as an additional parameter for accessing different bond anharmonicity degrees. Changing the pressure also played an important role for further variations in bond anharmonicity and anisotropy, which improve the thermoelectric performance.

EXAFS investigations were then conducted at different temperatures with high-quality data for allowing properly fittings of higher order cumulants, which are related to anharmonicity in the pair-potential (here, Sn–Se). The local atomic arrangement was probed using EXAFS measurements at the Sn *K*-edge up to a *k*-range of 17.5 $Å^{-1}$ (Fig. 1) The beamline was operating with two fixed-exit Si(311) crystals combined with Pt-coated KB focusing mirror system inclined to 2 mrad for the harmonic rejection. The beam size was set to 3×3 $μm^2$ (FWHM). The diamond anvil cell was equipped with two Boehler-Almax cut NPD diamonds of 300 μm culet size. Re gaskets with a hole of 150 μm and of 50 μm thickness was used as a sample chamber.

Data analysis is still in progress. However, the XANES region and the first derivative for run2 can be observed in Fig. 1(a) and 1(b), respectively. The extracted EXAFS oscillations (*k*-weight of 1) at 100 K from 0–25 GPa can be seen in Fig. 1(c), which attested the high-quality EXAFS data thanks to the provided nano-polycrystalline diamond anvils from GRC. We managed to properly model the FT-EXAFS using three single scattering paths (Sn–Se) at 2.709 Å (green), 2.824 Å (orange), and 3.476 Å (purple) [in Fig. 1(d)]. The disorder parameters derived were $0.65×10^{-3}$ $Å^2$, $0.16×10^{-3}$ $Å^2$, and $5.6×10^{-3}$ $Å^2$, respectively. The coordination number of each path was kept fixed to 2. With this dataset, we expect to draw a complete scenario on the local environment of SnSe and how the pressure can be employed for fine tuning the thermoelectric performance by the electronic band convergence.

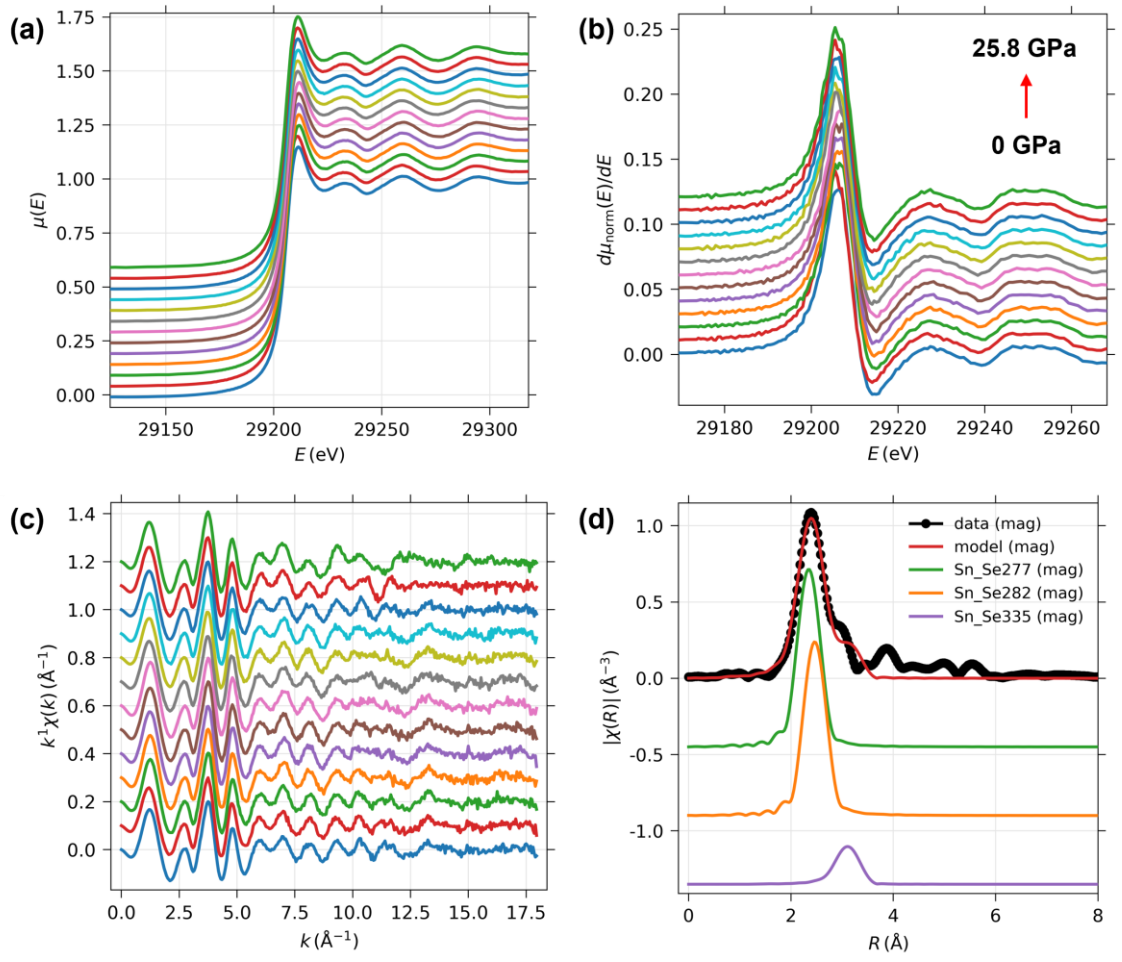

Figure 1. Sn *K*-edge XANES (a) and the first derivative (b) for SnSe sample loaded in Boehler-Almax NPD diamonds of 300 μm culet size. The extracted EXAFS oscillations χ(*k*) at 100 K from 0 up to 25 GPa (run2). EXAFS modelling for data point at 100 K and 8.4 GPa using three single scattering paths Sn–Se (d).

References

Currently, we are planning to report our findings in this project in a joint publication, as cited below:
J.E. Rodrigues, A.D. Rosa, J.Gainza, F. Serrano-Sanchez, G. Garbarino, J.L. Martínez, T. Irifune, J.A. Alonso, O. Mathon. *Local environment probed under high-pressure helps to fine tuning the thermoelectric performance of SnSe*. To be submitted for ACS journal *Chemistry of Materials*.