EUROPEAN SYNCHROTRON RADIATION FACILITY

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ESRF

Experiment Report Form

The double page inside this form is to be filled in by all users or groups of users who have had access to beam time for measurements at the ESRF.

Once completed, the report should be submitted electronically to the User Office via the User Portal:

https://wwws.esrf.fr/misapps/SMISWebClient/protected/welcome.do

Reports supporting requests for additional beam time

Reports can be submitted independently of new proposals – it is necessary simply to indicate the number of the report(s) supporting a new proposal on the proposal form.

The Review Committees reserve the right to reject new proposals from groups who have not reported on the use of beam time allocated previously.

Reports on experiments relating to long term projects

Proposers awarded beam time for a long term project are required to submit an interim report at the end of each year, irrespective of the number of shifts of beam time they have used.

Published papers

All users must give proper credit to ESRF staff members and proper mention to ESRF facilities which were essential for the results described in any ensuing publication. Further, they are obliged to send to the Joint ESRF/ ILL library the complete reference and the abstract of all papers appearing in print, and resulting from the use of the ESRF.

Should you wish to make more general comments on the experiment, please note them on the User Evaluation Form, and send both the Report and the Evaluation Form to the User Office.

Deadlines for submission of Experimental Reports

- 1st March for experiments carried out up until June of the previous year;
- 1st September for experiments carried out up until January of the same year.

Instructions for preparing your Report

- 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 frequency dynamics in amourphous and crystalline Carbon doped GeTe: investigating the origin of their similar ultra low thermal conductivity.	**Experiment number**: HC-2822
Beamline:	**Date of experiment**: from: 25/01/17 to: 31/01/17	**Date of report**: 28/02/17
Shifts:	**Local contact(s)**:Luigi Paolasini	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

A. Tlili*, V. M. Giordano*, S. Pailhes*, P. Noe*, J.-Y. Raty

Report:

Phase-Change Materials (PCM) exhibit a unique combination of properties from a reversible and ultra-fast amorphous/crystal transition to drastic differences in electronic properties, which put them at the forefront of research for optical and electronic storage. Among emerging non-volatile resistive memories, Phase Change Random Access Memories are at this day the most promising alternative technology in order to replace the current “flash memory”. This technology exploits the unique properties of chalcogenide based materials, with an electrical resistance changing by several orders of magnitude upon crystallization and a very low thermal conductivity in both phases, especially important as it allows decreasing the electric power needed for inducing the crystal-to-amorphous transition by Joule heating, and makes further electronic devices miniaturization accessible.

In this context, much attention has been given to binary GeTe, where carbon doping has been found to greatly improve the high temperature retention properties, specifically increasing the crystallization temperature. Surprisingly, doping GeTe with carbon dramatically changes its thermal properties: measurements performed on C-GeTe thin films show that while doping only slightly decreases the thermal conductivity in the amorphous phase, it dramatically reduces the one of the crystalline phase, of a factor larger than 10, making it very similar to the value in the corresponding amorphous phase. Such reduction can only be due to a dramatic change in phonon transport, as the crystalline electronic conductivity is reduced by only 30% for C doping in the 10-15% range (our work).

In order to get insight into the similarities or differencies in the vibrational properties of amorphuos and crystalline C-GeTe we have performed an IXS investigation at ID28. Measurements have been done on samples deposited as thin films onto a Si substrate, the standard preparation for use in microelectronics. For this experiment, we have prepared 1 micron thick films for getting the signal from a larger material quantity, Measurements have been done in a grazing incidence geometry, putting the sample vertically and impinging on it with the X ray beam at an angle close to the total reflection angle.

We used the Si 999 reflection of the monochromator, in order to have a larger flux, despite the lower resolution (3meV). In these conditions, we have succeeded in

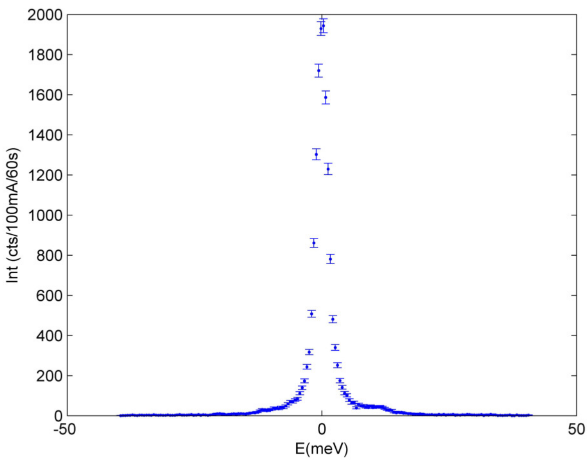

Fig.1: experimental spectrum collected on the crystalline film at $q=5.4nm^{-1}$

measuring the acoustic dispersion in the polycrystalline sample for wavevectors larger than 4 nm-1. Indeed, at smaller wavevectors the phonons were hidden by the elastic line, due to its important intensity and large width. An example of a spectrum collected at q=5.4nm^{-1} is reported in Fig. 1.

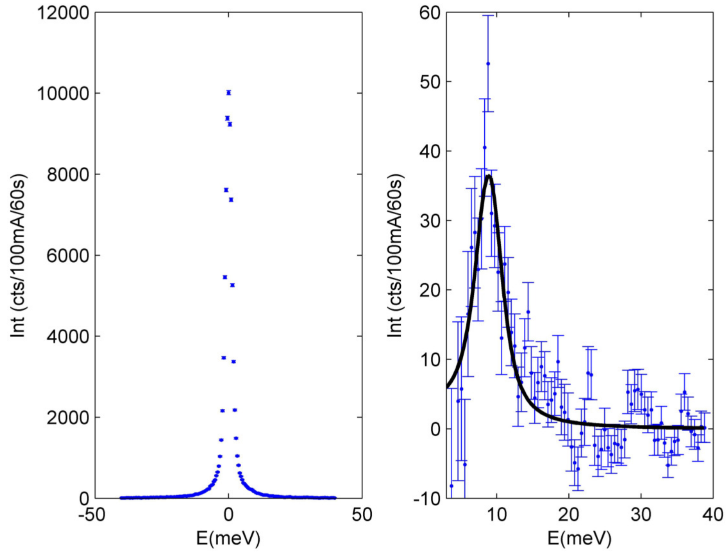

Fig.2: left: spectrum collected on the amorphous C-GeTe at q=5.4nm^{-1}. Right: Same data after subtraction of the intense elastic line, limited to the positive energy side. The black solid line represents the fit with an inelastic excitation.

Measurements on the amorphous sample turned out to be much more difficult due to the intense elastic line and to a smaller sound velocity. Nevertheless, we could extract phonon velocity and broadening in the limited 4-6 nm^{-1} range.
A spectrum collected at q=5.4 nm-1 is reported in Fig. 2 in the left panel. The right panel reports the same data after subtraction of the elastic line, together with the fit with a single excitation mode. Only positive energies are here reported for better visibility. Note the intensity values: 10000 counts for the elastic line and 40 counts for the phonon.
Our preliminary analysis indicates that the polycrystal has a larger average speed of sound but a comparable phonon broadening, leading to a mean free path of only about 1 nm for wavevectors larger than 5 nm-1.
At lower q, however, the mean free path is much longer, as the resolution-limited width of the phonon at q=4.2 suggests.

We also collected test data at high q (q~35nm^{-1}), where the spectrum should reflect the orientationnally averaged vibrational density of states. In this case the subtraction of the elastic line turned out to be quite difficult and not reliable for energies below 5 meV. These data have motivated us in submitting a DOS proposal at ID18, with the aim of exploring lower energies, thanks to the higher and sharper resolution.

Concerning the phonon dynamics, we would definitely need to complete our data by using the Si 12 12 12 on the crystalline and amorphous systems to access smaller qs. At the end of the beamtime, we could test the Si 12 12 12 on the polycrystalline sample in order to obtain the feasibility demonstration. However, there was no time to collect good statistics data. An example of spectrum at q=3.2 is reported in Fig. 4.

In the case of the amorphous sample, we plan to peel the film and prepare a powder sample between 2 diamond windows, with the optimal thickness of 80 microns. In this way we will be able to have a much stronger phonon signal.

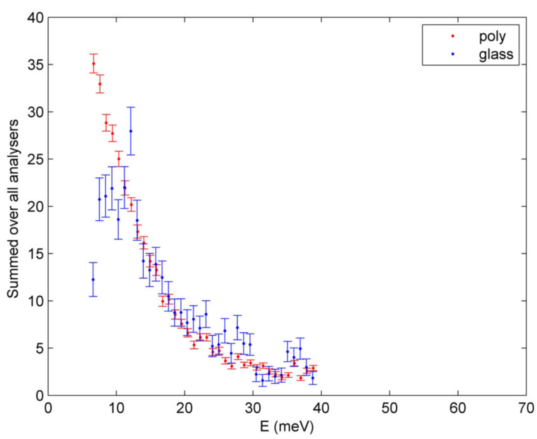

Fig. 3: high q spectra, as summed over all analysers after the elastic line subtraction.

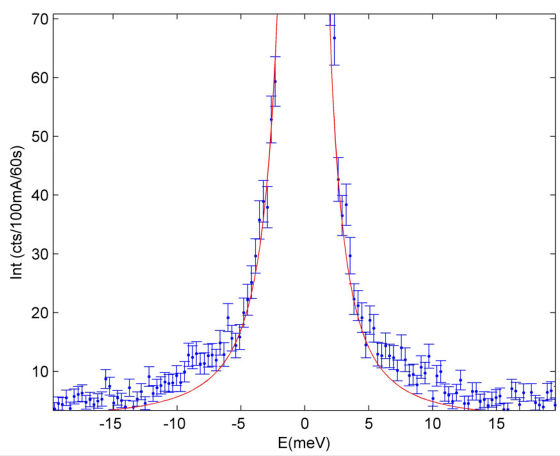

Fig. 4: Test spectrum on the polycrystalline film at the Si 12 12 12 reflection of the monochromator at q=3.2nm^{-1}. The red line corresponds to the elastic line, to improve the visibility of the inelastic signal.