	Experiment title: The effect of carbon doping on the phonon dynamics of crystalline GeTe: a microscopic insight into the drastic thermal conductivity reduction	**Experiment number**: HC-3415
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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 a previous experiment (HC-2822) we have investigated the vibrational properties of amorphuos and crystalline C-GeTe with 10% atomic content of carbon, called here GeTeCy.

Measurements were done in a grazing incidence geometry, on 1 micron thick C-GeTe layers deposited on a silicon substrate, using the 999 Si reflection of the monochromator, in order to have a larger flux, despite the lower resolution (3meV). We succeeded in 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. 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 a slightly crystallized sample, in the limited 4-6 nm^{-1} range, obtaining indications that the phonon mean free path in the amorphous sample is much smaller than in the polycrystal, shedding a doubt on the reliability of thermal coductivity measurements from literature.

The present experiment was meant to complete previous measurements focusing on the comparison of vibrational properties between C-GeTe and GeTe.
The same kind of samples and experimental setup was used in this run, and two more samples explored: polycrystalline GeTe and polycrystalline C-GeTe with a carbon atomic content of 15%, here called GeTeCz.
We measured both with the Si 999 and Si 12 12 12 reflection, this latter meant to access smaller q values reducing the width of the elastic line, despite a lower incident flux. However, we could not detect any phonon below 3.8 nm-1, the elastic line being extremely intense.

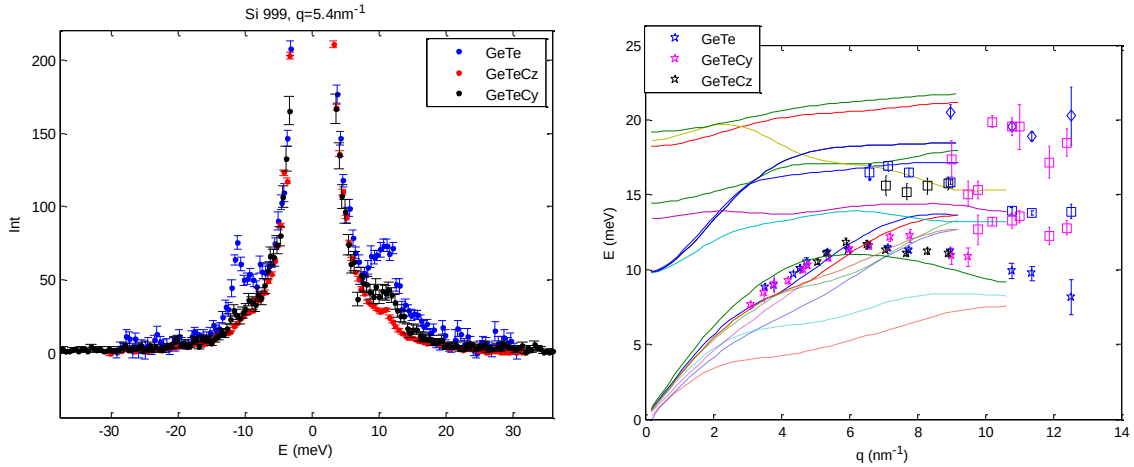

Figure 1: Left: IXS spectra collected with the Si 999 reflection of the monochromator on polycrystalline GeTe, GeTeCy and GeTeCz (see text). Right: the experimental acoustic (stars) and optic (squares and diamonds) modes of the three samples, compared with ab-initio calculations performed by JY Raty. Dashed lines are transverse acoustic modes

Our results indicate that there is no difference in the acoustic dispersions among the three samples, and the phonon width is similar as well, excluding a dramatic decrease of phonons lifetime, comparable to the amorphous case. Interestingly, the elastic to inelastic ratio increases with C-content, thus making the phonon detection more and more difficult (Fig. 1).

While we can exclude that carbon doping induces a thermal conductivity similar to the one of the amorphous sample, we cannot exclude a phonon lifetime shortening, beyond our experimental resolution.
For this, if on one side we are conducting new thermal conductivity measurements on these samples, for solving the contradiction with litterature reports, we have as well performed an experiment on ID18 to measure the density of states and get thus information on the q,E region inaccessible in this experiment, which could turn out to be the most relevant.