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Experimental Report HC2504

Temperature dependence of the acoustic/optic coupling in crytalline tetrahedrites.

Proposal Summary :

Sulphur-based compounds known as tetrahedrites, of chemical formula $Cu_{12}Sb_4S_{13}$, are well known from mineralogists due to their natural occurrence. While their crystallographic and chemical compositions were studied in-depth, little was known until recently on their transport properties, which have been found to be interesting.[2,3] The TE properties were reported in the quaternary derivatives $Cu_{12-x}T_xSb_4S_{13}$ where T is a transition metal (Ni, Co, Fe, Zn or Mn),[4] where a semiconducting behaviour was found for $x = 2$, and an exceptionally low thermal conductivity at the limit of the so-called minimum thermal conductivity (0.55 $W.m^{-1}.K^{-1}$ at 300 K in *e.g.* $Cu_{12}Sb_2Te_2S_{13}$, see ***Fig. a***). Their good TE performances mainly originate from this poor ability to conduct heat. We recently investigated the PDOS spectrum of $Cu_{12}Sb_2Te_2S_{13}$ and its temperature dependence upon cooling by means of neutrons TOF on the IN6 spectrometer of ILL (***Fig. b***). These measurements revealed a very low energy (~3 meV) phonon peak (***inset Fig. a***).[5] Its energy is much lower than the one (~ 7 meV) of the rattling vibrations in clathrates supposed to be responsible for their low thermal conductivity (~1.5 W/mK@300 K). Furthermore, it strongly softens upon cooling whereas phonon modes at higher energies behave classically, *i.e.* their energy increases.

In order to determine the interaction mechanism between the acoustic and low energy optical phonons, the goal of the experiment HC2504 was to investigate the temperature dependence of the longitudinal acoustic (LA) phonons by Inelastic X ray Scattering (IXS) between 10 K and 300 K. The experiment has been done on a high-quality single-crystalline specimen, $Cu_{10.1}Zn_{1.2}Fe_{0.7}Sb_4S_{13}$,for which, a complete characterization of its physical properties has been carried out.

The experiment has been recently performed on ID28 and was successful. First, the measurement clearly revealed an-anticroosing with a very low energy (~3 meV) phonon peak, corresponding to the non-polar out-of-plane vibrations of the Cu2 atoms in the cubic crystal structure of tetrahedrites (***inset Fig. a***) the data are not yet completely analysed

Scientific background:

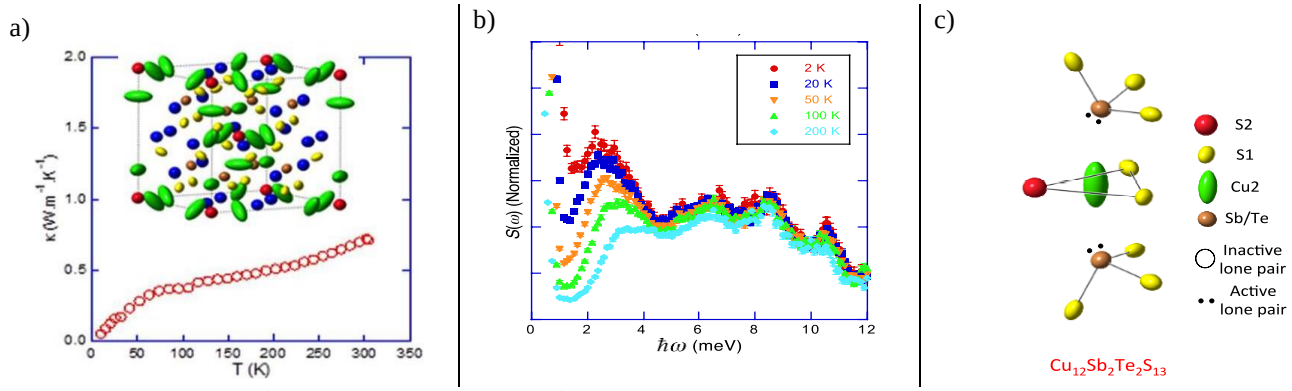

Figure 1 : a) T-dependence of the lattice thermal conductivity of $Cu_{12}Sb_2Te_2S_{13}$. Inset: perspective view of the crystal structure of $Cu_{12}Sb_2Te_2S_{13}$ (space group I-43m, a=10.35015 Å) showing the large thermal ellipsoids of the Cu2 atoms (atoms colour scheme is shown in panel c). **b)** Dynamical structure factor measured down to 2 K by neutron TOF in $Cu_{12}Sb_2Te_2S_{13}$ showing the strong anharmonicity of the low-energy mode below 4 meV. **c)** Atomic environment of the Cu2 atoms in of $Cu_{12}Sb_2Te_2S_{13}$. The $5s^2$ electron lone pairs of the Sb atoms are sketched.

Experimental data and initial findings

We first mapped at 300 K the LA phonons dispersions along the directions 100 and 110. We then focused the temperature dependence study on few q-points lying on the LA100 branch around the Bragg peak (4,0,0). We used the (12 12 12) monochromator silicon reflection and obtained a resolution of 1.4 meV. A sample with the optimal thickness of 140 micron was prepared and aligned in the scattering plane [100][011] in order to be mounted on a cold finger.

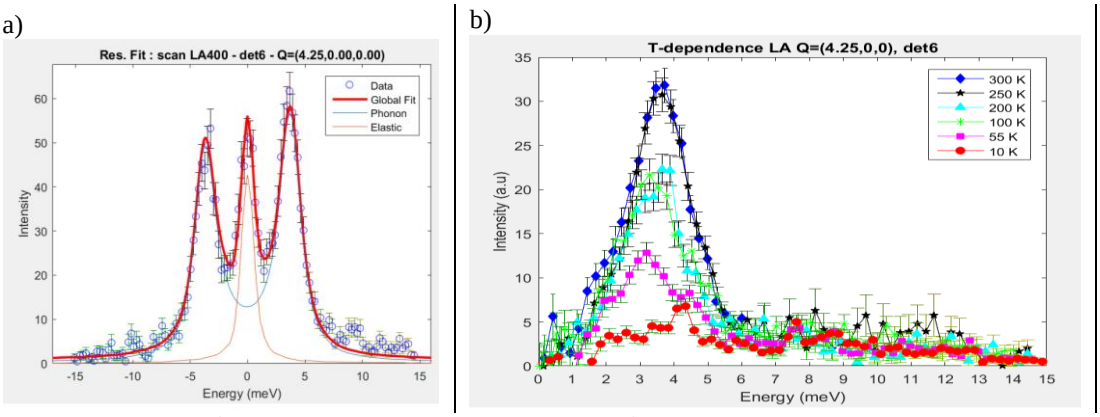

Figure 2 : a) Raw data of an IXS measurement on ID28 (exp. HC2504) of LA phonons in $Cu_{10.1}Zn_{1.2}Fe_{0.7}Sb_4S_{13}$ at 300. **b)** Temperature dependence of the low energy optical modes which was found to strongly interact with LA phonons.

In Fig 2a), we show an example of raw data measurement of a LA mode. As the experiment was performed in September, the data analysis is not yet finished and our conclusions are not definitive. However, the initial findings are:

- the IXS measurements revealed a very low energy (~4 meV) phonon peak, corresponding to the non-polar out-of-plane vibrations of the Cu2 atoms in the cubic crystal structure of tetrahedrites (***inset Fig1. a***) and the existence of a strong coupling with the longitudinal acoustic phonons. We observed an anti-crossing and a broadening of the acoustic phonons profiles when their energy approaches the energy of this optical mode
- Furthermore, the energy of the optical phonon strongly softens upon cooling whereas phonon modes at higher energies behave classically, *i.e.* their energy increases

This data will clearly help us to understand the origin of the very low thermal conductivity in crystalline tetrahedrites (0.55 $W.m^{-1}.K^{-1}$ at 300 K) at the limit of the so-called minimum thermal conductivity.

References

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