ESRF	**Experiment title:** Acoustic dynamics of a single crystal thermoelectric clathrate : Ba_8Si_{46}	**Experiment number**: HS 4653
Beamline: ID28	**Date of experiment**: from: 2012 to:	**Date of report**: 08/09/2015
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Report:

We have investigated the mechanism at the origin of the low thermal conductivity in cage based materials by mapping the phonon states in the simplest representative intermetallic clathrate, Ba_8Si_{46} (see Figure 1), using Inelastic X-ray Scattering (IXS) at beamline ID28. Phonons propagating along the main crystallographic directions were studied and the corresponding IXS cross sections were simulated by ab initio density functional theory (DFT) calculations.

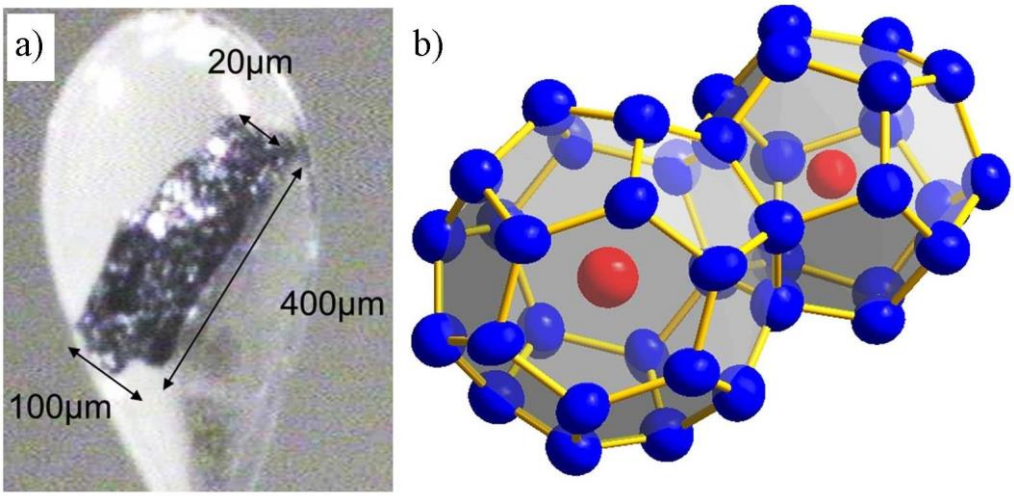

Figure 1: a) the single-crystal measured b) the cage-structure: in red the Ba atom encapsulated in the Si cages (blue)

In Figure 2, raw data of constant Q-scans, along the [100] direction, are shown together with the corresponding simulated IXS spectra, convoluted with the instrumental resolution function.

A surprisingly good agreement between the experimental and the simulated energy profi les can be observed for both the position and the energy width of the phonons.

For phonon wave vectors close to the Brillouin zone centre (q –> 0), all phonon spectra consist of a main peak at energies distinctly below the optical (op) guest excitations, which stems from the acoustic (ac) branch and follows a linear dispersion. No energy broadening was needed to fit the acoustic and optic phonon profiles. The main effect that was observed in our experimental data was an abrupt decrease of the intensities of the acoustic phonons for wave vectors higher than a critical wave vector, qc, concomitant with an increase of the intensities of the guest phonons. This was accompanied by a strong bending of the dispersion relation

of the acoustic excitations, with its slope approaching zero. qc was interpreted as the limit of the acoustic regime above which the acoustic character of the modes vanishes. The abrupt changes of the acoustic intensities were remarkably well reproduced by the ab initio simulation.

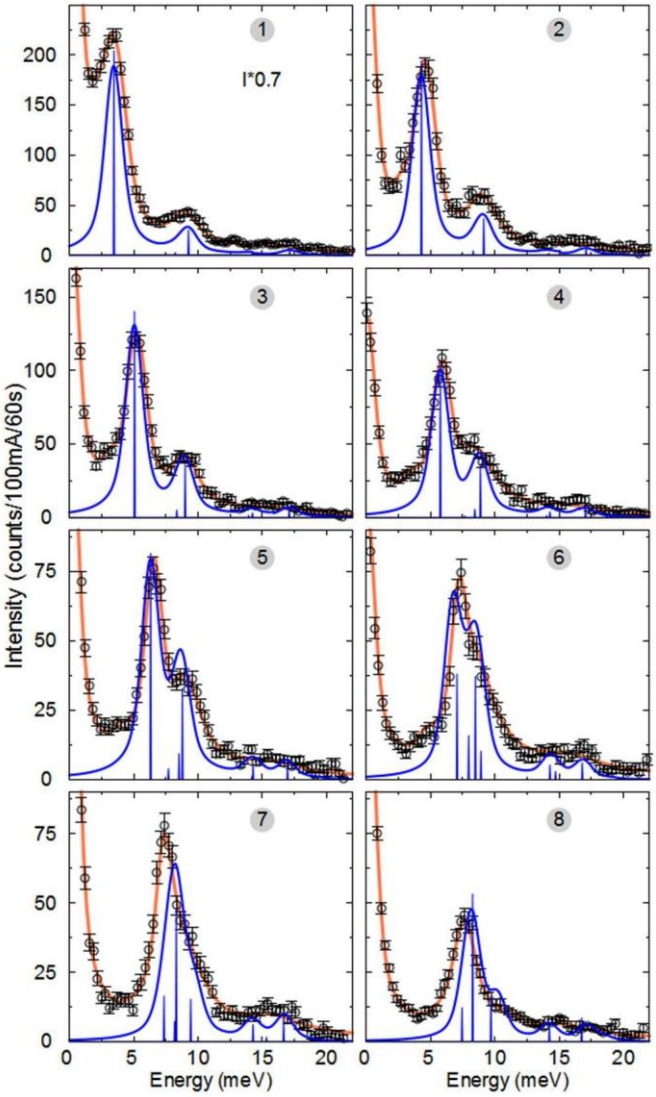

Figure 2: Example of constant Q-scans for phonons propagating along the 001 direction. Orange lines are fits of the data. Blue profiles correspond to the abinito simulated IXS spectra, convoluted with the instrumental resolution function. The blue vertical lines indicate the simulated phonon positions without the convolution.

In conclusion, the filling of the cages with guest atoms leads to the suppression of host propagative phonons, which are highly efficient at carrying heat, over a wide range of energies and wave vectors in phase space. The guest-host interaction can be understood as a purely harmonic process, i.e. it is not dominated by phonon-phonon scattering. The acoustic phonons preserve a very long lifetime and their propagative nature, until a critical wave vector is reached: at this point the character of the acoustic phonons changes, resulting in modes with an increasing contribution of the guest atoms. A careful theoretical analysis provides evidence that the guest modes are not propagative. These modes release their energy locally in an isotropic manner, leading to a change from a propagative to a diffusive energy transport mechanism, which may, in turn, be responsible for the low lattice thermal conductivity.

S. Pailhès, H. Euchner, V.M. Giordano, R. Debord, A. Assy, S. Gomès, A. Bosak, D. Machon, S. Paschen, M. de Boissieu, Phys.Rev. Lett. ***113****, 025506 (2014).- ESRF Highlight*