	Experiment title: Influence of vacancies on phonon modes in the thermoelectric clathrate BaCuGeGa	**Experiment number**: HC-3112
Beamline: ID28	**Date of experiment**: from: 26/05/17 to: 02/05/17	**Date of report**: 26/02/18
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Report:

The low thermal conductivity of type I clathrates is generally attributed to their cage-like crystal structure, with weakly bound guest atoms rattling in oversized host cages. The micorscopic mechanisms at play remain however still unknown.

Most puzzling is the weak temperature dependence of the thermal conductivity in many clathrates, which lack the typical 1/T behaviour, in some cases displaying a plateau like in glasses. We have recently succeeded to synthesize a series of high quality single crystals with varying vacancy content in the system $Ba_8Cu_{4.8}Ge_{41.2-(x+y)}\square_y Ga_x$ and have shown that the phononic properties (lattice thermal conductivity, phonon contribution to specific heat) are dramatically influenced by this variation. Specifically, a crystal-like to glass-like behaviour crossover takes place in the thermal conductivity as the vacancy content increases. This experiment was meant to pin down the microscopic mechanism underlying this effect, answering the question whether acoustic phonon branches are modified by this structural change or it is a mere scattering rate effect. The experiment, where we measured longitudinal phonon modes, was to complete measurements performed by inelastic neutron scattering, focusing on the transverse modes.

a. $Ba_8Cu_{4.8}Ge_{38.8}\square_{1.2}$ **b.** $Ba_8Cu_{4.8}Ge_{38.8}\square_{0.2}Ga$

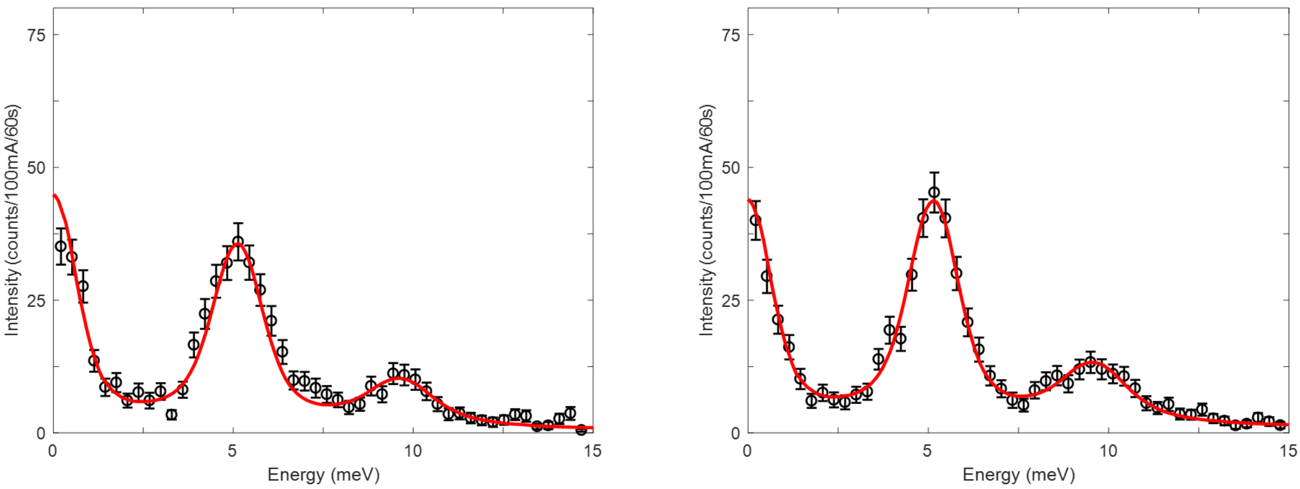

Fig. 1. Examples of Energy Scans. *Fig. 1a and Fig. 1b depict energy scans for the $Ba_8Cu_{4.8}Ge_{38.8}\square_{1.2}$ and $Ba_8Cu_{4.8}Ge_{38.8}\square_{0.2}Ga$ samples, respectively. Black, empty circles mark the data points, and the red line is a fit of the data points as damped harmonic oscillators, which are then convoluted with the instrumental resolution. Vertical error bars are statistical errors.*

Two Germanium-based, Type-I clathrate samples, synthesized by our group, were chosen for their large variation in vacancy count: $Ba_8Cu_{4.8}Ge_{38.8}\square_{0.2}Ga$ and $Ba_8Cu_{4.8}Ge_{38.8}\square_{1.2}$ and their longitudinal acoustic modes measured at room temperature. Samples were aligned into the [1 0 0] [0 1 1] scattering planeand data collection focused around the (6,0,0) Bragg peak. The 12 12 12 reflection of the Si monochromator was used for getting a resolution of 1.35 meV. For each sample, Analyzer 6 was brought directly into the scattering plane, and the spectrometer was moved to 10 different positions in order to map the respective phonon dispersions in reciprocal space. **Fig. 1** provides an example of an energy scan for each of the two samples. This particular energy scan was taken at $\vec{Q} = (6.35,0,0)$, near the Bragg peak $\vec{Q}_B = (6,0,0)$, with a phonon wave-vector $\vec{q} = (0.35,0,0)$.

Fig 2 summarizes the results of this experiment. The acoustic phonon branch disperses from zero to 6 meV for each sample, where the end of the first Brillouin zone is marked by the dotted line at 0.29 Å^{-1}. An optical branch centered at 10 meV is also visible. There are two main conclusions that our team can draw from this graph:

1) as observed in other experiments on clathrates, **the acoustic phonon mode is being filtered, or cut off, by the low-lying optical modes.**

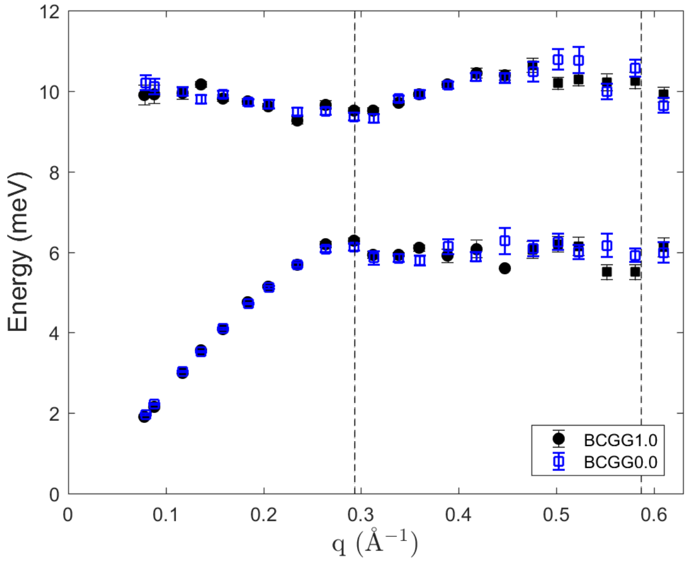

Fig. 2. Experimental Phonon Dispersions. *The measurements shown include data collection from the (6,0,0) Bragg peak to the (7,0,0) Bragg peak. The $Ba_8Cu_{4.8}Ge_{38.8}\square_{0.2}Ga$ sample has been labelled as BCGG1.0 and with filled black circles, and the $Ba_8Cu_{4.8}Ge_{38.8}\square_{1.2}$ sample as BCGG0.0 with open blue squares.*

2) The samples appear to have the same acoustic and optical phonon dispersions. This suggests that the change in lattice thermal conductivity due to vacancy variation is not due to a change in the sound velocity, but could be due to a phonon lifetime reduction, which still remains beyond our experimental resolution.

Inelastic neutron experiments gave the same results on the transverse modes.

It is however important to remind that the main difference in the thermal conductivity between these two samples arises at low temperature, below ~50K.Therefore, low temperature measurements should be performed, as different scattering mechanisms could be active at low temperature in the two samples, and the vibrational dynamics could thus turn out to be different. Specifically, recent theoretical calculations suggest a key role of the low-lying optic mode, whose temperature dependence could determine the one of the thermal conductivity. The suppression of the Umklapp peak could be related to a softening of the optic mode at low temperature. A following of the optic modes position with temperature with high resolution, better than 1 meV, would provide more insight as to the possible microscopic mechanisms responsible for this change in lattice thermal conductivity.