Experimental report

05/09/2019

Proposal: **7-01-494** **Council:** 10/2018

Title: The role of the quartic anharmonicterm in the thermal conductivity of complex crystals

Research area: Physics

This proposal is a new proposal

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Samples: $Ba_{7.81}Ge_{40.67}Au_{5.33}$

Instrument	Requested days	Allocated days	From	To
IN12	7	4	15/07/2019	19/07/2019

Abstract:

Low thermal conductivities (~ 1-2 W m-1 K-1) are observed in structurally complex crystals with a large number of atoms in the unit cell (more than 50 atoms), such as guest-host structures (clathrates and skutterudites), where however the measurement of phonon lifetimes remains beyond the standard resolution limit. Moreover, in some of them the typical Umklapp peak in the K(T) dependence (1/T) is smoothed out and replaced by a weakly temperature dependent glass-like 'plateau', whose origin in crystals is intensively debated. Recently, theoreticians have proposed that the strong quartic anharmonicity within perturbation theory, to the first order, of rattling guest atoms causes an anomalous hardening of the vibrational frequencies of low-lying optical modes with temperature, resulting in an improved agreement with experimental results, including the deviation of phonon lifetimes and thermal conductivity from the expected 1/T dependence. We propose here to track the low-lying optical modes energies as a function of temperature on the clathrate $Ba_{7.81}Ge_{40.67}Au_{5.33}$ to validate this theoretical finding. This proposal is part of the PhD thesis work of S. Turner.

Quantifying the Hardening/Softening with Temperature of Low-lying Optical Branches in a Type-I Clathrate

As stated in the original proposal, the goal of this experiment was to determine the temperature and energy dependence of the low-lying optical branches found in the Type-I clathrate $Ba_{7.81}Ge_{40.67}Au_{5.33}$. This branch has a specific behavior since its energy increases with increasing temperature, whereas optical branches in this system are expected to decrease in energy with increasing temperature. This hardening/softening difference between the lowest-lying optical branch and the next-lowest optical branches was the reason for selecting a high-resolution cold triple-axis instrument like IN12. Determining the energy of the lowest branch with temperature is important since this branch acts as a low-pass filter on the acoustic branch, not allowing the mode to continue after intersecting it. Quantifying how this branch moves with temperature plays a part in understanding the overall lattice thermal conductivity of the system. (See proposal for further background information.)

The experimental setup on IN12 included a cryofurnace, Be filter, velocity selector, and a k_F of 1.55 Å^{-1}. Four temperatures were measured: 200, 300, 400, and 500 K. The single crystal sample $Ba_{7.81}Ge_{40.67}Au_{5.33}$ was aligned on the [001][110] scattering plane. Each temperature was measured for approximately 14 hours in order to have proper statistics. (The last ~10 points of each scan had to be done without the optimization of the velocity selector, and therefore the counting time started to increase quickly.) The rest of the experiment time was used for alignments, temperature changes, and choosing the q that we would use at the beginning of the experiment. The raw data is shown in **Fig. 1.**

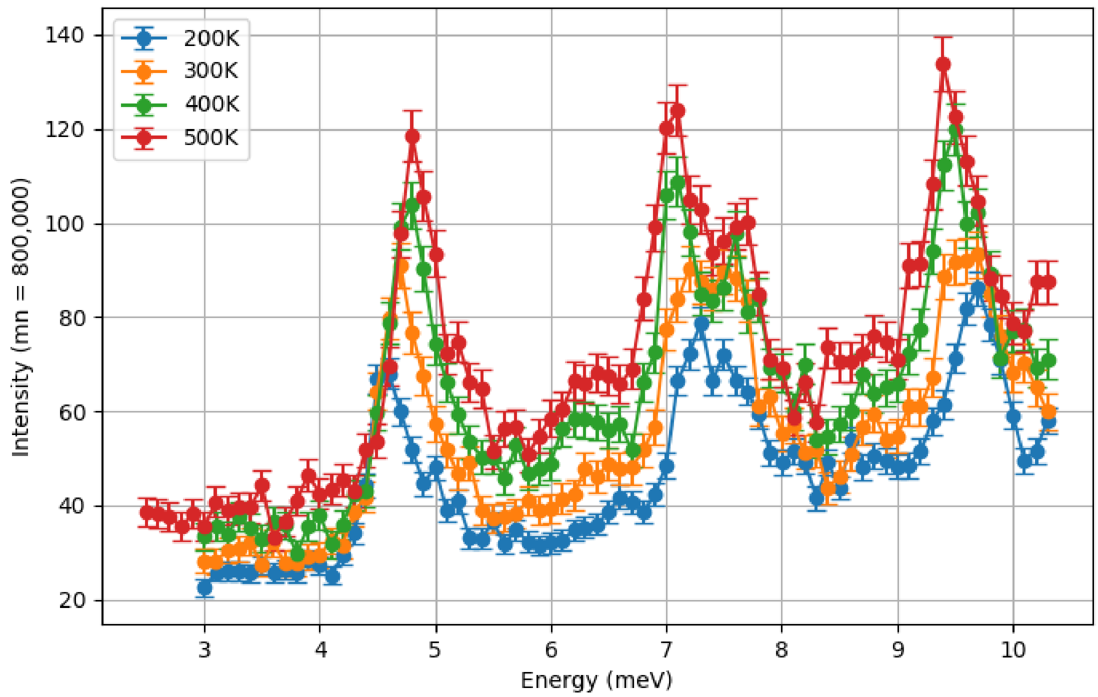

Figure 1: Temperature dependence of low-lying optical branches taken at (1 1 3) in reciprocal space in the scattering plane [001][110] of the single crystal Type-I clathrate $Ba_{7.81}Ge_{40.67}Au_{5.33}$.

As expected, the lowest branch at 4.9 meV shifts higher in energy with temperature while the next two branches shift down in energy with temperature. Further analysis will have to be done in order to understand why the second branch appears to split into two modes at higher temperature. This is most likely due to the fact that optical phonon branches are each a series of modes, and therefore it is possible that not all modes in a given branch have the same temperature dependence.

The scans in **Fig. 1** were fit assuming each peak was Gaussian in nature as a first approximation. Preliminary analyses of this experiment show that the branch at 4.9 meV has a completely linear temperature dependence, as seen in **Fig. 2.** This will allow us to predict the energy of the mode at temperatures that we did not have time to measure.

This experiment helped bring us one step closer to drawing overall conclusions about the lattice thermal conductivity of complex crystalline systems such as clathrates.

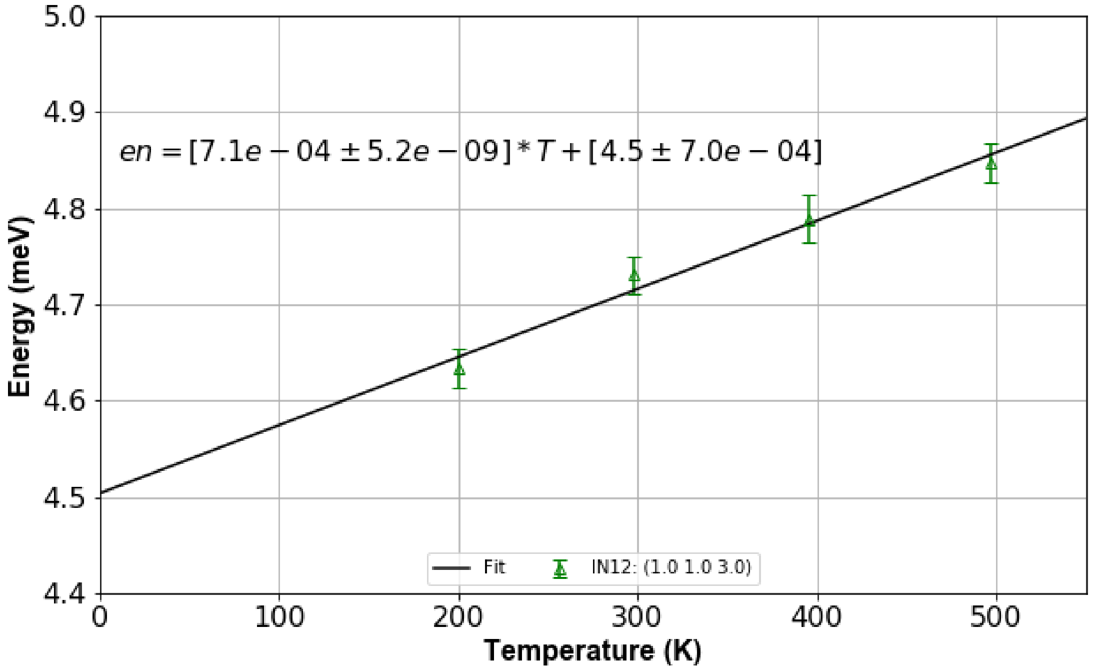

Figure 2: Plot depicting the change in energy of the lowest branch at 4.9 meV with increasing temperature. Fits of **Fig. 1** scans were done assuming Gaussian fits.