Experimental report

15/02/2023

Proposal: **7-01-547** **Council:** 10/2020

Title: Skrutinizing the phonon Kondo effect in thermoelectrc clathrates

Research area: Physics

This proposal is a new proposal

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Samples: Ba8Cu4.8Ge40.2Ga

Instrument	Requested days	Allocated days	From	To
IN3	1	1	07/07/2021	08/07/2021
IN8	5	5	07/07/2021	14/07/2021
ORIENTEXPRESS	1	2	22/02/2021 17/06/2021	23/02/2021 18/06/2021

Abstract:

Intermetallic clathrates are of great interest, not only for their potential as thermoelectric materials but also for fundamental interest in their unusual lattice dynamics. It is now well documented that these materials exhibit energetically low-lying optical phonon so-called Einstein corresponding to the rattling motion of the guest atoms in the structural cages. However, how these interact with the heat-transporting acoustic modes to produce ultralow lattice thermal conductivities is an open question. Recently, a phonon-Kondo effect was proposed to explain striking deviations between lattice dynamics predictions and experimental observations for various thermal transport and thermodynamic quantities. The proposed experiment sets out to scrutinize this model. We will study the temperature dependence of the low-energy phonon dispersion in the vicinity of the optic-acoustic mode interaction ("anticrossing") on the type-I clathrate Ba8Cu4.8Ge40.2Ga, a particularly well pre-characterized compound available as large single crystal. We expect a characteristic disentanglement of the two modes above the phonon Kondo temperature.

Introduction

The Kondo effect between a local magnetic moment and conduction electron is a well-known phenomenon. Much less appreciated is that the Kondo effect more generally describes non-commutative scattering of an extended wave from a localized entity with internal degree of freedom, and its occurrence in an all phononic context was proposed only very recently [1]. Energetically low-lying optical phonon modes, also known as Einstein modes, describe the rattling motion of the guest atoms in the structural cages [2, 3, 4]. They are associated with the localized entity (“the spin”). The acoustic phonon modes of the clathrate framework represent the extended wave (“conduction electrons”). Striking deviations between thermal transport experimental data and state-of-the-art ab initio lattice dynamics calculations support this model and call for further investigations on a microscopic level [1]. In addition, the inverse difference of calculated and experimental phonon thermal conductivities of the clathrate $Ba_8Ga_{16}Ge_{30}$ demonstrates a ln T temperature dependence, which is a hall-mark of incoherent Kondo scattering in the spin Kondo effect above T_K (Fig. 1a). A recent inelastic neutron scattering investigation of the type-I clathrate $Ba_{7.81}Ge_{40.67}Au_{5.33}$ revealed a distinct change of the transverse acoustic phonons profile when cooling from 300 to 10 K [4]. This difference vanishes at small q and it is anticipated to be larger at larger q where the Einstein and acoustic modes interact more strongly.

Experimental configuration

For the experiment we have selected the type-I clathrate $Ba_8Cu_{4.8}Ge_{40.2}Ga$ since its thermodynamic and thermal transport properties are well characterized [1]. Measurements were performed on a single crystal with mass of ~ 2 g, grown by the floating zone technique in a 4-mirror furnace [5]. The sample was mounted in an orange cryostat along its crystallographic (100) axis with the aim of studying the interaction between the transverse acoustic phonons and the lowest-energy Einstein modes as a function of temperature between 15 and 300 K.

Summary and outlook

We started the measurement sequence by checking the Bragg’s scattering intensities at different q vectors to choose the most intensive one. In addition, it was of paramount importance to verify the sample mosaicity (~ 0.5°) and the absence of twin reflections, since structural defects would have been a dramatic hindrance. Another key aspect was to define the needed ratio between inelastic intensities and energy resolution, therefore we tested different experimental set-ups (without collimator, 30- and 40-minutes collimator).

Firstly, we mapped the longitudinal and transverse phonon dispersions starting at q = (6, 0, 0) at 50 and 200 K (Fig. 1b), to identify the “anti-crossing” wave-vector. To optimize the counting time, it was necessary to define the Bose-Einstein factor beforehand at the energy range of interest, due to the low-temperature intensity loss. Here we see that q = (6, -0.48, -0.48) corresponds to the wave-vector where the modes’ hybridization is strongest (Fig. 1c), and the transverse acoustic phonon dispersion becomes flat at close to the Brillouin zone boundary. This effect has not been observed in the longitudinal dispersion both in our current experiment and in previous measurements on this sample by means of inelastic x-ray scattering.

Furthermore, to fully access the mode disentanglement we studied the temperature dependence of three selected wave-vectors (6, -0.45, 0.45), (6, -0.48, -0.48) and (6, -0.51, -0.51) above and below T_K, demonstrating a logarithmic relation of the phonon's energy shift above 50 K, consistent with the proposed model of phonon Kondo scattering (Fig. 1d). The newly found results are in good agreement with the measured phonon thermal conductivity of the type-I BGG clathrate [1].

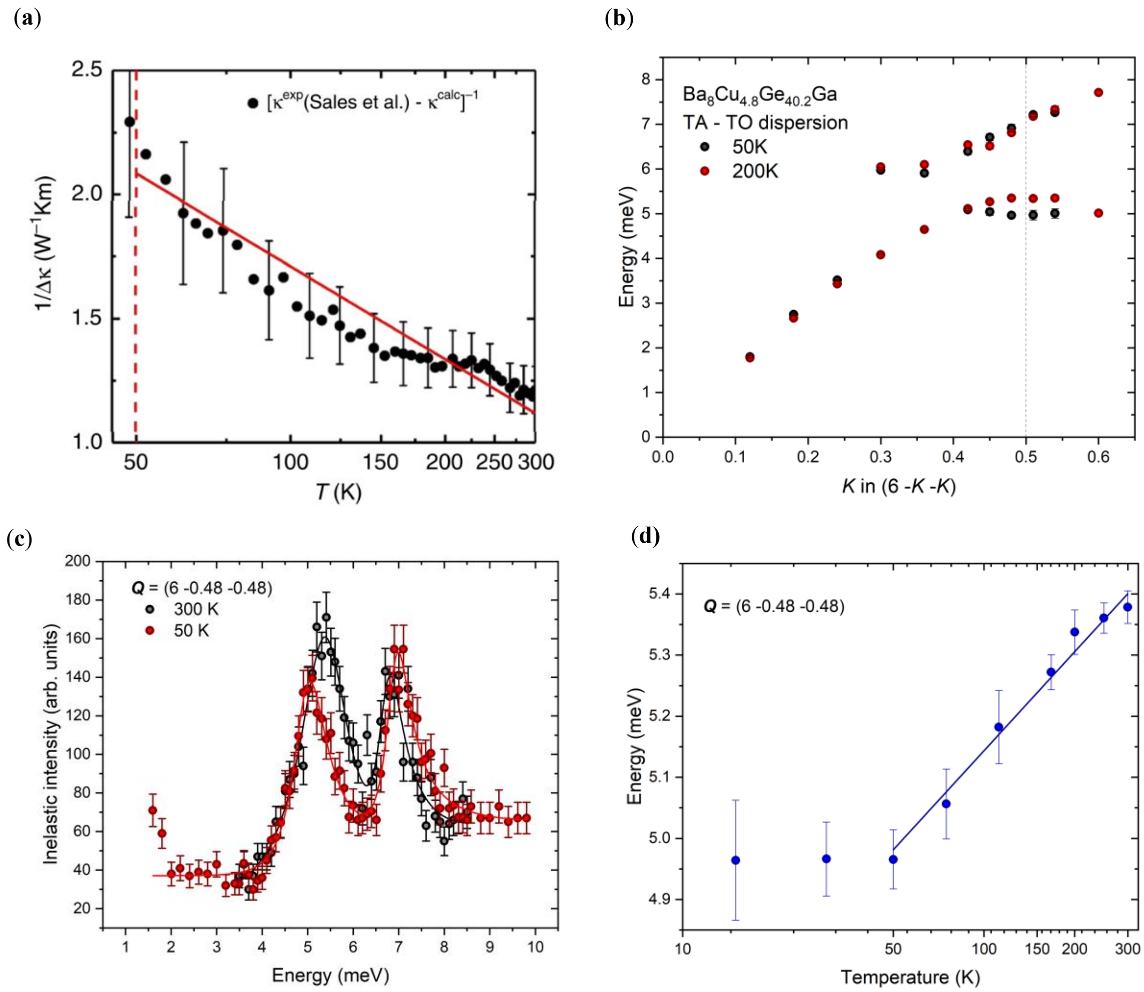

Fig. 1: (**a**) Inverse difference of calculated and experimental phonon thermal conductivities of $Ba_8Ga_{16}Ge_{30}$ above the Kondo temperature (dashed vertical line). (**b**) The transverse phonon dispersion of $Ba_8Cu_{4.8}Ge_{40.2}Ga$ measured at 50 and 200 K. (**c**) Energy scan of the inelastic neutron intensities at the anti-crossing wave-vector measured at 50 and 200 K. (**d**) The logarithmic dependence of the fitted peak position as a function of temperature above 50 K.

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