Experimental report

14/02/2020

Proposal: **CRG-2610** **Council:** 4/2019

Title: Dispersion relation and phonon lifetime of the Rb2ZnCl4 incommensurately modulated phase (970)

Research area:

This proposal is a new proposal

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Samples: Rb2ZnCl4

Instrument	Requested days	Allocated days	From	To
IN6-SHARP	3	3	02/07/2019	05/07/2019

Abstract:

CRG-2610 Dynamical properties of the Rb_2ZnCl_4 incommensurately modulated phase

Background and context

Aperiodic crystals are materials that possess long-range order but lack lattice periodicity. They comprise incommensurately modulated structures, incommensurate composite crystals and quasicrystals [1]. The aperiodic long-range order leads to new excitations named phasons. In the longwavelength limit they are predicted to be diffusive excitations. Phason modes have been measured and evidenced only in very few systems [1], and we propose to measure them in the well-characterized Rb2ZnCl4 incommensurately modulated phase.

Rb2ZnCl4 belongs to the family of the A_2BX_4 ferroelectric materials [2]. This system is particularly interesting since the incommensurate phase exists between 303 and 196 K, and goes from a harmonic modulation close to 303 K to a strongly anharmonic modulation just above the lock-in transition at 196 K [3] [4], where the structure becomes a 3-fold superstructure of lower symmetry [5] [6] [7]. This system gives us the opportunity to investigate the effect of anharmonicity in an incommensurately modulated phase.

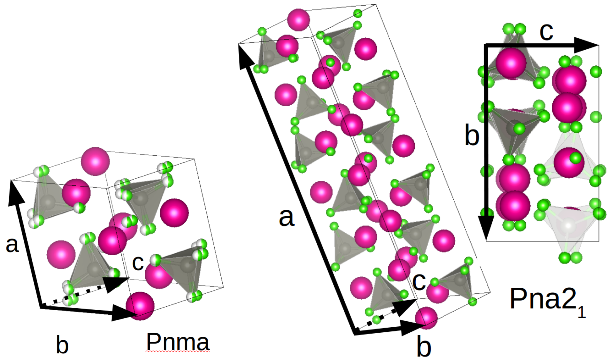

FIGURE 1 – Rb_2ZnCl_4 primitive cell in high temperature commensurate phase (left) and in lock-in phase (right).

Phase IV	Phase III (lock-in)	Phase II (incommensurate phase)	Phase I
75K	T_C=196K	T_i=303K	

TABLE 1 – Rb_2ZnCl_4 phases.

Experiment

Rb_2ZnCl_4 dynamics have been investigated with inelastic neutron scattering. Measurements were performed on the IN6-SHARP time of flight spectrometer at the ILL, using a powder sample wrapped in an aluminium foil, and inserted in a cylindrical aluminium can. We used a neutron incident wavelength of 5.1Å, at 315, 295, 264, 235, 200 and 180K. Complementary measurements were made for 4.1Å at 295K and 200K, with the sample and with the empty can.
In our convention, the lattice parameters are : a=9,233Å, b=7,278Å and c=12,736Å at 300K.
Data were processed using Mantid [8].

Results

We have followed the phase transition looking at Bragg peaks position and their intensity distribution. A clear signal was visible on the $(131\bar{1})$ satellite, allowing to locate the phase transition temperature in agreement with literature and specific heat measurements (tab. 1). For comparison with the theory, a calculation of the expected powder diagram in the two commensurate phases has been performed on VESTA [9] using [10] data. The sample exhibits a texture so that the relative intensities of Bragg peaks differ from the theoretical calculation. According to the measured evolution of the amplitude of the $(131\bar{1})$ satellite, the two phase transitions where found around the expected temperatures. The generalised vibrational density of state was extracted from data with Mantid, taking into account the Bose-Einstein correction. It exhibits a large gap in energy between 20 and 33 meV (fig.2). The experimental results have been compared to DFT calculation [11] (ref. mp-608314 in Material Project) using the high T model and 0K calculation, and the phonopy package [12] and found to be in good

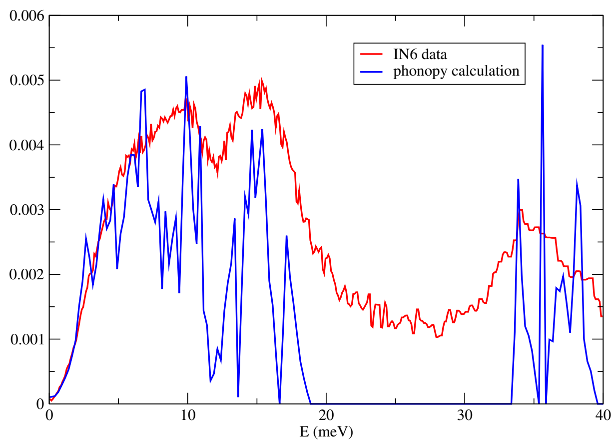

FIGURE 2 – Measured and calculated density of state as a function of energy at 317K

agreement with experiment as illustrated in fig. 2. It also appears that an excess of modes was present at 199K around 1meV, just above the lock-in transition, and disappeared at 180K.

We also studied the quasielastic signal, in a first step integrating the measured signal over all Q positions. Results for four temperatures are compared in fig. 3. A clear quasi-elastic signal is observed at high T, both in the phases I and II. This signal has disappeared at low T. We suggest that this quasi-elastic signal signal is related to the $ZnCl_4$ tetrahedrons re-orientations between the two positions available in the phase I, as pictured on figure 1. Further analysis as a function of Q are underway to confirm this hypothesis.

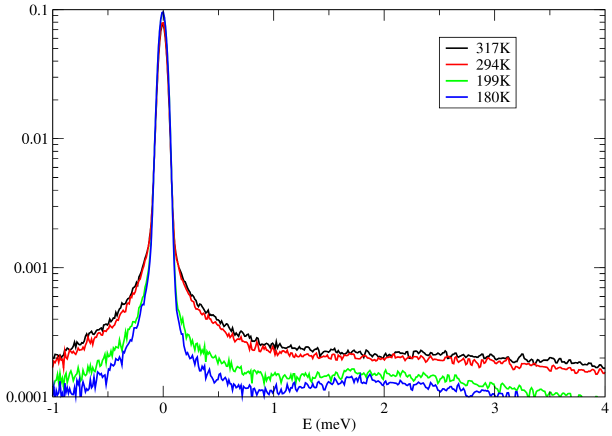

FIGURE 3 – Measured energy transfer around the two phase transitions for 5.1Å neutrons

We have also observed the apearence of an excess of modes around 2meV near T_C temperature. This might be the signature of a low energy phonon mode discovered in the similar compound Rb_2ZnBr_4 [13] and called amplitude mode. Further analysis will be conducted in order to determine the Q-space location of this mode and determine its nature.

Références

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