Dynamical properties of the incommensurately modulated Rb_2ZnCl_4 phase

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Aperiodic crystals are long-range ordered crystals that lack periodicity. A good description of these materials is provided by the superspace approach [1, 2]. Although their structure is in general well described, the atomic realisations and properties of their dynamics are more debated. Phason modes that should arise from the new degrees of freedom due to the aperiodic order have been experimentally observed in very few incommensurately modulated phase and quasicrystals [1, 3]. Also, low thermal conductivity in those systems asks for an investigation of their dynamics.

The Rb_2ZnCl_4 phase displays several transitions [4]. Above T_i = 303 K the high temperature phase is described as a crystal structure where the orientations of $ZnCl_4$ tetrahedrons are randomly oriented with a space group *Pmcn* and lattice parameters a =7.3 Å, b = 12.7 Å and c = 9.2Å. From T_i = 303 K, down to TC = 195 K, the orientation of the $ZnCl_4$ tetrahedrons gets incommensurately modulated along the c* axis with an increasing anharmonicity [5, 6]. Below TC, the modulation gets locked-in with a 1/3 ratio of the periodicities, the c cell parameter is then tripled. As theory predicts a different behaviour of phasons depending on the harmonicity regime. This material fits well as a probe of the incommensurate phases' dynamics. We probed the dynamical properties of this material through inelastic neutron scattering with the IN6-SHARP, IN5, IN12, IN22 and THALES instruments of the ILL, and with the 1T spectrometer of the LLB. In order to cover the whole incommensurate phase and go beyond the commensurate and the lock-in phase transitions, working temperatures ranged from 350K to 140K.

We have measured and compared the temperature dependence of transverse acoustic phonons around a few main Bragg reflections as well as some of the satellite reflections that sign the incommensurability. In the lock-in phase, to the tripling of the cell is manifested by superstructure reflections. At 140 K, all the measured acoustic phonons have consistent integrated intensities whether they are associated to superstructure or substructure reflections. Although they all presented a similar sound velocity around 9 meV.A, the superstructure phonons were found to widen faster. As temperature increases, the relative integrated intensity of superstructure related acoustic phonons decreases. At the same time, a large quasi-elastic signal localised around the superstructure reflections appears and increases in intensity with temperature, evidencing a relaxation process we relate to local reorientation of $ZnCl_4$ tetrahedrons. During the phase transition at TC, the superstructure reflections are splitted along the c* axis into satellite reflections and we observe a jump in intensity of the localised quasi-elastic signal. This signal continues to grow with increasing temperatures in the incommensurate phase while the relative intensity of the acoustic phonon associated to satellite reflections continues to decrease. Above T_i, the satellites reflections disappear into large diffuse elastic spots. At 350 K the localised quasi-elastic signal dominates, but despite the absence of a reflection defining the centre of a Brillouin zone, a weak and large mode is found to disperse as an acoustic-like phonon around these diffuse elastic spots, indicating weak long range correlated modes are remaining despite the prevailing disorder in the $ZnCl_4$ tetrahedrons orientations.

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Keywords: aperiodic crystals; incommensurate modulation; lattice dynamics; phason mode; inelastic neutron scattering

The project is funded by the Agence Nationale de la Recherche (ANR, French Research Agency).