Experimental report

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Proposal: 7-02-152 **Council:** 4/2014

Title: Phonon dispersions related to the incommensurability near the structural instabilities in the intercalation compound alkane-urea

Research area: Materials

This proposal is a new proposal

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Samples: Deuterated Alkane-urea C19D40-CO(ND2)2

Instrument	Requested days	Allocated days	From	To
IN5	7	7	01/12/2014	08/12/2014

Abstract:

In this proposal we aim at mapping the excitations of the prototype incommensurate uniaxial intercalation compound c19D40-urea in order, on the one hand, to measure the dynamics related to the incommensurability along the incommensurate axis and, on the other hand, the dynamics related to the structural phase transition.
At the same time, a complete mapping of the excitations will allow to observe for the first time the excitations specific of the incommensurability and to understand the role of the phonons modes responsibles of the ferroelastic transition in this material in the plane perpendicular to the incommensurability axis. A complete mapping of the reciprocal space in this system appears to be a way of assigning unambiguously the dynamical features of different origin (host and/or guest) and to estimate the coupling between them. Measurements will be made on an available large single crystal.

Phonon dispersions related to the incommensurability near the structural instabilities in the intercalation compound alkane-urea

The aim of this proposal was at at mapping the excitations of the (fully deuterated) incommensurate uniaxial intercalation compound alkane-urea ($C_{19}D_{40}$ - $CO(CD)_2$) in order, on the one hand, to measure the dynamics related to the incommensurability along the incommensurate axis and, on the other hand, the dynamics related to the host structural hexagonal to orthorombic structural phase transition.

1 Introduction

Alkane-urea lattice is made of a host urea honneycomb-like channeled frame filled by the guest alkane chains. The hexagonal structure exists only in the "symbiotic" clathrate compound, pure urea having a tetragonal structure. The hexagonal channels can host linear alkanes of various lengths, whose lengths have no reason to match the urea lattice periodicity. From the non-rational ratio of the host and guest periodicities results an incommensurate intermodulation of the two sublattices with, in particular, apparition of extra Bragg reflections which can only be indexed in a four-dimensional superspace symmetry group $P6_122(00\gamma)$. A remarkable property results in the dynamics from the infinitely degenerated ground state of the incommensurate structure: a free slidding of one sublattice with respect to the other without restoring force.

In the plane perpendicular to the incommensurate direction, the host structure is also affected by the guest molecules. While lowering the temperature, the urea tends to minimizes its energy by distording to an orthorombic structure leading to a ferroelastic transition around 150 K in the nonadecane case of this study. Despite the transition is rather abrupt and even close to a 1^{st} order transition, the dynamics is expected to be affected through a softening of the corresponding host lattice acoustic transverse modes.

2 Experimental

A $\sim$ 20mm long 2.5 mm diameter single crystal with a mass around 200 mg mouted in the $[hh0] - [00\ell]$ plane has been use in this study, A mapping of the excitations have been made at three temperatures, one far from the ferroelastic transition (200 K) and two close to the transition (155 and 150 K), the exact transition temperature being difficult to extimate in a standard cryostat.
A rotation of the crystal around the $[\overline{h}h0]$ axes over a range of 200 degrees in order to map the hexagonal plane and the incommensurate axis has been performed at each temperature. A wavelength of 3 Å was chosen in order to reach at least the first host Bragg spot on the $c*$ axis which is rather far because of the extinction rule along this axis ($\ell = 6n$) for the crystal hexagonal space group.

3 Results

Elastic scattering (Figure 1) along the (11ℓ) can be indexed within the subspaces of the host or guest lattices (either $\ell \neq 0$,$m = 0$ or $\ell = 0$,$m \neq 0$ in the $(hklm)$ notation) but no

mixed ($\ell \neq 0$, $m \neq 0$) satellites.

Figure 3 shows the pretransitional diffuse scattering *vs.* temperature in a cut in the $[hh0] - [\bar{h}h0]$ crossing the urea Bragg positions. Surstructures appears from the diffuse scattering on the line joining the urea Bragg spots. A cut along the $[hh0] - [\bar{h}h0]$ lines (Fig. 4) confirms that at 155 K the compound is still in the high temperature phase since the correlations of the peaks at 3/2 are not yet diverging.

The inelastic scattering shows, however, no clear evidence of any pre-transitional effect due to the ferroelestic transition unless very weak intensities that seems not to change with the temperature (Fig. 2).

The intense and broad scattering slightly above the $(\frac{3}{2}\frac{3}{2}4)$ position of the host lattice is due to the fast relaxation of the CH_2 subunits of the alkane guest molecules, The weak intensity visible close to $\ell = 1$ or 3 is expected to be related to the ferroelstic transition.
However, no softening of this non-acoustic phonon branch can be detected before the transtion ($T_c \simeq 150$ K).

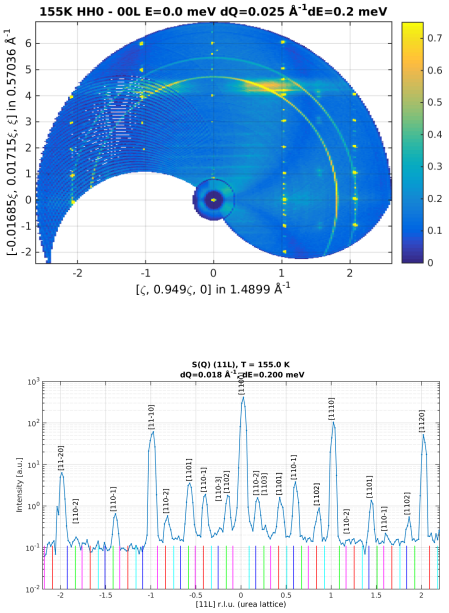

Figure 1: Elastic scattering at 155 K.*(top)* Map in the $[hh0] - [00\ell]$ plane. *(bottom)* Cut along the (11ℓ) direction (intensity in log scale).

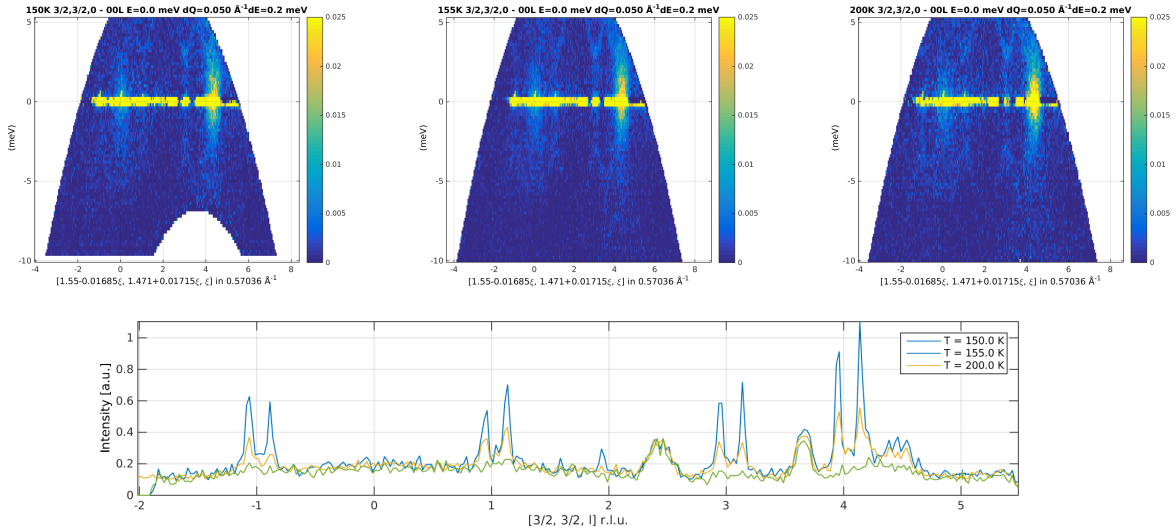

Figure 2: *(top)* Inelastic scattering along the $(\frac{3}{2}\frac{3}{2}\ell)$ line at 150, 155 and 200 K. Pretransitional inelastic scattering appears at $\ell = 1$ and 3.*(Bottom)* Elastic scattering along the same line with temperature.

Along the same line in the reciprocal space the elastic intensity change substantially with the temperature as shown on Fig. 2*(bottom)* indicating a structural change in the lattice. Despite a clear evidence that the chosen temperatures were adequate, it was thus not possible to observe any inelastic scattering that could be related to the transition.

Along the particular axis related to the incommensurability $[00\ell]$ no inelastic scattering is visible in the spectra up to $\sim \ell = 7$n and energies up to 5 meV at least. This might come from symmetry reasons, which appears natural for the host substructure but not for the whole crystal, or because of too weak intensties to be observable with the time-of-flight technique. At this stage there is no clear explanation, the analysis of the data are still ongoing.

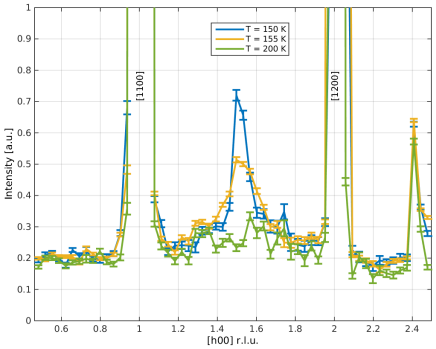

Figure 4: Elastic scattering along the (1,10,0)-(1±200) urea Bragg position.

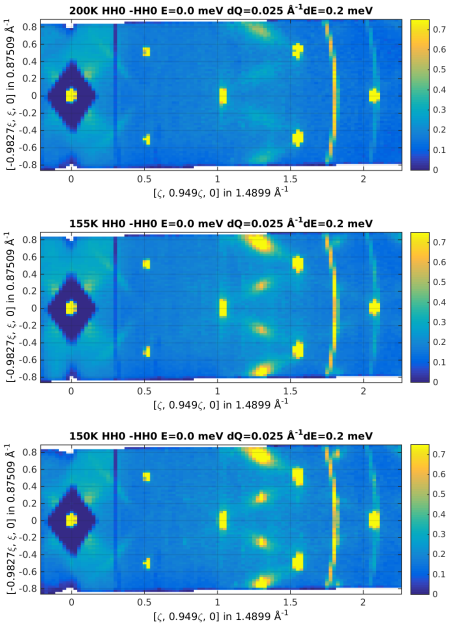

Figure 3: Pretransitional elastic scattering above, close to and at the transition temperature. In particular the surstructures appearing from the diffuse scattering on the lines joining the (1100) to the (1±200) Bragg spots.