Experimental Report

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Proposal: **7-02-143** **Council:** 10/2012

Title: Critical pretransitional dynamics within crystallographic superspaces

This proposal is a new proposal

Researh Area: Physics

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Samples: C19D40/CO(ND2)2

Instrument	Req. Days	All. Days	From	To
D10	10	10	04/03/2013	14/03/2013

Abstract:

The goal of this proposal is to study the critical dynamics around a phase transition involving high dimensional spaces in an aperiodic material. Recently, we reported a quite original phase transition in the composite crystal, n-nonadecane/urea, revealing an incresase of the dimension of the crystallographic superspace at Tc1=149K, from 4 (phase I : hexagonal superspace group P6122(00gamma)) to 5 (phase II: orthorhombic superspace group C2221(00gamma) (10delta)). Afterwards, a very high resolution study of the static aspect of the critical phenomena revealed quite anomalous long correlation lengths along the incommensurate direction. This could be tentitatively interpreted in terms of a soft phason at a critical wave vector qs characterized by five independent vectors. Only inelastic measurements can prove this assessment and only a coupled four circles, triple axis spectrometer permits this study at such a complex qs location.

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Critical pretransitional dynamics within crystallographic Superspaces

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The proposal concerned the study of the critical pretransitional phenomena within crystallographic superspace considering incommensurate composites structures made of two interpenetrating and mutually incommensurate periodicities in at least one direction. Here we consider n-nonadecane/urea, where the n-alkanes are imbedded in parallel channel of the host urea sublattice. Very recently, we have shown that it presents a phase transition going from four (Phase I hexagonal group $P6_122(00\gamma)$) to five (Phase II: orthorhombic space group $C222_1(00\gamma)(10\delta)$) dimension [1,2]. Five indices $(h\ k\ l\ m\ n)_o$ defined in the orthorhombic basis are thus associated with each Bragg peak at positions $\mathbf{Q}_{hklmn} = h\,\mathbf{a}_o^* + k\,\mathbf{b}_o^* + l\,\mathbf{c}_h^* + m\,\mathbf{c}_g^* + n\delta\mathbf{c}_{h^*}$. The critical wavevector associated with the order parameter is found at (0 1 0 0 1),corresponding to $\mathbf{q}_s = \mathbf{b}_o^* + \delta\mathbf{c}_{h^*}$. The value of δ was found to be 0.09.
Critical static diffuse scattering was measured by very high resolution synchrotron diffraction in *n*-nonadecane/urea as shown in the figures of the reference [3]. The pretransitional effects seem to be associated with quasi-one-dimensional fluctuations along the aperiodic direction **c** showing a lateral ordering in the (**a**, **b)** plane upon approaching T_{c1}. The aim of the experiment is to study, in the three reciprocal space directions, the critical inelastic scattering function around several critical wavevectors.

The experiment is performed on a fully deuterated large single crystal (0.4 x 0.4 x 2.5) cm^3. The incident wavelength is k_i=2.662Å. The cryogenic system runs very successfully finding the phase transition at T_{c1}=149K, as expected.
Several small problems were encountered during the experiment but not preventing his successful realisation:

- This is an unique experiment performed these last years in the inelastic mode on D10, with some consequences as the absence of the knowledge of the four dimensional resolution function and also the lack of the analysis programs for the inelastic data.
- Some mechanical problems appeared concerning the displacement of the analysers generating some wrong positions and a certain waste of time during some scans.

Due to the experimental challenge which is measuring dynamical critical phenomena in the reciprocal space, there is no doubt that the retained spectrometer D10 (triple axis analysis on four circle diffractometer) is the only instrument suited. The neutron flux on D10 being weak compared to the other triple axis spectrometers, we focused on low energy transfer. It is well-known that the spatial resolution of D10 is excellent. This has been confirmed as illustrated in the figure 1, which so nicely illustrated the large separation between the five dimensional critical wavevectors (2 3 0 0 1) and (2 3 0 0 -1) (separate in the reciprocal space by less than 0.1Å, that is giving a resolution lower than 0.01Å HWHM) It should be stressed that such an observation has been possible only thanks to the exceptional mosaicity of the large fully deuterated crystal used.

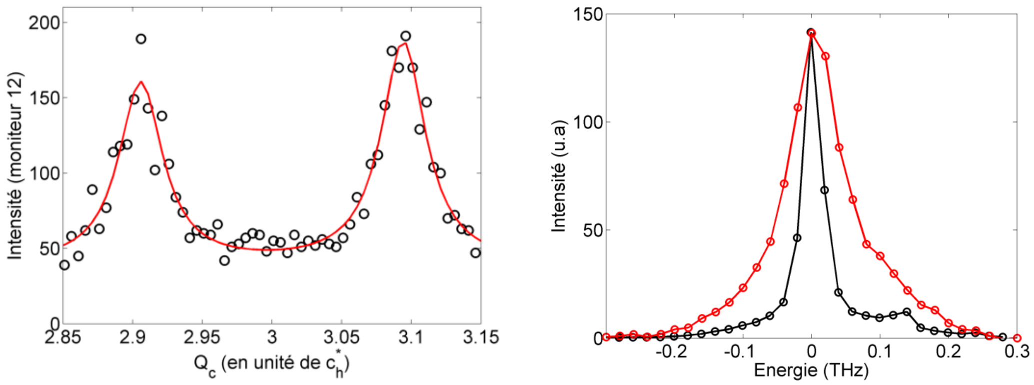

FIG.1.Right) A Q scan performed along the aperiodic direction at superlattice positions (3 0 3 m n) revealing the critical wavevectors at $-q_s$ (3 0 3 0 -1) and $+q_s$ (3 0 3 0 1) at 150K (T_{c1}+1K). Left) Energy analysis of the pretransitional phenomena performed at the critical positions q_s (2 3 0 0 1) at T_c+3K: comparison between positions (2 3 0 0 1) et (3 0 3 0 1), normalized to their respective maximum intensity.

It appears during the experiment that the energy resolution is quite good, the cut in energy of a Bragg peak has a HWHM of 10GHz. Most of the experiments will take advantage of these two properties (high resolution in q and in energy), making the measurements very close to the Bragg positions and considering narrow energy ranges (maximum 500 GHz).

Results obtained during the experiment on D10:

All the possible measurements from the proposal were performed but only at one temperature (T=152K that is 3K above the transition temperature).

1) A series of longitudinal and transverse phonons were performed around two different Bragg peaks of the basal plane (2 0 0 0 0) and (0 4 0 0 0). They confirm the quality of the experimental conditions and determine the focusing conditions of the spectrometer.

2) Several measurements were performed at the five dimensional critical wavevectors close to the basal plane (3 2 0 0 1) and with a large component in the aperiodic direction (3 0 3 0 1) (Fig.1). These critical wavevectors characterize the increase of the dimensional superspace as associated to a doubling of the internal variable in the internal superspace. The figure 2 gives a typical energy analysis of this critical wavevector. It appears that the signature is not resolved in energy for the satellite close to the basal plane (n=1, l=0), (note that a quasielastic contribution of about 100GHz HWHM is clearly evidenced but as discussed in the point 3 it is not attached to this critical point). On the contrary, the satellite with a large component along the aperiodic direction (n=1, l=3) presents a main quasielastic feature. The lack of time did not allow to pursue the study in q space and versus temperature of this very exciting and totally new result.

3) Several measurements were performed in the (a*, b*) plane in order to study the dynamics of the critical phenomena leading to the concomitant structural change from hexagonal to orthorhombic. As shown in figure 3 at the point (2 2.75 0 0 0), and as

already noted at the point q_s (2 3 0 0 1), there is an inelastic component. Its width in energy is found about 100GHz and its norm is modulated in space maximum in the (a*,b*) plane and with two maximum along c* one around the structure Bragg position (2 2 0 0 0) and the other around the superstructure (2 3 0 0 0) point.

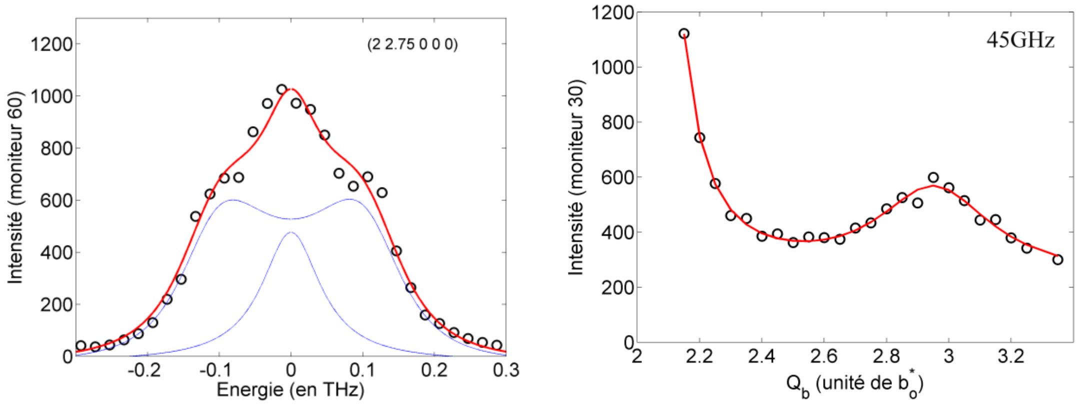

FIG. 3: Right) Energy analysis of the pretransitional phenomena performed in the (a*, b*) plane at the position (2 2.75 0 0 0) at T_c+3K. Left) A 45GHz constant energy scan in the same conditions.

The experiment brought several exciting answers for the questions raised in the proposal. Due to the limited neutron flux, not a fully dispersion analysis in space could be performed and only one temperature was studied.

[1] B. Toudic, Garcia P., Odin C., Rabiller P., Ecolivet C., Collet E., Bourges P., McIntyre G.J., Hollingsworth M.D., Breczewski T., Science **319**, 69 (2008).
[2] B. Toudic, P. Rabiller, L. Bourgeois, M. Huard, C. Ecolivet, G. J. McIntyre, P. Bourges, T. Breczewski, and T. Janssen, Europhys. Lett. **93**, 16003 (2011).
[3] C. Mariette et al. Physical Review B **87**, 104101 (2013).