

## HIDDEN DEGREES OF FREEDOM IN APERIODIC CRISTALS.

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A fundamental concept in the description of the states of matter and the associated physical properties is that of order. For the solid state this has long been synonymous with periodicity, which is the basis of the notion of a crystal lattice, and a paradigm underpinning numerous fields of condensed matter. One way to probe the structure of matter on the atomic scale is to use scattering of radiation of a suitable wavelength, for example X-rays, neutrons. The existence of long-range order is then characterised by the appearance of diffraction spots which form a pattern with the symmetry of the crystal lattice. It is thus that non-periodic, yet still ordered, structures were discovered during recent decades. These *aperiodic* structures can be described in a periodic manner in a superspace with dimensions  $3+d$ , where 3 represents the usual *real* 3D space, and  $d$  the dimension of an *internal* space.

We are interested in aperiodic structures where a host framework forms subnanometric channels, which can contain and confine a network of guest molecules. We have now observed that there exists phase transitions where the structural changes correspond just to degrees of freedom *hidden* in the internal superspace. Experiments were performed on the cold-neutron triple-axis spectrometer 4F1 at LLB. In the studied nonadecane-urea inclusion compound, linear alkane molecules pack end-to-end in the channels of a honeycomb-like framework of urea molecules (figure 1). Because the ratio of repeat lengths along the channel axis of the urea host (the  $c$  axis) and the alkane guest is irrational the crystal as a whole is not periodic. The diffraction pattern requires four indices  $h, k, l, m$  with  $l$  and  $m$  the coefficients of the parallel reciprocal vectors  $c_{host}^*$  and  $c_{guest}^*$  respectively.

The average structure of the urea is described by the  $hk0$  reflections, the average structure of the alkane by the  $hk0m$  reflections, and the reflections  $hklm$  with  $l, m \neq 0$  are due exclusively to the mutual interaction between the lattices (figure 1). The high symmetry phase is described by an hexagonal four dimensional superspace group.

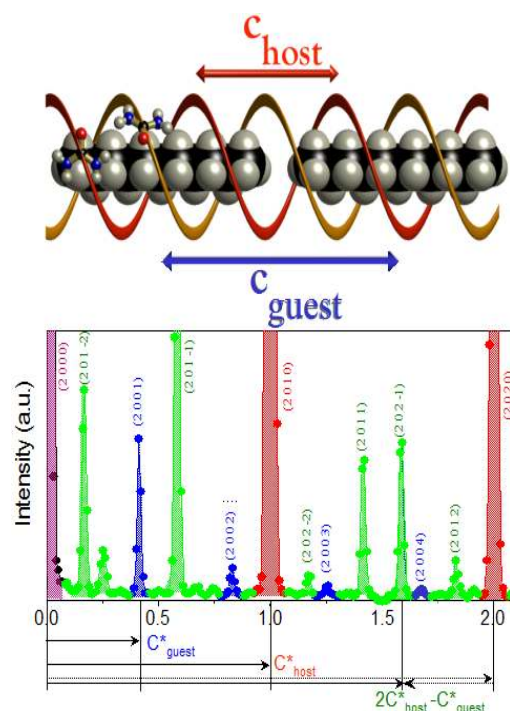


Fig 1: Real and reciprocal images of a self-assembled aperiodic material. Alkane/urea crystals are prototypical examples of nanotubular intergrowth compounds. Along the channel, the periodicity of the host urea subsystem is  $c_{host} = 1.102$  nm at room temperature, whereas the guest periodicity,  $c_{guest}$ , is roughly a linear function of the number of carbon atoms in the alkane molecule. The irrational ratio,  $c_{host}/c_{guest}$ , defines a misfit parameter  $\alpha$ . The reciprocal image is characterized by four different types of diffraction peaks. The common Bragg peaks in purple are located at  $(h, k, 0, 0)$ . The scale refers to the host periodicity, so host Bragg peaks  $(h, k, l, 0)$  in red are at integer positions along  $c^*$ , and guest Bragg peaks  $(h, k, 0, m)$  in blue are at multiple values of  $\alpha$  (which is also equal to  $c_{guest}^*/c_{host}^*$ ). Intermodulation satellite Bragg peaks, in green, are along  $c^*$  at the summation positions  $(h, k, l, m)$  with  $l$  and  $m$  different from zero. The presence of these satellites shows that each sublattice is modulated by the periodic potential of the other one [1].

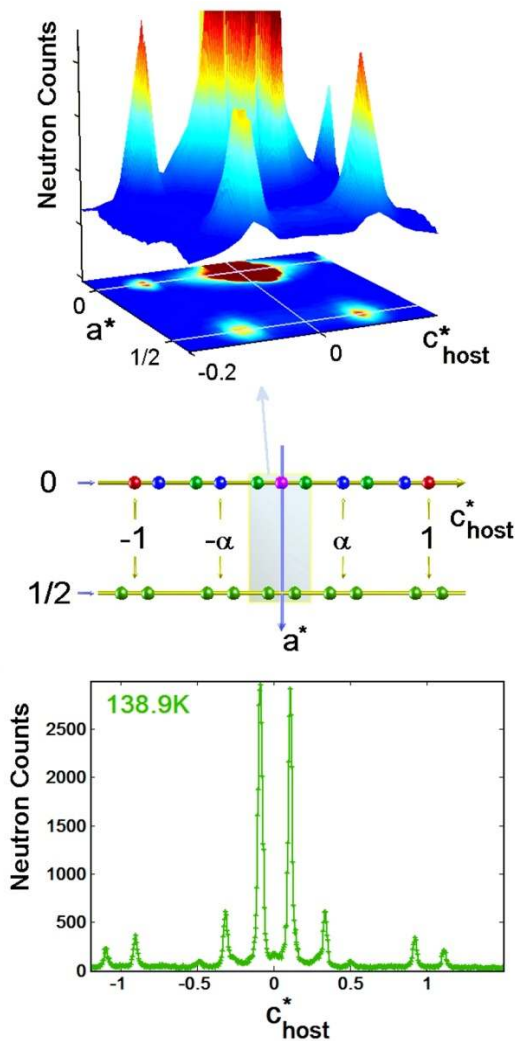


Fig. 2: Superstructure lines are generated in  $h=1/2$  (in the high symmetry hexagonal notation) at a first transition ( $T_{c1}=149\text{K}$ ). This doubling concerns only the internal dimension of the crystallographic superspace: there are no host, no guest, no common superstructure Bragg peak, but only satellites superstructure at  $138.9\text{K}$  [2].

We show that, at  $T_{c1}=149\text{K}$ , the crystal presents a structural instability towards an orthorhombic superspace with a doubling which concerns only its fourth superspace dimension [2,3]. Indeed, only satellite reflections of type  $1/2klm$  with  $l, m \neq 0$  appear in the superstructure reciprocal line (figure 2). There is thus an intermodulation of the host and guest lattices that alternates from channel to channel in the  $a$  direction, yet the average positions of the host and guest molecules are the same from channel to channel

On further cooling below  $T_{c2}=129\text{K}$ , a second phase transition appears revealing the four different types

of superstructure Bragg peaks (figure 3). So, the doubling now concerns also the mean host and guest substructures in addition to the previous doubling of the intermodulation.

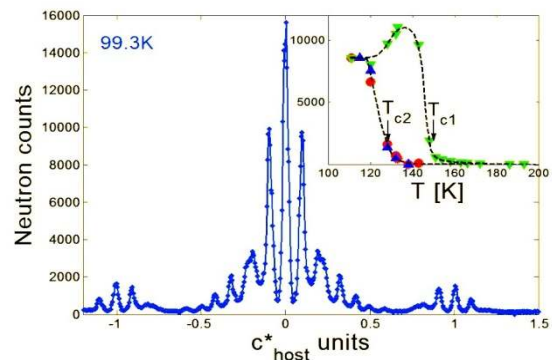


Fig 3: In *nonadecane\_urea*, a second ordered crystallographic phase appears below  $T_{c2}=129\text{K}$ . This phase is an orthorhombic superspace phase which is characterized by the appearance of host, guest and common superstructure in addition to the satellite ones already present in the first ordered phase. Whereas in the first ordered phase, the doubling concerns only the intermodulation, it concerns now also the mean host and guest substructures [2].

The unusual phase between  $149\text{K}$  and  $129\text{K}$  shows that nature can use the degrees of freedom hidden in the internal space to form states that cannot be envisaged in the usual 3D real space. This observation suggests a wider perspective for our understanding of the organisation of complex structures, manipulation of materials on the nanometric scale, sub-nano-fluidity, or translocation of polymers. In addition, these additional structural degrees of freedom of structure may couple with new dynamical ones to lead to new and tuneable properties of nanoscale and biological materials.

#### References:

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