INTERACTIONS IN SELF-ASSEMBLIED MOLECULAR CRYSTALS

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Self-assembly is ubiquitous in nature. The key elements are chemical complementarities and structural compatibility through non-covalent bonds [1]. A fundamental question in organic supramolecular and biological materials is the knowledge of the actually involved interactions. Peptides are short molecules yielding to numerous examples of molecular self-organized systems. Urea, which is the smallest molecules containing the peptide linkage and urea inclusion compounds constitute a prototype family of intergrowth nanoporous crystals [2]. In these crystals, the host network is made of honeycomb-like channels formed by helical ribbons of urea molecules. Each infinite and parallel channel exhibits an available diameter of ca. 5.25 Å in which linear guest molecules are densely packed in a one-dimensional arrangement. Aperiodicity in these materials generate quite new properties, such as a specific diffraction pattern [3], a matter transport through molecularly selective capillaries [4] or a selective compressibility [5].

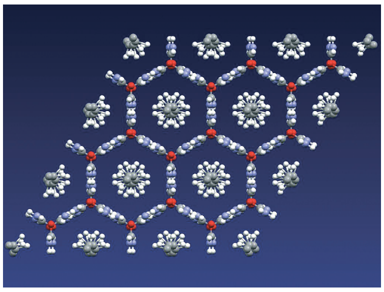

Figure 1. A projection in the basal hexagonal plane of the urea-alkane molecules within the disordered high symmetry phase.

Inside the urea hexagonal channel, alkane molecules occupy at room temperature a six-fold symmetry site which requires an orientational disorder about the long molecular axis, as illustrated in the figure 1. The urea sublattice has been characterized by the space group $P6_122$ with cell parameters in the commensurate plane: a = b = 8.22 Å at 295 K.. At atmospheric pressure, this structure transforms into an orthorhombic phase, which has been described for urea by $P2_12_12_1$. The transition temperature, T_c, is 150 K for fully deuterated nonadecane-urea. It increases versus pressure with a rather linear slope of 10K/kbar up to 6kbar.

Diffraction techniques at best identify symmetry breakings. Neutron scattering experiments were performed at the Laboratoire Léon Brillouin (Orphée reactor, Saclay, France). The data were collected on a triple axis spectrometer installed on a cold neutron source (4F). The incident wave vector was $k_i = 1.55$ $Å^{-1}$ with a refrigerated beryllium filter removing higher order contaminations.

At atmospheric pressure, the symmetry lowering, by the loss of threefold symmetry, generates three families of ferroelastic orthorhombic domains. They are related to the deformation of three orthohexagonal sublattices of metrics $b_o = \sqrt{3}\, a_o$ and shifted by 120°. This ferroelastic phase transition generates then six equivalent twinned domains which impose the splitting of the Bragg reflections into six peaks, two of which being superimposed along the crystallographic axes. In the figure 2, is shown this already known splitting [6], characteristic of the low temperature ordered phase at atmospheric pressure.

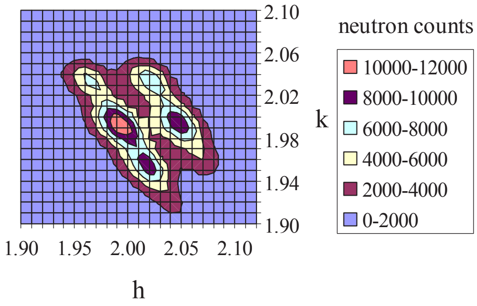

Figure 2. A neutron diffraction map of the (2 2 0) Bragg peak measured at in the orthorhombic ordered phase at atmospheric pressure at T=120K.

Such Bragg peaks of the structure have been measured versus temperature and pressure going through the transition line which is evidenced by the appearance of superstructure Bragg peaks. The same map performed at 5.3kbar and 120 K, then far below the transition temperature T_c' (≈ 200 K), is shown in the figure 3. This measurement does not show any splitting of the Bragg reflections in the ordered phase on the contrary to the atmospheric pressure case. In this high-pressure low symmetry phase, hexagonal metrics is kept within the limit of the spatial resolution, meaning that no significant shearing occurs in the structure.

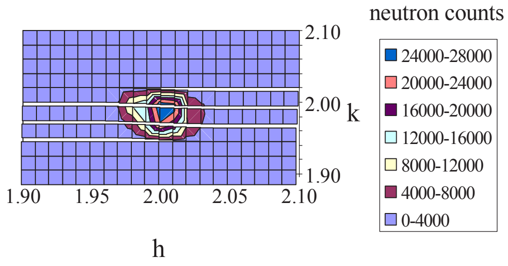

Figure 3. same as figure 2 but in the high pressure ordered phase (P=5.3kbar, T=120K): no splitting of the Bragg proves no apparent shearing of the structure.

This structural analysis of the mechanism triggering the phase transitions in self-organized supramolecular crystals is of fundamental importance for a deeper understanding of the actual interactions between the different networks. A first theoretical approach of this atmospheric pressure phase transition, based on a basal plane picture, considers it as resulting from a translation-rotation coupling between the rotational ordering of the chains and the shearing of the host sublattice [7]. This model describes the regime of this transition as both order-disorder and displacive. It was expected to be quite general, since to our best knowledge, in similar systems, the architecture of all the ordered structures at atmospheric pressure exhibits a large shearing of a few degrees. Clearly, the diffraction results reported here rule out this interpretation, at least under pressure.

Elastic properties are, of course, also very sensitive to structural modifications and provide for interactions changes through temperature or pressure anomalies. Sound velocity anomalies are related to the order parameter and conveniently studied by Brillouin scattering. Ferroelastic phase transitions are usually characterized by a splitting of Brillouin lines resulting from the appearance of domains at low temperature which induce scattering along non equivalent crystallographic directions.

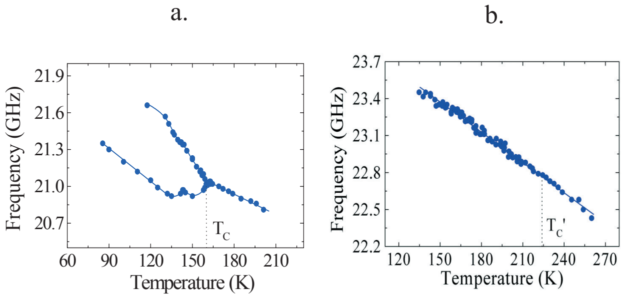

Figure 4. Brillouin longitunal shift versus temperature a) at atmospheric pressure, b) at 5kbar.

Experimental results are here presented at atmospheric pressure and 5kbar. At atmospheric pressure, the figure 4a shows a splitting below 160 K, where each curve is due to different ferroelastic domains. The frequency change is typical of a static biquadratic coupling between the elastic strains and the square of the order parameter, independently of its fluctuation dynamics. At 5kbar, no elastic anomaly and therefore no splitting is observed (figure 4b), indicating no measurable coupling between the order parameter of this transition and the elastic strains of the composite structure. As the elastic properties mainly correspond to the rigid hydrogen-bonded urea network, it indicates that, in average, no significant urea reorientation occurs which could modify the elastic interactions at the scale of the phonon wavelength.

In conclusion, for the first time, we show that the ordering in self-organized materials may occur without any significant deformation of the host matrix. It invalidates at high pressure models which would consider the large shearing of the host sublattice as a driving force of the phase transition. This fundamental observation reported here could be of essential importance when considering the interactions in more complex architectures involving mutually interpenetrating supramolecular or tubular biological networks.

References

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