ONE-DIMENSIONAL STRESS-STRAIN EXPERIMENT INSIDE AN APERIODIC INCLUSION SINGLE CRYSTAL

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Certain small molecules, such as urea, thiourea, perhydrotriphenylene can co-crystallise with long-chain hydrocarbon molecules to form aperiodic inclusion compounds[1]. The guest chains are confined to narrow, approximately cylindrical channels created by the host small-molecule lattice. The stoichiometry and the conformations of the chains included inside the channels are function of internal interactions such as intrachain interaction, but also of overall co-operative properties of the resulting three dimensionally ordered single crystal. The feasibility of a selective stress-strain experiment inside such a composite relies on the aperiodicity of the structure, which theoretically enables an homogeneous displacement of one sublattice with respect to the other one without any restoring force. This property results from an infinitely degenerate ground state for an infinite aperiodic structure. The stiffness of the matrix is a further necessary condition since this matrix plays the role of a compression cylinder.

This is the case with urea host molecules which are known for their ability to form, via hydrogen bonds, solid 1d channels, almost cylindrical with an available diameter of 5.5 Å, which can accommodate linear guest molecules like n-alkanes. Inside these honeycomb-like channels, these latter are confined in an ordered 1d dense packing with some 3d ordering despite some rotational and translational disorder.

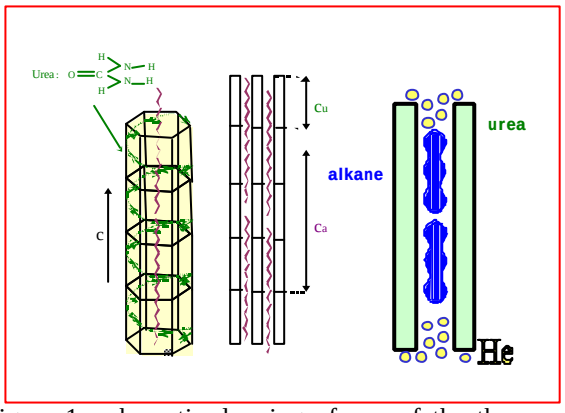

Figure 1. schematic drawing of one of the three urea helices building a channel occupied by alkane molecules. Middle: Schematic representation of the urea and alkane periodicities. Right: principle of the "molecular press" with helium pressure gaz.

The compound we have studied is the nonadecane ($C_{19}D_{40}$) / urea ($CO(ND_2)_2$) which is a paradigm of such intergrowth crystals. The mean high symmetry structure of the urea host subsystem is described by the hexagonal $P6_122$ space group, with cell parameters a = b = 8.22 Å and c_u = 11.02 Å at room temperature and atmospheric pressure. The a and b parameters are shared by both subsystems. The aperiodicity of the composite results from the two independent periods of the sublattices: the alkane lattice parameter (C_a=26.36 Å at 300K and 1bar) and the pitch of the urea helices constituting the host structure independently of the guest length. Their ratio is called the misfit parameter. In composites, a major consequence of aperiodicity is the existence of four kinds of Bragg reflections located at different positions in the reciprocal space. We distinguish common reflections (h k 0 0) generated by both sublattices in the commensurate plane, and along the incommensurate direction, either main sublattice reflections labeled (h k l 0) for the host and (h k 0 m) for the guest, together with pure intermodulation satellites at combinatory positions (h k l m)[2,3].

A convenient way to directly measure the lattice and sublattice strains is to apply hydrostatic pressure and to perform neutron diffraction. This experiment was performed on the triple axis spectrometer **4F1** with an incident wave vector k_i = 1.55 $Å^{-1}$. Hydrostatic pressure up to 5.3 kbars was obtained in a helium gas pressure cell at room temperature. The retained scattering plane was (**a***,**c***) with a fully deuterated single crystal.

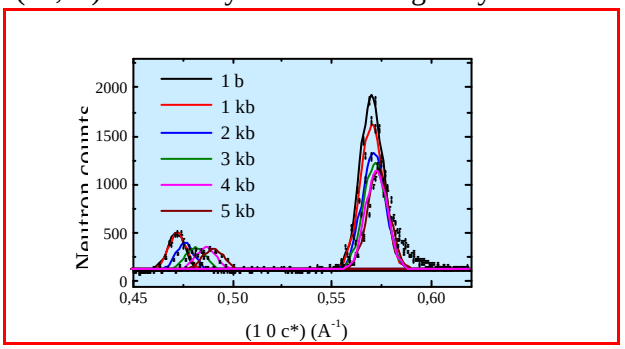

Figure 2. Evolution of two Bragg peaks related respectively to the alkane (1 0 0 2) (left) and to the urea (1 0 1 0) (right) sublattices.

The figure 2 shows the evolution versus pressure of two Bragg peaks observed on the reciprocal line (1, 0, *l*, *m*) which are (1 0 1 0) and (1 0 0 2). Obviously, these peaks, related respectively to the urea and the alkane sublattices, shift with a different pressure sensitivity.

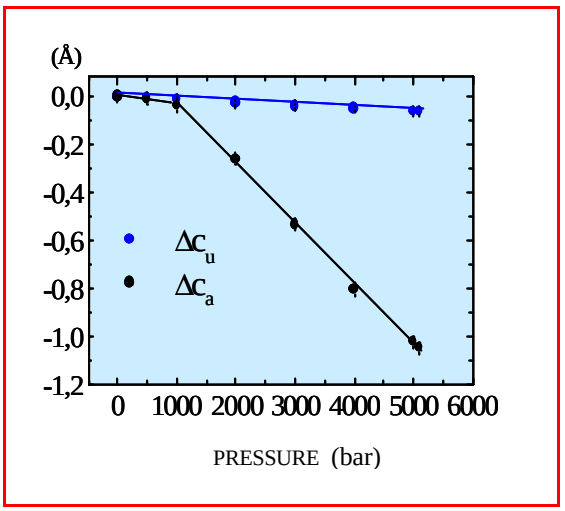

Figure 3. Evolution versus pressure of the sublattice parameter variations along the incommensurate direction c for the alkane (?) and the urea (•) one (lines are guides for the eye)

Original features appear along this incommensurate direction [4]:

- Below 1 kbar the measured strains are comparable within the experimental accuracy to the computed values of the elastic constants measured in standard conditions where the composite behaves as a regular crystal.

- Above 1 kbar, one observes different strains for the two sublattices direction, which appear as the individual responses of each sublattice. The variations observed which are an order of magnitude larger for the alkane sublattice than for the urea one are reversible and so indicate that the composite is neither destroyed nor altered under pressure. One can interpret the alkane behavior as due to the application of pressure at both ends of the urea channels by the He atoms on the alkane molecules. Then, on increasing pressure, He atoms with a Van der Waals diameter of ca 2.8 Å can play the role of a piston inside each cylinder made of urea molecules by pushing the alkanes towards the inside of the crystal.

From the lattice parameter variation shown in figure 3, it is possible to determine experimentally the elastic properties of the alkane sublattice. One can estimate the pushing force by multiplying the pressure by the free area of the hexagonal channel 19 ± 1 Å^2. A pressure of 5kbars corresponds then to a force of 95 ± 5 pN acting on the far ends of the alkane sublattice. This force is acting mainly on the inter-molecular degrees of freedom and lead to a compression end-to-end of the molecules

The slope of the alkane deformation versus pressure shows that for 5 kbars, the elongation of the alkane sublattice should be 1.3 Å. However it has to be corrected from the influence of the conformational defects of the chain ends which also alter the chain length [5]. This correction leads to an actual elastic displacement of 1.0±0.1 Å. Consequently, the alkane intermolecular force constant k is found equal to 1.0±0.15 N/m.

In conclusion, we have observed selective compressions in a crystal due to its aperiodic nature. This experiment shows furthermore that the relative motion of a sub lattices are pinned at low pressures and that a depinning occurs under the effect of pressure like CDW under the effect of an electric field above some threshold. The knowledge of the inter alkane force constant will help the definition of better experimental conditions for the sliding mode observation in this family of aperiodic organic composite.

References

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