

## Pressure-Induced Lock-In in an Aperiodic Nanoporous Crystal

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This Letter reports on the first observation of a commensurate lock-in inside an aperiodic composite. This result is obtained by neutron diffraction, under hydrostatic pressure, in the prototype self-assembled crystal of hexadecane urea. A selective compressibility of the sublattices is a required condition together with the existence of a lock-in energy term in these supramolecular materials. This measurement, under one-dimensional confinement, opens the way for the use of continuously controlled forces to manipulate molecular properties or functions.

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Self-assembly underlies the formation of a wide variety of biological [1,2] and supramolecular structures [3]. The key elements are chemical complementarities and structural compatibility through noncovalent bonding. Self-assembled compounds are often constructed from two interpenetrating sublattices, defining host and guest subsystems. Very recently self-hosting was reported in metallic [4] and organic [5] materials. Nanopeapods of fullerene arrays inside single-wall carbon nanotubes constitute a new type of hybrid structures [6–8]. The common feature of all these materials is to present the ultimate one-dimensional confinement for the guest molecules. Aperiodicity in these materials may appear rather naturally due to the misfit of host and guest parameters along the channels or the tubes. The idea of free sliding, which rapidly emerged in aperiodic materials [9,10], generates very recent developments [11,12]. Nested carbon nanotubes, where inner and outer tubes may be incommensurate, show remarkable nanotribological properties [13]. The understanding of the interactions involved is of fundamental importance with a wide area of theoretical issues as well as practical applications. Potential uses of nanometer-sized containers is huge for molecular manipulation, chemical reaction, and nanofluidics. A very challenging goal is to use the one-dimensional confinement to manipulate molecular properties or functions under external forces.

In this Letter, we report on the first continuously controlled commensurate lock-in in a composite crystal. Urea is one of the smallest molecules containing the peptide linkage, and urea inclusion compounds constitute a very simple paradigmatic example of nanoporous intergrowth crystals. They are known for their ability to form, via host urea hydrogen bonds, solid 1D channels, almost cylindrical with an available diameter of 5.5 Å which can accommodate linear guest molecules such as alkanes  $C_nH_{2n+2}$  [14]. The mean high-symmetry structure of the urea host subsystem is then described by the hexagonal  $P6_122$  space group, with cell parameters  $a = b = 8.22$  Å and  $c_h =$

11.02 Å at ambient conditions [15–17]. The basal  $a$  and  $b$  parameters are shared by both subsystems. The alkane-urea composites are typically incommensurate crystals since the guest lattice parameter  $c_g$  is a function of the number  $n$  of carbons in the alkane molecules, according to the empiric expression  $c_g(n) = [1.277(n - 1) + 3.48]$  Å [18]. In the diffraction pattern, sharp diffuse layers with superimposed Bragg peaks reflect the guest sublattice periodicity [19,20]. A misfit parameter  $\alpha$  is defined by the ratio of the host and guest periodicities ( $\alpha = \frac{C_h}{C_g}$ ). The structure of aperiodic composites is described in the frame of the superspace crystallography [21,22]. In the present case, a four-dimensional superspace description gives the positions of the whole set of Bragg reflections:

$$\mathbf{q}_{hklm} = h\mathbf{a}^* + k\mathbf{b}^* + l\mathbf{c}_h^* + m\mathbf{c}_g^*,$$

where  $\mathbf{a}^*$ ,  $\mathbf{b}^*$ ,  $\mathbf{c}_h^*$ , and  $\mathbf{c}_g^*$  are the conventional reciprocal-lattice vectors. The different components of the diffraction pattern can be classified as follows:  $(hk00)$  are common reflections from the basal periodic plane,  $(hk10)$  and  $(hk0m)$  render account of the mean periodicity of, respectively, the host and the guest sublattices, and  $(hklm)$  with nonzero  $l$  and  $m$  integers are intermodulation satellites [22]. This characteristic diffraction signature is reported in urea-alkane crystals [23,24]. Quite new properties, such as a molecularly selective capillary [25] and a selective compressibility [26] were recently reported in these materials. These remarkable features rely on the aperiodicity of the structures, which theoretically enables a 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 [9,10]. In the stress-strain experiment, the stiff hydrogenated bonded host matrix plays the role of a compression cylinder whereas He atoms play the role of a piston. The selective compressibility for the different sublattices provides a unique opportunity to observe an induced commensurate lock-in in a composite crystal. The

main condition relies on the existence of a commensurate lock-in energy term in the material. To achieve it experimentally with hydrostatic pressure, a second condition is to have a misfit parameter in the vicinity of a simple rational number. The guest compound we retained in the present work is hexadecane ( $C_{16}H_{34}$ ), which has a sublattice parameter just slightly larger than 2 times the urea periodicity.

Single crystals of hexadecane urea were prepared by a slow evaporation of a mixed solution of urea and hexadecane in a mixture of ethanol and isopropyl alcohol. Neutron scattering experiments were performed at the Laboratoire Léon Brillouin at the Orphée reactor (Saclay, France). The data were collected on the triple-axis spectrometer  $4F_1$  installed on a cold neutron source. The retained scattering plane was  $(\mathbf{a}^*, \mathbf{c}^*)$ . The incident wave vector was  $k_i = 1.55 \text{ \AA}^{-1}$ . The diffraction pattern has been followed with a refrigerated beryllium filter to remove higher-order contaminations. Hydrostatic pressure up to 6 kbar was obtained in a helium gas pressure cell installed inside a liquid-helium cryostat. Figure 1 shows the reciprocal line  $(30lm)$  measured at room temperature at the pressure of 6 kbar, with indices referring to the urea reciprocal-lattice parameter. It shows the common  $(3000)$ , alkane  $(300 \pm 1)$ , and urea  $(30 \pm 10)$  Bragg peaks. All the presented studies were performed along this reciprocal line. Measurements performed on a cold neutron triple-axis spectrometer have a very high spatial resolution for the Bragg peak locations. Although the absolute values of the lattice parameters may not be so accurate on triple-axis spectrometers, the relative variations of the parameters are very precise:  $0.005 \text{ \AA}$  for urea and  $0.01 \text{ \AA}$  for alkane. At ambient conditions, the experimental misfit parameter was found to be 0.487, the predicted value.

The initial measurements were performed at room temperature in the hexagonal phase up to a pressure of 6 kbar. The pressure evolution of the misfit parameter is shown in Fig. 2. At low pressures, one must reach a threshold pressure of about 1 kbar before obtaining the selective com-

pressibility. This result is consistent with the one previously reported in nonadecane urea [26] and is assigned to structural defects. Above the threshold pressure, we observe the selective compressibility of host and guest sublattices through the pressure variation of the misfit parameter. The slope is

$$\frac{d\alpha}{dP} = 4.7 \times 10^{-3} \text{ kbar}^{-1}.$$

Original features appear around 4 kbar where the misfit parameter meets the 0.5 value and remains constant over a pressure range of 800 bars. There, the system behaves as a usual crystal. This is the first evidence of a commensurate lock-in inside an aperiodic crystal. It proves the existence in this self-assembled crystal of a well-defined lock-in interaction energy term that favors periodicity between host and guest sublattices. This interaction competes with the one that provides structural intermodulation. Its existence is expected to break the analyticity of the displacive intermodulation function and consequently to affect specific dynamics creating a zero energy gap for the sliding branch [27].

At higher pressures, the crystal presents again a depinning. The same value for the slope is found above and below the commensurate plateau showing that the process involves the same compressibility in the whole pressure range. The compressibility is found larger in hexadecane urea than in nonadecane urea, as expected. The ratio of these values are slightly larger than the ratio of their inverse molecular lengths.

The hexagonal room-temperature phase is a thermally disordered one with important rotational and translational degrees of freedom of the guest molecules [28,29]. These motions are expected to average the interactions between host and guest sublattices. Temperature is then an important parameter since it would strongly affect the thermal fluctuations. Furthermore, alkane-urea compounds present a structural phase transition to an orthorhombic symmetry

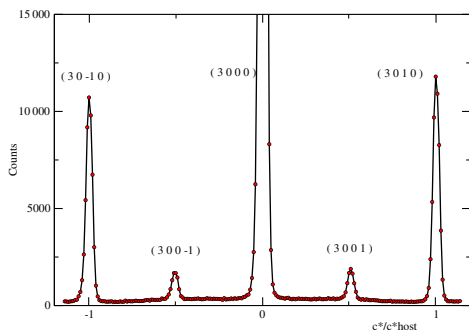


FIG. 1 (color online). Neutron diffraction study of hexadecane urea performed on a triple-axis cold neutron spectrometer ( $4F_1$ , L.L.B.,  $k_i = 1.55 \text{ \AA}^{-1}$ ): reciprocal line  $(30lm)$  measured at 300 K and 6 kbar.

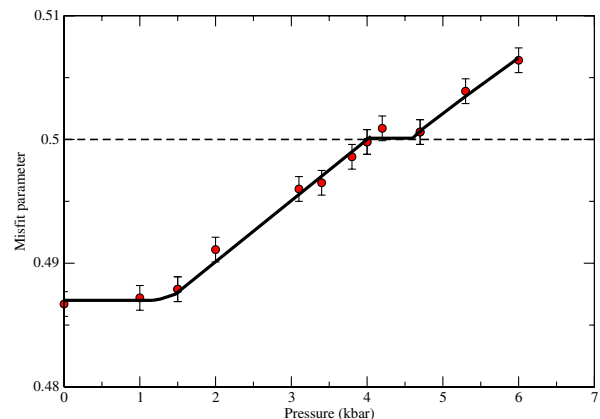


FIG. 2 (color online). Pressure evolution of the misfit parameter measured at room temperature.

at low temperature [15,16] and under pressure [30]. It is associated to a shearing of the hexagonal lattice and a simultaneous decrease of the translational [28] and rotational [20,31,32] dynamical disorder of the guest subsystem. In order to measure the influence of the ordering on the host-guest interaction, we performed a pressure study of the compressibility far below the transition temperature near 150 K in this compound. In order to avoid solidification of the helium pressure gas at high pressure, the experiment was conducted at 60 K. Thus, all of the presented measurements are obtained under hydrostatic pressure. The crystal was cooled from 300 to 60 K at 4.2 kbar, that is, on the commensurate plateau obtained at 300 K. Upon passing through the phase transition, the structural problem is complicated by the appearance of different low-symmetry orthorhombic induced domains [16]. Triple-axis cold neutron diffraction allows one, without difficulty, to select the domains, thus all of the results will concern one chosen domain.

The pressure evolution measured at 60 K is presented in Fig. 3. Experimentally, pressure was first decreased from 4.2 to 1 kbar. This revealed a depinning below 2 kbar in which the crystal recovers aperiodicity along the channels. Then, the pressure was increased. In the figure, a very broad commensurate 1:2 plateau is present from 2 kbar to a pressure of 6 kbar, the maximum limit of our hydrostatic pressure cell. Since this measurement begins in an incommensurate state, this result does not correspond to a metastability of the composite with the value 1:2. It should be noted that when the lock-in is obtained at room temperature and at 60 K, intensities of the Bragg reflections associated with the guest subsystem do not significantly increase. In other words, the interchain correlations are not fundamentally increased. This means that inside each channel the system is periodic, but from channel to channel, decorrelation remains. This shows the pronounced 1D character of the guest sublattice even when it is locked with commensurate ratios between host and guest sublattices.

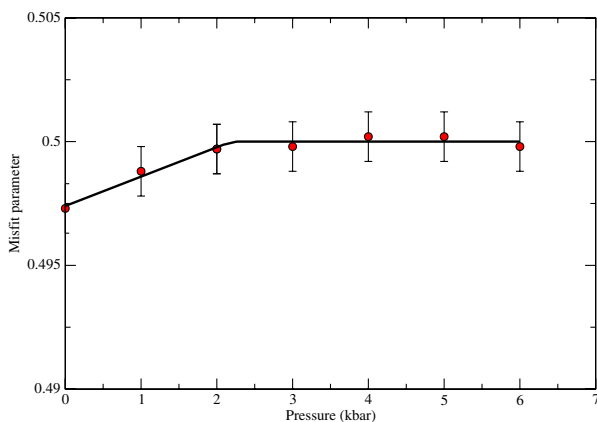


FIG. 3 (color online). Pressure evolution of the misfit parameter measured at 60 K.

When pressure is returned to 1 bar at 60 K, one sees in Fig. 3, that the misfit parameter, even if it is different from 0.5, does not recover exactly the one found at room temperature (here 0.497 instead of 0.487). This brings us to study the misfit parameter as function of the temperature after decreasing the pressure to atmospheric pressure. Figure 4(a) shows the temperature evolution of the  $a$  and  $b$  parameters, which clearly reveal the orthorhombic hexagonal phase transition at 150 K, the usual transition temperature for the structural instability at 1 bar. Figure 4(b) shows the misfit parameter from 60 K to room temperature. A clear decrease in this parameter appears when increasing temperature. This is the first evidence of a thermal evolution of the misfit parameter in these crystals. Because it concerns an incommensurate state, the change of the periodicity may reveal a change in the mean alkane length as the proportion of *gauche* defects changes [33,34]. Moreover, the mean square amplitude of the thermal fluctuations increases as the system transforms into a disordered phase. The very fundamental point is that, coming back to room temperature, one recovers the same value of the misfit parameter obtained at the beginning of the  $(P, T)$  cycle. This proves that there are no memory effects and no deterioration of the crystal in this pressure cycle.

In conclusion, in this Letter, we report on fundamentally new observations concerning lock-in properties in nanoporous self-assembled materials. The temperature evolution of the width of the commensurate plateau is of fundamental importance to quantify the interaction and, in particular, the magnitude of the lock-in energy term in these supramolecular crystals. The strong change of the width between 60 K and room temperature suggests that the plateau should vanish slightly above 300 K. This defines an equivalent interaction energy that is of the order of  $1 \text{ kcal mol}^{-1}$ . Further *ab initio* and molecular dynamics calculations should be done considering the simple com-

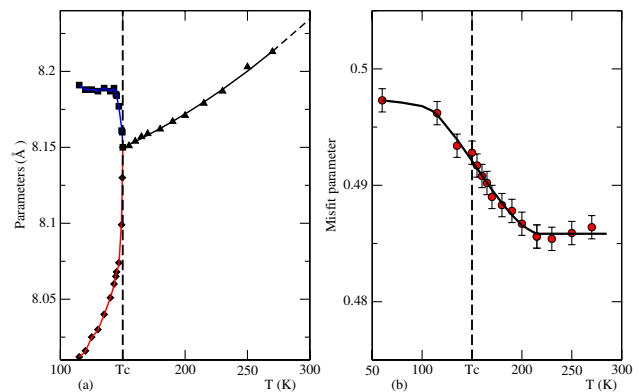


FIG. 4 (color online). Measurements performed at 1 bar after decreasing the pressure (end of the pressure cycle) (a) temperature evolution in the basal plane of the orthorhombic ( $a, b/\sqrt{3}$ ) parameters below  $T_c$  and the  $a = b$  hexagonal parameters above  $T_c$ ; (b) temperature evolution of the misfit parameter.

mensurate state both to identify the origin and the quantitative values of the energy lock-in term. This is of fundamental importance to determine the stability of such self-assembled materials with strong hydrogen-bonded host systems and weaker van der Waals cohesive interactions. This observation raises the question of the actual interactions in other similar supramolecular or biological tubular systems. It could explain essential structural features, like incommensurate intermodulation [24] and original symmetry breaking [35] together with special collective dynamics. The continuous control of the guest repeat gives a unique tool for tuning and studying 1D properties of confined compounds. These results open a broad field of scientific subjects that can be tackled combining the low friction of incommensurate nanoporous materials with conformational, optic, or electronic properties of guests.

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