Interactions in Self-Organized Nanoporous Organic Crystals

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This Letter reports on the structural analysis of a self-assembly material, the prototype host-guest urea-alkane nanoporous crystal. Different spectroscopic techniques, under hydrostatic pressure, reveal a totally unexpected ordered phase where ordering does not require any apparent deformation of the host. This fundamental observation raises the question of the actual interactions in other similar supramolecular or biological tubular systems.

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Self-assembly is ubiquitous in nature. The key elements are chemical complementarities and structural compatibility through noncovalent bonds [1,2]. 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 [3]. Urea, which is one of the smallest molecules containing the peptide linkage, forms several polymorphs of extended linear [4], orthogonal [5], or helicoidal [6] networks of hydrogen bonds. Urea inclusion compounds constitute a prototype family of intergrowth nanoporous crystals. They offer, in a very simple paradigm crystal, a unique opportunity to address at a fundamental level the nature and the roles of the interactions in self-organized architectures. The effect of pressure on such soft systems is of interest to a wide range of disciplines going from physical chemistry to microbiology. Medium hydrostatic pressure of some kbars are enough to affect macromolecular structures, conformations, and functions and can therefore be used as a means of investigating fundamental processes in a continuous thermodynamically controlled manner.

In the simplest case, self-assembly molecular compounds are constructed from two interpenetrating sublattices. In urea inclusion 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 [6]. Most guests are alkanes C_nH_{2n+2}, or chains with terminal groups like hydroxides, halogens, or carbonyls. The shape of these confined chains influences the symmetry of the rigid hydrogen-bonded host network.

Alkane-urea crystals are incommensurate composites. Their stoichiometry and aperiodicity are defined by the ratio of the host and guest periodicities along the incommensurate channel direction, respectively determined by the pitch of the urea helices and the guest length. The characteristic diffraction pattern is described in terms of superspace crystallography [7,8]. The incommensurability feature combined with the relatively rigid host structure of this crystal generates quite new properties, such as a matter transport through molecularly selective capillaries [9] or a selective compressibility [10,11].

Inside the urea hexagonal channel, alkane molecules occupy at room temperature a sixfold symmetry site which requires an orientational disorder about the long molecular axis. 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 [12]. On lowering temperature, this structure transforms into an orthorhombic phase, which has been described for urea by $P2_12_12_1$ [13]. The transition temperature, T_c, increases with the alkane length and is 160 K for hydrogenated nonadecane-urea. This weakly first order, cell doubling phase transition, is characterized by both a shearing of the structure in the basal plane and a herringbone-like arrangement of the alkanes inside the channels giving an unambiguous antiferro character. An antiferro signature is revealed by the appearance of superstructure Bragg peaks with orthorhombic Miller indices verifying $h + k$ odd [14,15]. The shearing induces orthorhombic ferroelastic domains which make very tough any structural resolution of this ordered phase. However, crystallographic information coming out from single crystal ^2H solid state NMR shows that the carbon-carbon planes of alkane chains are pointing towards corners of the distorted urea hexagonal frame [16].

The 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. Here, it could either be considered that the host sublattice shears and orders the structure as soon as the orientational alkane dynamics slow down, or that the herringbone

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ordering of alkanes induces a shearing of the host sublattice. In other words, the possibility to define a primary order parameter related only to a single sublattice, whereas the secondary order parameters would be related to the other one, is often questioned. The answer obviously requires a better knowledge of the interplay between the guest orientational ordering and the structure shearing. However, in each mechanism, it seems obvious that the urea sublattice mediates a long-range order through long-range elastic interactions. A first theoretical approach of this atmospheric pressure phase transition, based on a basal plane picture, considers it as resulting from a linear translation-rotation coupling between the rotational ordering of the chains and the shearing of the host sublattice [17]. This model describes the regime of this transition as both order-disorder and displacive. It is 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.

In this paper, we present and discuss results obtained on *n*-nonadecane/urea using neutron and light scattering under hydrostatic pressure. A first evidence of a new kind of phase transition leads to reconsider the interactions in these supramolecular crystals.

All studies were performed on single crystals prepared by a slow evaporation of mixed solution of urea and nonadecane in a mixture of ethanol and isopropanol. Samples used in neutron experiments were fully deuterated ($T_c = 150$ K) as in our previous studies [10,11], whereas light scattering ones were fully hydrogenated. A He gas hydrostatic pressure was produced by a primary compressor followed by a pressure multiplier. It was transmitted by a capillary to a pressure cell, made of aluminum (neutron) or “Marval” steel with sapphire windows (light scattering), cooled by a nitrogen gas flow. The investigated pressure range was between atmospheric pressure and 7 kbar, with a regulation stability of ± 10 bars even during temperature changes or small gas leaks. All the pressure changes were operated at 295 K. Temperature was measured by a Si diode (light scattering) or a platinum resistor (neutron diffraction) in thermal contact with the pressure cell.

Raman scattering is a sensitive probe for detecting phase transitions and can provide for information concerning the symmetry properties of the structure. Spectra were recorded by using a Kr ion laser and a *Z*24 Dilor triple monochromator with a resolution about 1 cm^{-1}. On a commensurate basis, most of the expected modes below 300 cm^{-1} are the external urea modes. In the $P6_122$ urea space group, corresponding to the D_6 factor group with six molecules per cell, the vibration representation decomposes into $2A_1 \oplus 5E_1 \oplus 6E_2$. The two irreducible bidimensional representations E_1 and E_2 correspond to twofold degenerated modes, respectively, observable with (xz) and (xy) polarizations. In the same frequency range, the intramolecular “longitudinal acoustic modes” of nonadecane can also appear in the (zz) polarization. All these peaks are not resolved at room temperature due, probably, to a noticeable damping and the frequency proximity of several modes. By taking into account the aperiodicity of the composite, additional modes activated by the intermodulation of both sublattices could also occur. It should however be noticed that the recorded spectra seem weakly affected by the aperiodic nature of the compound with no strong additional component in that frequency range.

In the $P2_12_12_1$ phase with a D_2 factor group, the 12 molecules per urea cell can be decomposed into three independent families. The external modes, for one of them, are described by the representation $\Gamma = 6A_1 \oplus 6B_1 \oplus 6B_2 \oplus 6B_3$ involving only one-dimensional representations [18]. Obviously, due to the ferroelastic domains in the scattering volume, these different modes cannot be easily sorted out. The breaking of the hexagonal symmetry into any low symmetry group like the orthorhombic one transforms each bidimensional representation into one-dimensional representations. This implies that the mode degeneracy is lifted out, permitting a splitting of Raman bands. A study versus temperature was performed under pressure using the (xz) polarization related to the E_1 symmetry. Results are here presented at atmospheric pressure and 6.5 kbar only. Shown in Fig. 1(a) are the (xz) spectra recorded at atmospheric pressure above and below the phase transition, in agreement with [18]. The splitting of the intense band about 100 cm^{-1} seems to be the sole modification and, in particular, no soft mode is observed. The same behavior, with an obvious larger damping, is observed at 6.5 kbar in Fig. 1(b). These spectra reveal that no bidimensional representation exists up to this pressure in the vibration representation of the low temperatures phases, indicating a lower symmetry than a hexagonal one. The transition temperature under pressure T_c^l and further features were deduced from the fit by Lorentzian functions of the spectra at different temperatures. T_c^l, ca. 225 K at 6.5 kbar, is close to the value extrapolated from previous results at lower pressures [19]. The evolutions versus temperature of the frequency and the linewidth (convoluted by the apparatus function) of this band are presented in Figs. 2(a) and 2(b). The splitting amplitude independent of pressure indicates a

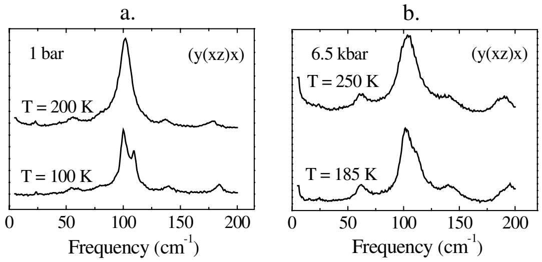

FIG. 1. (xz) Raman spectra showing the splitting of the E_1 mode at ≈ 100 cm^{-1} (a) at atmospheric pressure (200 and 100 K); (b) at 6.5 kbar (250 and 185 K).

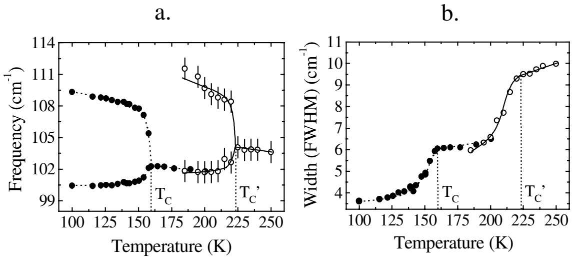

FIG. 2. Temperature evolution of (a) the frequency and (b) the linewidth of the E_1 mode at $\approx 100\ \mathrm{cm}^{-1}$. Full symbols represent atmospheric pressure and open symbols represent 6.5 kbar.

similar modification of the neighborhood of the urea molecules, consisting of urea and alkane molecules. Despite a stronger broadening of the peaks at high pressure, the same linewidth evolution is observed in the vicinity of the phase transition. This behavior is expected for such an order-disorder transition involving the rotational motions of the guest sublattice.

Diffraction techniques clearly 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 ($4F$). This spectrometer has been chosen to offer the best spatial resolution in the ($\mathbf{a}^*, \mathbf{b}^*$) diffraction plane. The incident wave vector was $k_i = 1.55\ \text{Å}^{-1}$ 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 [12]. They are related to the deformation of three orthohexagonal sublattices of metrics $b_0 = \sqrt{3}a_0$ and shifted by 120°. In fact, this nonsymmetric deformation is accompanied by a further small disorientation $\pm\delta$, required in order to align their diagonals along the ones of the high symmetry orthohexagonal lattice. This ferroelastic phase transition generates then six equivalent twinned domains which impose the splitting of the Bragg reflections into six peaks, two of which are superimposed along the crystallographic axes. This splitting affects Bragg peaks in the whole reciprocal space except along the channel direction [14]. The study of these reflections in the basal plane allows us to investigate the structural minute evolutions of symmetry and metrics.

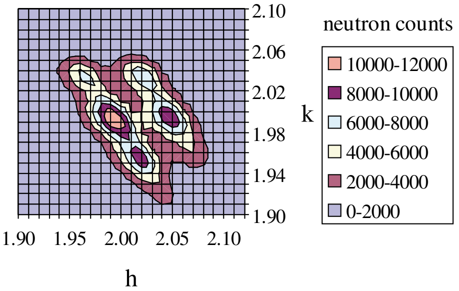

FIG. 3 (color online). Intensity map in the (a^*, b^*) plane of the $(2\,2\,0)_O$ Bragg spot at 120 K as obtained by neutron diffraction in the ordered phase at atmospheric pressure. Measurements are performed with an incident wave vector $k_i = 1.55\ \text{Å}^{-1}$ and a monitor rate $M = 20$ (2.2 s/pt).

Bragg peaks have been followed versus temperature up to 5.3 kbar. Shown in Fig. 3 is the above discussed splitting, characteristic of the ordered phase, measured at atmospheric pressure and 120 K. The same map performed at 5.3 kbar and 120 K, then far below T_c' ($\approx$200 K), is presented in Fig. 4. This measurement does not show any splitting of the Bragg reflections in the ordered phase 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. An orthorhombic lowering of the crystal symmetry is unambiguously evidenced by the appearance of the superstructure Bragg peaks which verify the same existing conditions: $h + k$ odd, as previously found at atmospheric pressure. Of course, due to the hexagonal metrics conservation under pressure, superstructures, like structure reflections, do not split in this new ordered phase. So, at all pressures, the cell is doubling in the basal plane implying an orthorhombic symmetry in agreement with Raman scattering. All these observations suggest that the two ordered phases have certainly the same symmetry. Phase transformation between them is then expected to be reconstructive with a strong first order character. The recorded structural signatures indeed exhibit such an important metastability: for instance, by decreasing pressure at low temperatures, the high-pressure phase can still be observed at pressures close to the atmospheric one.

Elastic properties are very sensitive to structural modifications and provide for interaction changes through temperature or pressure anomalies. Sound velocity anomalies are related to the order parameter and conveniently studied by Brillouin scattering. Measurements were performed with an Ar ion laser (514.5 nm) and by using as frequency analyzer, a tandem of Fabry-Perot interferometers (Sandercock type) where each interferometer is triple passed giving a contrast larger than 10^{11}. 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 nonequivalent crystallographic directions. The variation

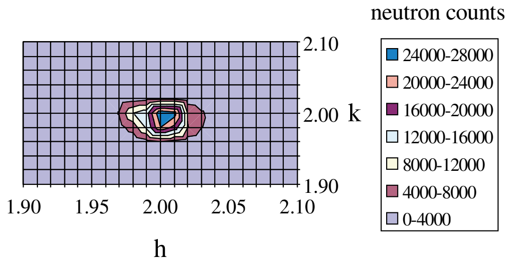

FIG. 4 (color online). Same as Fig. 3 except the pressure is 5.3 kbar.

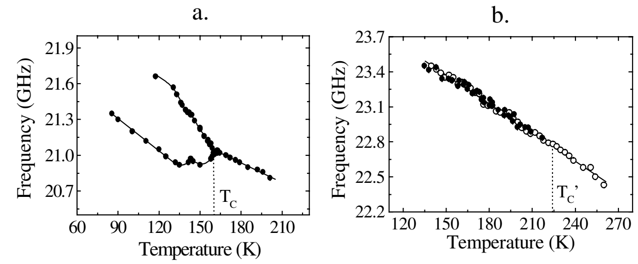

FIG. 5. Evolution of the longitudinal Brillouin shift vs pressure in the basal plane (a) at atmospheric pressure; (b) at 5 kbar, deduced from spectra recorded in a backscattering geometry (open and full symbols for increasing and decreasing temperatures).

of the Brillouin shifts, versus temperature or pressure, reflects the coupling between the order parameter and the deformations. Consequently, the study of the Brillouin shift versus temperature of the longitudinal acoustic mode propagating along a direction in the isotropic (**a**, **b**) plane can bring us information about the shearing of the high-pressure phase.

Experimental results are here presented at atmospheric pressure and 5 kbar only. At atmospheric pressure, Fig. 5(a) 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 5 kbar, no elastic anomaly and therefore no splitting is observed, 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 [20,21], the latter result shows that no large deformation characterizes the structure of the urea sublattice at high pressure. This result is in agreement with the metrics conservation reported above from neutron diffraction. Furthermore, it indicates that, on average, no significant urea reorientation occurs which could modify the elastic interactions at the scale of the phonon wavelength.

At high pressure, all these results prove that the large shearing is not the primary order parameter. Therefore, the importance of the guest molecules in this new kind of phase transition in nanoporous structures is probably predominant. A tentative explanation could involve the pressure induced conformation changes of the guests. The increase of the proportion of *gauche* conformers [11,22] could, perhaps, by a stronger steric hindrance, impede the shearing possibility of the host channels wall and generate this orthohexagonal phase. A further argument is also given by the behavior of the proportion of *gauche* conformers which, so far, seems to follow the metastability of the ordered high-pressure phase [11].

In conclusion, medium hydrostatic pressure appears as the dedicated tool to study the collective organization and the interactions in such a nanoporous host-guest material, yielding unexpected results concerning the actual interactions. A coherent interpretation of all these thermodynamic, structural, and dynamical results forces a total reconsideration of the interaction in these self-organized compounds. For the first time, this Letter shows 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. The fundamental observation reported here could be of essential importance when considering the interactions in more complex architectures involving mutually interpenetrating supramolecular or biological tubular networks.

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