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Céline Mariette, Laurent Guérin, Philippe Rabiller, Yu-Sheng Chen, Alexei Bosak, Alexander Popov, Mark D. Hollingsworth and Bertrand Toudic*

The creation of modulated monoclinic aperiodic composites in *n*-alkane/urea compounds

Abstract: *n*-Dodecane/urea is a member of the prototype series of *n*-alkane/urea inclusion compounds. At room temperature, it presents a quasi-one dimensional liquid-like state for the confined guest molecules within the rigid, hexagonal framework of the urea host. At lower temperatures, we report the existence of two other phases. Below T_c=248 K there appears a phase with rank four superspace group $P6_122(00\gamma)$, the one typically observed at room temperature in *n*-alkane/urea compounds with longer guest molecules. A misfit parameter, defined by the ratio $\gamma=c_h/c_g$ (c_{host}/c_{guest}), is found to be 0.632±0.005. Below T_{c1}=123 K, a monoclinic modulated phase is created with a constant shift along ***c*** of the guest molecules in adjacent channels. The maximal monoclinic space group for this structure is $P12_11(\alpha 0\gamma)$. Analogies and differences with *n*-heptane/urea, which also presents a monoclinic, modulated low-temperature phase, are discussed.

Keywords: alkane/urea crystals; aperiodic crystals; crystallographic superspace; diffraction; phase transitions.

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Introduction

Incommensurate composite crystal structures result from the intergrowth of two or more subsystems that have incommensurate lattice parameters in at least one direction in real space [1, 2]. These compounds are aperiodic by construction. To a first approximation, the diffraction pattern of such a structure consists of the main reflections of the first subsystem (often called host), the main reflections of the second subsystem (often called guest), and satellite reflections due to the subsystem interactions [1–5]. For uniaxial composites, which have a single incommensurate direction (***c***), the reciprocal image is characterized by a four-dimensional superspace description

$$\mathbf{Q}_{hklm}=h\boldsymbol{a}^*+k\boldsymbol{b}^*+l\boldsymbol{c}_h^*+m\boldsymbol{c}_g^*, \quad (1)$$

where $\boldsymbol{c}_h^*$ and $\boldsymbol{c}_g^*$ are, respectively, the independent host and guest reciprocal vectors.

According to the above construction, Bragg peaks from the commensurate ***a*****b** plane are indexed (*h k* 0 0) and are called common Bragg peaks; host diffraction peaks are indexed (*h k l* 0); guest diffraction peaks are indexed (*h k* 0 *m*); and finally, satellite peaks, which characterize the intermodulation of one substructure by the other, are indexed as (*h k l m*) with *l* and *m* ≠ 0. In the following, the structure is scaled to the host periodicity, so (*h k l* 0) Bragg peaks from the host are at integer positions along $\boldsymbol{c}^*=\boldsymbol{c}_h^*$.

Certain organic molecules can be co-crystallized with long-chain hydrocarbon molecules to form channel inclusion compounds [6–11]. In these materials, the guest chains are confined to narrow, approximately cylindrical channels created by the host. Prototype examples of such intergrowth crystals are the *n*-alkane/urea inclusion compounds ($(C_nH_{2n+2})/(CO(NH_2)_2)$), where the italic "*n*" refers to straight-chain (i.e., linear) guest molecules [11–15]. In these supramolecular systems, urea molecules build up a network of infinite, hexagonal, parallel channels with diameters of 0.53–0.58 nm [6]. Most of these materials exhibit incommensurate composite features since periodicity along the channel of the guest alkane does not fit rationally with the helical parameter of the host urea matrix (Figure 1). Direct evidence of the mutual intermodulation of the two substructures was demonstrated by the existence of satellite Bragg peaks in this family

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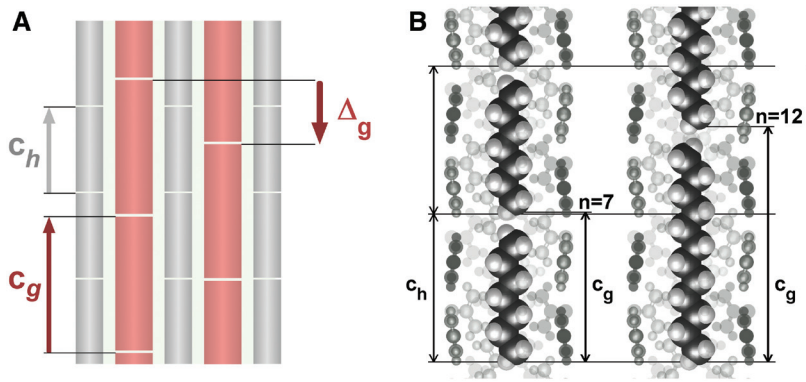

Fig. 1: (A) Definitions of the different parameters along the channel direction for a uniaxial composite made of ultimately confined guest molecules within a host subsystem (c_h (c_{host}), c_g (c_{guest}), and Δ_g, the relative shift of the guest chains from channel to channel); (B) the *n*-alkane/urea prototype family with n=7 (*n*-heptane/urea) and n=12 (*n*-dodecane/urea).

of inclusion compounds [16, 17]. It should be noted that the host lattice parameter c_h is essentially independent of the chain length of the alkane guest and is approximately 11.02 Å at room temperature. Years ago, Lenné found an empirical relationship between the guest repeat along the channel axis (c_g) and the number of carbon atoms in the alkane guest molecule [18]:

$$c_g(n)=[(n-1)\times 1.277+3.48]\text{Å} \quad (2)$$

This family of materials can be characterized by the ratio of host and guest periodicities along the channel direction. In the following, this value will be called the misfit parameter $\gamma=c_h/c_g$.

Dynamical and structural properties have already been investigated heavily by a variety of techniques [19–25]. Information on the "individual" dynamical disorder of guest molecules in the high-symmetry phase has been obtained by means of incoherent and coherent quasielastic neutron scattering, computer simulations, and deuterium and proton nuclear magnetic resonance (NMR). These studies demonstrated that in the high-temperature phase, guest molecules undergo both rapid reorientations about the channel axis and rapid, restricted translations along the channels. Such organic materials, with internal and/or external degrees of freedom, often present phase transitions well below room temperature. The family of *n*-alkane/urea inclusion compounds fulfills this condition and therefore presents a unique opportunity to explore sequences of phases within crystallographic superspaces [26–29]. As previously reported, most of these materials require four independent lattice parameters at room temperature, so these crystals are not periodic in three dimensions, the periodicity being recovered in four-dimensional crystallographic superspace. A systematic, theoretical analysis of all of the possible sequences of four dimensional superspace groups in urea inclusion compounds has been presented in the literature [26]. Here we compare the sequence of phases in two compounds, *n*-dodecane/urea and *n*-heptane/urea, which are made of rather short guest molecules.

Experimental details

Crystals of *n*-dodecane/urea were formed by heating a mixture of *n*-dodecane (1.47 g, Aldrich 99+%), urea (2.76 g, Sigma Ultra), methanol (43 mL, Fisher ACS) and isobutyl alcohol (10 mL, Fisher ACS) to 49°C and cooling slowly to room temperature. Even larger crystals were formed by evaporation at room temperature of this same solution over seven days after collection of a first crop of crystals. The first X-ray diffraction measurements were performed with laboratory equipment using a monochromated Cu-K_α radiation from a Nonius FR591 rotating anode source together with a Ge-111 bend monochromator and a high resolution Mar345dtb imaging plate (Marresearch GmbH). To achieve the required resolution and signal to noise ratio, synchrotron experiments were conducted on beamline 14-BM-C at the APS with an ADSC Quantum 315 CCD detector and on beamline ID23 at ESRF with a DECTRIS PILATUS 6M detector. In all cases, full data collections were performed with a single rotation axis and 1°, 0.8°, and 0.1° oscillations per frame, respectively, on the three devices given above. Reciprocal planes were reconstructed using CrysAlisPro software from Agilent Technologies.

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The quasi-liquid phase – Phase QL (T>248 K)

The reconstructed ***b**c*** plane, which was generated with room temperature data, is shown in Figure 2A. This image clearly reveals the host subsystem with strong Bragg peaks. On the other hand, the signature of the guest contains no Bragg peaks. The space group of the crystal can be assigned solely to the host structure and is hexagonal with space group $P6_122$, in agreement with the systematic absences of $l \neq 6n$ for the (0 0 *l*) line.

Many studies were previously devoted to *n*-alkane/urea crystals with rather long guest molecules [30–35]. In these materials, the mean value of the offset between guests in adjacent channels (defined by Δ_g in Figure 1) was found to be zero. In the case of short-chain guest molecules, the mean squared amplitude of the vibration along the channels is larger due to their lower mass and weaker interaction with the host, thus allowing new structures to be explored. Such large fluctuations may indeed destroy the interchannel guest ordering [10, 17]. Kim and co-workers recently reported translational diffusion of alkane guest molecules along the channels using pulsed field gradient NMR [36]. Such diffusion permits the use of such crystals as selective capillaries [37, 38]. From the diffraction point of view, the guest subsystem mainly appears as sharp, parallel diffuse planes, called s-planes by Boysen et al. [39, 40]. In the diffraction patterns of *n*-dodecane/urea at room temperature, such s-planes can be seen in reconstructions from synchrotron data using a Quantum 315 detector (Figure 2), but they are much more clearly evident in the synchrotron data using the PILATUS 6M detector (Figure 3). Similar observations have been reported in the literature for completely different materials [41–43]. Such disorder has been described as the "paracrystalline state."

The Fourier transform of a static, one-dimensional (1-D) system with long-range order is a set of diffuse Bragg sheets perpendicular to the 1-D axis. It is well known, however, that in real 1-D systems, no long-range order can exist: fluctuations broaden the Bragg diffraction peaks in the diffuse ("s") planes along ***c****. The intensities of the s-planes are not uniform perpendicular to the channel axis, due to some weak lateral ordering. We verified that this does not affect the broadening of these planes, their widths being independent of the position where they are measured. The width of these planes along the channel reciprocal direction is found to vary as the square of the order of the plane (*m*) [39]. Such a description of the experimental data, measured at room temperature on ID23 at ESRF, is presented in Figure 3. Using Gaussian lineshapes,

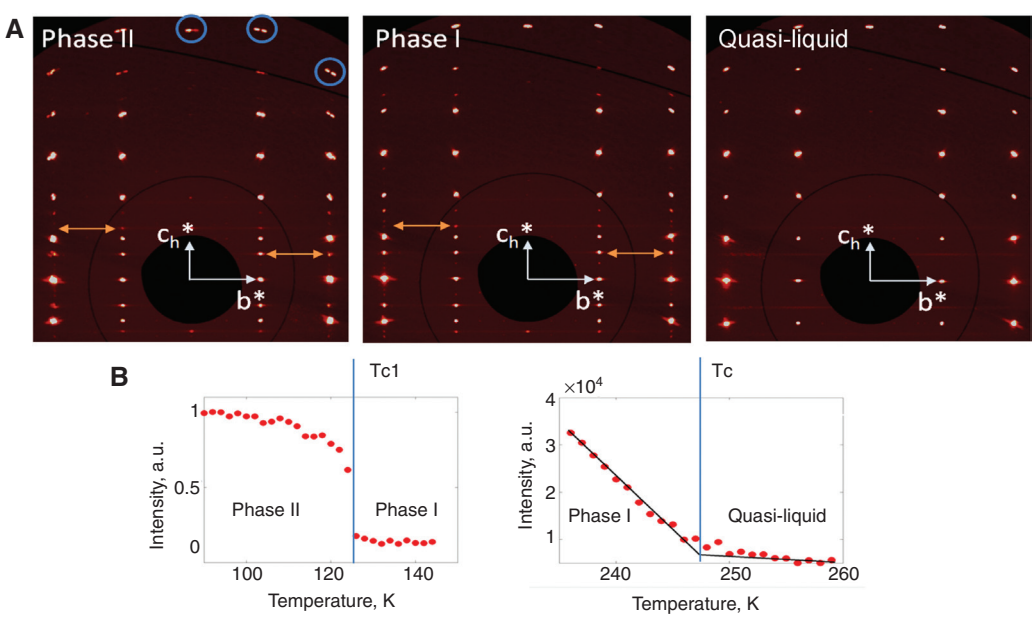

Fig. 2: (A) The reconstructed ***b**c*** plane as measured at the APS: right at room temperature, middle at 160 K, left at 80 K. In this figure, the circles point out some Bragg splitting resulting from a ferroelastic transition. In the left and middle images, double-headed arrows show the Bragg peaks that have appeared in these phases on the guest diffuse layer lines. (B) Right: temperature evolution of Bragg peaks appearing on s-planes as a signature of the creation of the four-dimensional aperiodic composite of *n*-dodecane/urea (extracted from laboratory data): a large set of Bragg peaks appearing in the first s-plane were integrated in order to obtain this curve. Of course the intensity does not vanish above T_{c1} since at this position remains the s-plane. The fit of the data in blue yields a transition temperature of T_c=248 K; left: evolution of the intensity of a set of new Bragg peaks appearing at alkane guest reciprocal positions in phase II (T_{c1}=123 K).

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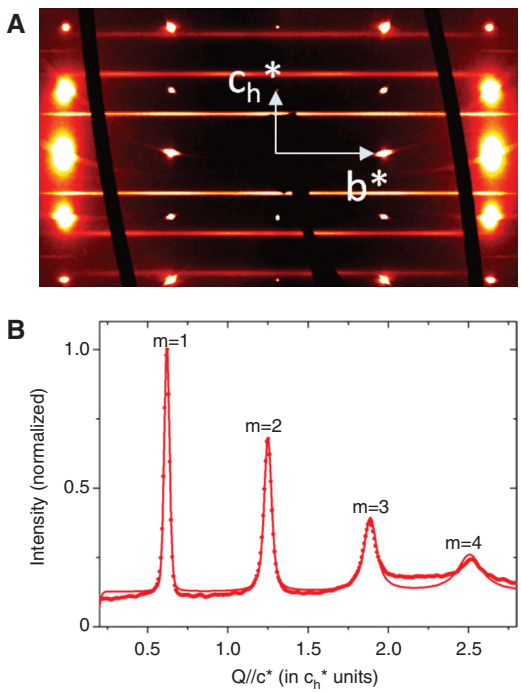

Fig. 3: (A) The reconstructed ***b**c*** plane from data collected at the ESRF ID23 beamline. (B) Profile along the ***c**** direction showing the broadening of the planes with their order *m*.

the data from four reconstructed diffuse planes were fit at mean positions that are multiple values of the misfit parameter (γ) of 0.63, which defines a mean guest repeat distance of 17.5 Å. Here, the mean squared displacement δ^2 of the guest molecule is linked to the width W along $\boldsymbol{c}^*$ of the s-plane of order m by the relation shown in equation 3, which is a function of the mean guest repeat distance:

$$W(m)=\frac{\pi^2 m^2}{\bar{c}_g^3}\delta^2 \tag{3}$$

The value of δ, which characterizes the liquid-like feature, is found to be 0.61 Å in *n*-dodecane/urea, in agreement with the those reported previously by Weber et al. in other *n*-alkane/urea compounds (n=14, 17) [39].

The hexagonal (248-123 K) and monoclinic (T<123 K) rank four phases

Figure 2A shows that below 248 K, a new phase (Phase I) emerges with a set of Bragg peaks corresponding to the periodicity of the guest along the incommensurate direction, indicating 3-D ordering of the guest subsystem. The temperature evolution of the intensity of one "guest" Bragg peak is shown in the right panel of Figure 2B and reveals a transition from the quasi-liquid guest state to a real four-dimensional host-guest composite. Close to the transition temperature, it is difficult to estimate the intensities of the guest Bragg peaks due to the large amount of diffuse scattering at the same position in reciprocal space. However, this phase transition appears to occur continuously, and the transition temperature (T_c) is found to be about 248 K, according to these data. Below this temperature, this rank four structure has a maximal hexagonal superspace group of $P6_122(00\gamma)$, according to the observed systematic extinctions. The value of the misfit parameter (γ) is found to be 0.632±0.005.

The left panel of Figure 2A reveals a different phase, called phase II. From the splitting of the Bragg peaks in this image (see circles), it is clear that this phase is characterized by a ferroelastic distortion. In phase II, the basic vector $\boldsymbol{a}$ is defined to be parallel to $\boldsymbol{a}_{hex}$. The transition from phase I to phase II can be monitored with two different signatures, the splitting of the structure Bragg peaks of the high temperature phase, and the appearance of superstructure Bragg peaks at *h+k odd* in the low symmetry notation. The intensity evolution of this last signature as function of temperature gives a transition temperature from phase I to phase II of T_{c1}=123 K. This value is in good agreement with the one reported in the literature (123.2 K) from differential scanning calorimetry [44]. In the low temperature phase, symmetry reduction gives rise to twinning, as demonstrated in the (*h*, *k*, 0, 1), (*h*, *k*, 0, 2) and (*h*, *k*, 0, 3) layers shown in Figure 4 (A, B, C and E) which reveals six $\boldsymbol{c}_g^*$ vectors. One of them, $\boldsymbol{c}_g^*=\alpha\boldsymbol{a}^*+\gamma\boldsymbol{c}_h^*$, is shown with red lines in Figure 4 (D and E). The six $\boldsymbol{c}_g^*$ vectors are independent, and a single domain is associated with each one. Indeed a domain characterized by a pair of vectors $\boldsymbol{c}_{g+}$ and $\boldsymbol{c}_{g-}$ is excluded since it would create a Bragg peak generated by the vector $\boldsymbol{c}_{g+}^*+\boldsymbol{c}_{g-}^*=2\gamma\boldsymbol{c}_h^*$ in the (*h*, *k*, 0, 2) position, which does not exist (Figure 4B). The measured α parameter is irrational and is found to be 0.160±0.002. In the limit of precision of our measurements, the value of α is found to be constant as function of temperature from 90 to 123 K. In this phase, all of the Bragg peaks can be indexed with the four basic vectors given in equation (1). This proves that the superspace dimension remains equal to four. The key feature of phase II is that the reciprocal vectors $\boldsymbol{c}_h^*$ and $\boldsymbol{c}_g^*$ are no longer parallel. This indicates that the two sublattices do not have the same mean crystalline system. Within the limit of precision of our measurements, the angle β_h of the host subsystem is found to be 90°. This subsystem could therefore be either orthorhombic or monoclinic with a very small distortion. As with the host in *n*-heptane/urea [45], the presence of a 2_1 screw axis (here along $\boldsymbol{b}$), the absence of C-centering, and the chirality of the structure excludes orthorhombic

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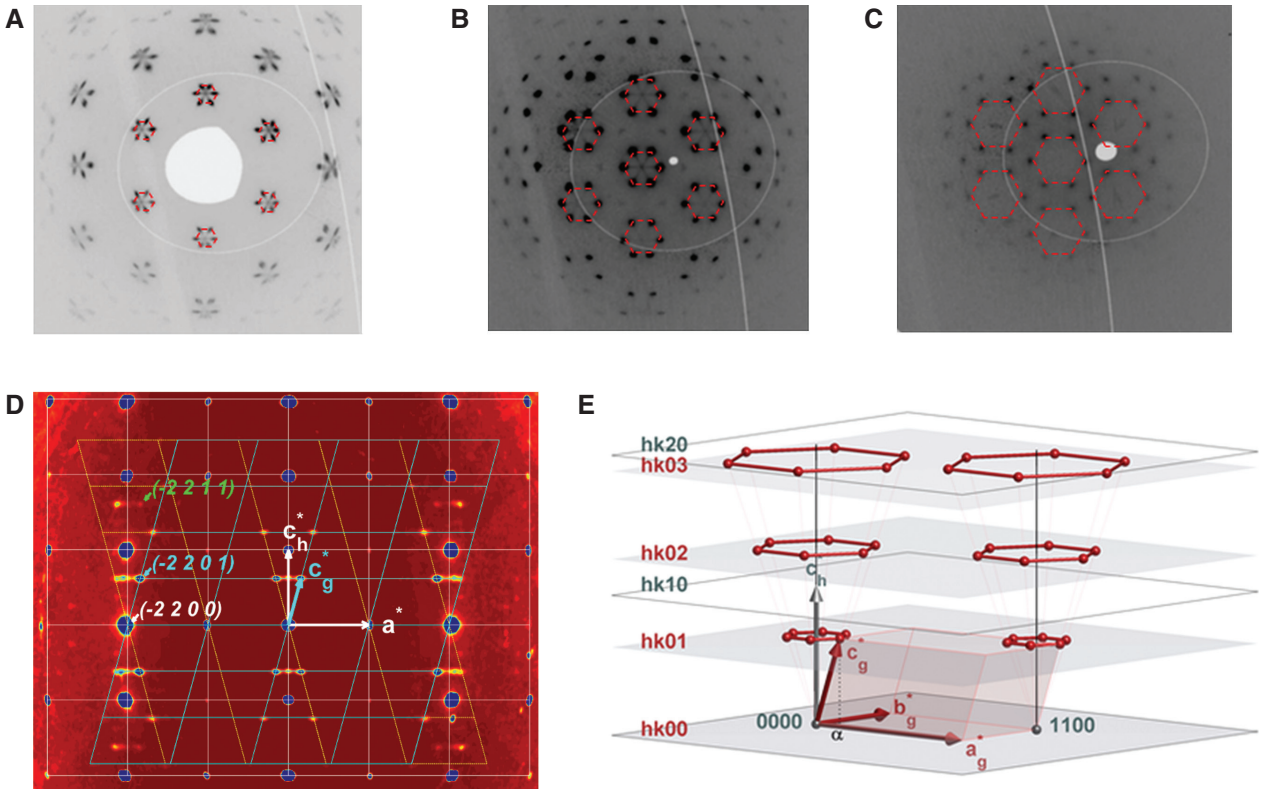

Fig. 4: (A), (B) and (c) Reciprocal planes (*h k* 0 *m*) with *m*=1 (A), 2 (B) and 3 (C) reconstructed from measurements in the low symmetry phase of *n*-dodecane/urea (T=100 K, 14-BM-C, APS). Red hexagons are guides for the eyes. (D) reconstructed (*h* 2 *l m*) plane of *n*-dodecane/urea in the same phase. The red lines represent the monoclinic cell, and the green arrow points to an intermodulation satellite. (E) 3-D schematic representation of the reciprocal space of *n*-dodecane/urea in the low symmetry phase.

space groups leads to space group $P2_1$ for the host. The observed systematic extinctions for *h*+*k* odd for (*h k o m*) Bragg peaks correspond to a centering of the guest subsystem. We can therefore assign it as the monoclinic space group C2, with the unique axis along the $\boldsymbol{b}^*$ direction. In this phase, the two subsystems are intermodulated, as revealed by the existence of intermodulation satellites characterized by *l* and *m* different from zero (Figure 4D). The four-dimensional superspace group, $P12_11(\alpha 0\gamma)$ is the maximal superspace group compatible with the observed extinction rules.

The low symmetry phase of *n*-dodecane/urea presents some similarity with the low symmetry phase of *n*-heptane/urea since both are described by a monoclinic rank four superspace group [45]. (Schematic representations of these systems are given in Figure 5.) However, the structural solutions are different since in *n*-dodecane/urea, the maximal monoclinic superspace group is $P12_11(\alpha 0\gamma)$, that is with the unique axis along ***b***, whereas in *n*-dodecane/urea, the maximal monoclinic superspace group is $P2_111(0\beta\gamma)$, with its unique axis along ***a***. In real space, the constant shift of the guest in *n*-dodecane/urea is along the "equivalent anthracene" direction, that is the ***a*** direction. In *n*-heptane/urea, the phase shift is along the "equivalent biphenyl" direction, that is the ***b*** direction. Of course, between these two compounds the main difference is the length of the guest molecule. According to our observed values, the misfit parameters γ are found to be constant as a function of temperature, with γ=0.981 for *n*-heptane/urea and γ=0.632 for *n*-dodecane/urea. These values, when referred to the room temperature parameter for urea (c_h=11.02 Å), yield guest repeat lengths of 11.23 Å and 17.44 Å, respectively, for *n*-heptane/urea and *n*-dodecane/urea. For *n*-heptane/urea, the phase transition at T_{c2} comes very close to a simple doubling of the unit cell parameter along the ***b*** direction. Indeed, the misfit parameter defined as the component along $\boldsymbol{b}^*$ (that is $\beta=2\Delta_g/c_g$) is 0.49 just below the transition temperature (T_{c2}=130 K) and evolves continuously away from this value down to 0.467 at 80 K. In related systems, the host repeat along the channel axis is known to vary quite gradually with temperature in this temperature range (about 0.02 Å per 100 K according to neutron diffraction data). Assuming a value of c_h=10.98 Å, c_g=11.19 Å, and the value of $2\Delta_g$ varies from 5.48 Å to 5.22 Å. The phase transition is then interpreted as the creation of a frustrated incommensurate monoclinic structure due to

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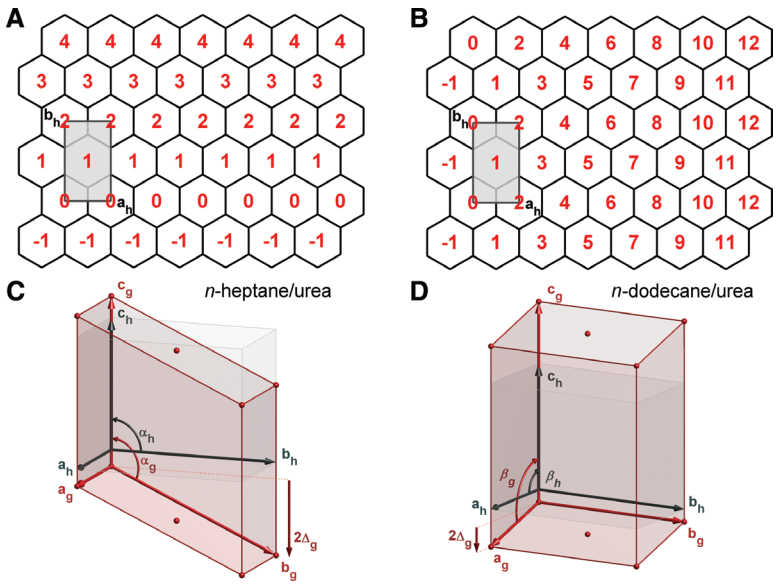

Fig. 5 Schematic real space representations of *n*-heptane/urea and *n*-dodecane/urea. (A) and (B) projections in real space along the *c* direction. The black hexagons represent the urea subsystem. The red numbers indicate the relative displacements of the guest molecules along ***c*** in Δ_g units. The black arrows indicate the basic vectors associated with the urea subsystem. (C) and (D) Schematic representation of the real unit cell associated with the host substructure in gray and the guest substructure in red, with an arbitrary shift of the two unit cells along ***c***. In the case of *n*-heptane/urea (C), the ratio $\gamma = c_h/c_g$ has been exaggerated to improve clarity.

the very small deviation of γ from the rational value of ½. In *n*-dodecane/urea, the misfit parameter defined as the (irrational) component along $\boldsymbol{a}^*$ (that is $\alpha = 2\Delta_g/c_g$) is 0.160. With the value of c_g equal to 17.40 Å, $2\Delta_g$ is found to be 2.78 Å. In *n*-dodecane/urea, the transition to Phase II is first order, as revealed by the temperature evolution of the new Bragg peaks (Figure 2B), and the value $2\Delta_g$ is found to be constant as function of temperature, in agreement with this discontinuous feature of the transition. No physical meaning can be attributed to the peculiar value of $2\Delta_g$ as long as the structure remains unsolved. Unfortunately, there are several serious issues with obtaining meaningful structural data in either of the two low symmetry phases. Most significantly, in the monoclinic phase, where one has the best chance to solve the structure because of the much smaller dynamic disorder of the guest molecules, the crystal exhibits six-fold non-merohedral twinning. To obtain sufficient data on the weak satellites without decomposing the crystal in the synchrotron beam, large crystals are required for these studies. This makes it difficult to scale the data properly for single crystal structure determination if the domains are not populated equally in different regions of the crystal. With regard to Phase I, because of the considerable static and dynamic guest disorder, there are no structures of alkane/urea inclusion compounds in the $P6_122(00\gamma)$ phase that have revealed any detailed information about the guest structure.

Conclusions

Many original phase transitions have already been experimentally observed in *n*-alkane/urea compounds. Short guest composites appear quite rich because they possess much larger mean square amplitudes of translation along the channels than longer guests. This is also why it has not been possible to obtain stable *n*-alkane/urea inclusion compounds with molecules shorter molecules than heptane. For *n*-dodecane/urea we show that at room temperature there is a liquid-like state for the guest subsystem confined within the rigid, hexagonal host matrix. In *n*-heptane/urea, a similar phase was reported with a second liquid-like phase within a monoclinic rigid matrix at lower temperature [45]. This is not observed in *n*-dodecane/urea, which presents a direct phase transition to the usual four-dimensional space group $P6_122(00\gamma)$. Of course, due to the different chain lengths, the transition temperature to the solid composite is at much higher temperature (T_c=248 K), in *n*-dodecane/urea than it is in *n*-heptane/urea. A fundamental feature of such aperiodic materials is that both host and guest subsystems never encounter the same local environment. In the superspace description this reflects the fact that the three-dimensional solution chosen by the crystal is the result of an arbitrary slice of the four-dimensional one. As a consequence, specific zero-energy motions along the internal direction are theoretically possible, neglecting defects. Such stable host

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matrices that confine short chain guests present promising opportunities for generating new kinds of phases that take advantage of the enhanced dynamical degrees of freedom associated with the guest molecules.

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