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Phase transitions within crystals that are aperiodic by construction

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Aperiodic crystals possess long-range order without translational symmetry. They constitute a state of matter that has forced a profound paradigm shift in solid-state physics. A common feature of aperiodic crystals is that they recover periodicity in higher dimensional spaces, the so-called crystallographic superspaces. Much work has been dedicated to the structural order within these superspaces and also to their specific dynamics. This paper focuses on the phase transitions within crystallographic superspaces. Aperiodic crystals are divided into three families: incommensurately modulated crystals, composite crystals, and quasicrystals. Incommensurately modulated crystals have been studied heavily and appear now to be relatively well understood, since they possess a periodic high-symmetry phase. The other two members of the family are aperiodic by construction. In this paper, we present a comprehensive and systematic study of a prototype composite host-guest family of *n*-alkane/urea inclusion compounds [$n-C_nH_{2n+2}/CO(NH_2)_2$]. For these materials, which exhibit a rich sequence of phases, the phase transitions are described in terms of group/subgroup symmetry breaking within crystallographic superspaces. Such phase transitions may decrease, increase, or maintain the dimension of the crystallographic superspace. These results highlight the multiplicity of specific structural solutions that aperiodicity offers.

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I. INTRODUCTION

Aperiodicity is found in a large variety of materials, including simple elements under pressure, minerals, oxides, high T_c superconductors, ferroelectrics, charge-density wave compounds, magnetic systems, intermetallic alloys, and organic molecular crystals. Such crystals are usually separated into three families [1–6]. Incommensurately modulated phases have an average three-dimensional periodic structure, but the atoms are periodically shifted from their average positions according to a modulation function with a period that is incommensurate with the periodicity of the basic structure. In contrast, incommensurate composite crystals are aperiodic by construction and are described as intergrowths of two or more idealized periodic substructures. The unit-cell dimensions of these substructures have a mutually incommensurate ratio in at least one direction and, moreover, interactions between them lead to incommensurate modulations in these substructures. Last, quasicrystals, which are also aperiodic by construction, present diffraction patterns with rotational symmetries that are incompatible with any translational invariance [5,7].

Periodicity has long been the foundation not only for crystallography but also for condensed-matter physics, whose fundamental tools and concepts, such as the Brillouin zone, are defined within the frame of periodicity. However, the presence of aperiodic long-range order means that the conventional theoretical models for physical properties can no longer be used. To restore periodicity, the concept of higher-dimensional superspaces of rank $= D+d$ was developed, where D is the dimension of the physical space and d refers to additional dimensions required for recovering periodicity [2–4,6]. Thus, the dimension (rank) of a crystallographic superspace is the number of independent vectors defining the basis vectors. Within a crystallographic superspace, each atom corresponds to a function defined along the d dimensions of this superspace (the so-called internal dimensions of the superspace). The basis of the reciprocal superspace has the same definition as in periodic crystals: $\boldsymbol{a_i} \cdot \boldsymbol{a_j}^* = 2\pi\delta_{ij}$ where δ_{ij} is the Kronecker delta function, with i and j varying from 1 to $D+d$.

Superspace crystallography is now well established, but one central question remains: "What are the rules that govern phase transitions from one aperiodic structure to another?" The question of phase transitions has been explored in the

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case of incommensurately modulated crystals, which have a periodic high-symmetry phase that greatly simplifies analysis. There, the concept of frustration plays a major role in the evolution of phases exposed to different temperatures or other external fields. For this class of materials, phase transitions may be well described by Landau theory, in which there is a group-subgroup relationship between the periodic high-symmetry phase and the incommensurate phase [1,4,6,8]. The problem is much more complex when the crystals are aperiodic by construction, such as aperiodic composite crystals and quasicrystals. Unlike incommensurately modulated crystals, where the modulation is treated as a perturbation of the periodic mean structure, with aperiodic composites, there are two intermodulated lattices, one for the host and another for the guest [4,9–12]. The host lattice is generally taken as the mean structure, since it tends to dominate the overall crystal symmetry. However, because the guest is not a perturbation but a separate lattice, which may or may not have the same symmetry, there may be limitations to applications of a formalism in which a single superspace group is used to describe the composite crystal [9,10]. This is a consequence of weak coupling between host and guest substructures with different symmetries, and in such cases, the host and guest structures are assigned to different superspace groups. For example, in one phase of the aperiodic composite of *n*-heptane and urea, the guest structure is C centered, even though the host adopts a primitive structure [13].

Nevertheless, application of a single superspace group using the host as the mean structure can provide much insight into the diffraction patterns and phase transitions exhibited by a given aperiodic composite compound, even if it is not a perfect description of the full crystal. Here we show how this approach, applied to a homologous series of aperiodic composite crystals, provides a unique opportunity to uncover unexpected sequences of phases within crystallographic superspaces.

II. APERIODIC COMPOSITE CRYSTALS

Aperiodic composites [4,6,9,12,14–17], which include channel-type composite crystals [15–17], have been studied extensively. In the organic channel inclusion compounds considered here, urea cocrystallizes with long-chain hydrocarbons and substituted analogs [18–20]. The long-chain guest molecules are confined to narrow, approximately cylindrical channels created by the urea host substructure. Prototype examples of such intergrowth crystals are the *n*-alkane/urea $[n-C_nH_{2n+2}/CO(NH_2)_2]$ inclusion compounds shown in Fig. 1. In this paper, we report results for these inclusion compounds from *n*-heptane/urea ($n = 7$) to *n*-tetracosane/urea ($n = 24$). In these supramolecular systems, urea molecules are hydrogen-bonded in helical arrays to generate a honeycomblike host network of infinite and parallel channels, with van der Waals diameters of approximately 5.5–5.8 Å [21], and a helix repeat of $c_h = 11.02$ Å at room temperature. The separation between channels, at room temperature, is $a_{\text{hex}} = 8.2$ Å. Apart from *n*-eicosane/urea ($n = 20$), which is commensurate by construction [22], *n*-alkane/urea inclusion compounds normally exist as incommensurate composites because host-guest interactions are

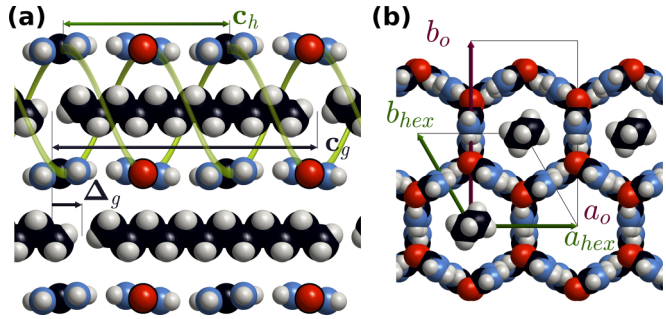


FIG. 1. Schematic representation of an *n*-alkane/urea inclusion compound. (a) View perpendicular to the channel axis of a sample compound, showing the periodicities of the urea host, c_h, and *n*-alkane guest, c_g, substructures. The offset between neighboring guest molecules in adjacent channels is defined as Δ_g. (b) View along the channel axis showing the unit cell axes of the high-temperature hexagonal phase and a conventional low-temperature orthorhombic one, here showing an example of ferro ordering of the guests (with the mean planes of the alkane backbones being parallel in adjacent channels).

weak. Thus the ratio of guest and host periodicities along the channel, given by the misfit parameter $\gamma = c_h/c_g$, is only rarely equal to a low denominator rational number. Using high-resolution diffraction techniques, we have measured the misfit parameter γ, at 260 K, as depicted in Fig. 2. In this figure, the continuous line corresponds to the function $\gamma = c_h/c_g$, where $c_h = 11.02$ Å and $c_g = [1.270\,(\text{n}-1) + 3.658]$Å. It is consistent with the one derived previously by Lenné *et al.* for a different range hydrocarbon chain lengths [23]. With the exception of $n = 8$ and 11, which become commensurate on cooling (discussed below), these misfit parameters remain constant across the range of temperatures measured between 260 K and 80 K. Several other members of this series are very close to commensurate at 260 K ($n = 7$, 16, 24), but remain incommensurate on cooling. Only for *n*-eicosane/urea

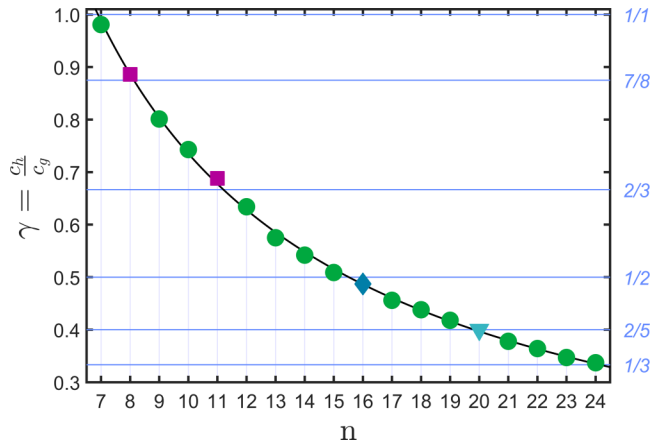


FIG. 2. Evolution of the misfit parameter γ in *n*-alkane/urea inclusion compounds as a function of the number of carbon atoms (n) in the *n*-alkane guest molecule. Apart from $n = 8$ and 11, the misfit parameter remains constant across the range of temperatures measured. For $n = 16$, the crystal becomes commensurate under hydrostatic pressure. For $n = 20$, the crystal is periodic by construction.

($n = 20$) is this parameter found to be a rational fraction ($\gamma = 2/5$) at room temperature and below. Here, the commensurate rank-3 structure has $c = 55.1$ Å at room temperature and the period of two n-eicosane molecules exactly equals the period of five turns of the urea helix [22].

Dynamical and structural properties of urea inclusion compounds have been investigated with a wide variety of techniques. Information on the individual dynamical disorder of guest molecules in the high-symmetry hexagonal phase has been obtained by means of incoherent and coherent quasielastic neutron scattering [24,25] and ^{2}H nuclear magnetic resonance [26–29]. These measurements demonstrate that in the high-symmetry phase, guest molecules undergo both rapid reorientations about the channel axis and rapid, restricted translations along the channels. At first, much of the literature concerning phase transitions of n-alkane/urea inclusion compounds was limited to the three-dimensional space based on the host lattice, neglecting the aperiodicity of the composite. The phase transitions in all these compounds were considered to be of a single type, a symmetry lowering from the hexagonal $P6_122$ space group to the orthorhombic $P2_12_12_1$ [30–35]. However, observation of satellite peaks, indicating long-range guest and host intermodulation within these composites [36,37], led us to consider their phase transitions within higher dimensional spaces, the so-called crystallographic superspace.

III. SYMMETRY BREAKING IN CRYSTALLOGRAPHIC SUPERSPACE

The present paper is based on high-resolution diffraction studies, many of them already discussed in the literature [13,38–46]. The guest molecules concerned are the linear molecules of n-heptane ($n = 7$), n-octane/urea ($n = 8$), n-nonane/urea ($n = 9$), n-decane/urea ($n = 10$), n-dodecane ($n = 12$), n-hexadecane ($n = 16$), n-octadecane ($n = 18$), n-nonadecane ($n = 19$) and n-tetracosane ($n = 24$). Results concerning the other compounds of the n-alkane/urea family are given in Ref. [47]. The structural characteristics of all the compounds were first determined with x-ray diffraction measurements using monochromatic Cu $- K\alpha$ radiation from a rotating anode source and a high-resolution mar345dtb imaging plate detector (Marresearch GmbH) at the Institut of Physique in Rennes. The richness of the phase transition paths observed in n-alkane/urea inclusion compounds has been summarized in the superspace group/subgroup tree shown in Fig. 3, where the numbers 7–24 refer to the number of carbons, n, in the linear alkane guest with formula $n - C_nH_{2n+2}$. Each color corresponds to a different maximal space group or maximal superspace group. In each case, the maximal superspace group was assigned by evaluating the systematic absences of Bragg peaks to determine the one of maximal allowed symmetry. This diagram is a generalization of Landau theory for group/subgroup phase transitions within crystallographic superspace for crystals that do not possess translational symmetry by construction. The phases are separated along the horizontal by their crystal system (hexagonal, orthorhombic, and monoclinic) and along the vertical by the dimension (rank) of crystallographic superspace ($3 + 0$, $3 + 1$, and $3 + 2$).

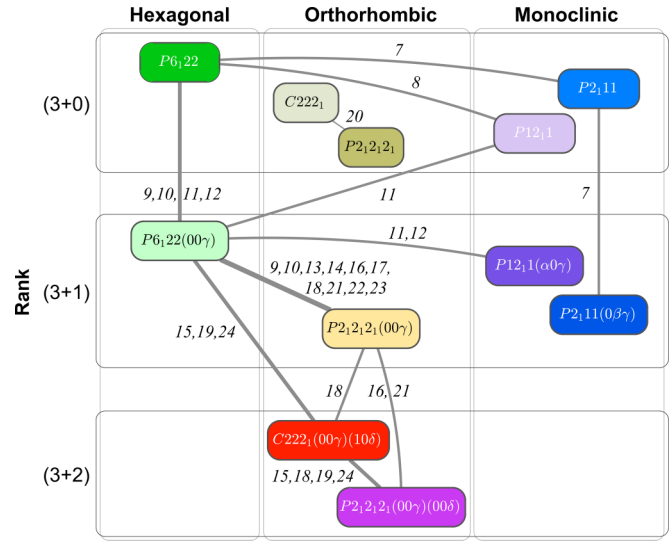


FIG. 3. The superspace group-subgroup tree of n-alkane/urea inclusion compounds. Numbers next to lines indicate which compounds exhibit that phase transition, given as the number of carbon atoms (n) in the n-alkane guest molecule. Color coding of phases is the same as in Fig. 4. The different superspace groups are discussed in the text.

To understand why a group/subgroup phase transition may be associated with an increase in the dimensionality of crystallographic space, we must bear in mind that a D+0 dimensional crystal may be described in a D+d dimensional space in which there are no supplementary modulations along the d internal dimensions of the superspace. This was done implicitly when describing phase transitions of incommensurately modulated crystals within Landau theory [1]. The development of an incommensurate phase is associated with an instability of a particular normal mode of the high symmetry space group [1]. Relations between groups allow subgroups according to the critical wave vectors of the incommensurate phase [48], the high temperature phase being embedded in a superspace of the same dimension as the incommensurate one [11]. Accordingly, there is a group/subgroup phase transition between a D+0 dimensional space group (the high-symmetry periodic crystal) and the corresponding D+d superspace group of lower symmetry.

The modulation along each of the d dimensions is characterized by a complex order parameter $Ae^{i\phi}$, where A is the amplitude of the structural modulation and ϕ is its phase, yielding the amplitudon and phason modes, respectively [1]. The amplitude A goes to zero at the transition temperature to the high-symmetry phase. Thus, periodic D+0 crystals may be described as a particular case within crystallographic superspace, i.e., D+d crystals in which the amplitudes of the supplementary modulations along the d dimensions are zero. In this paper, this concept is generalized to crystals that are already aperiodic by construction (here of $3 + 1$ dimension), regarding them as being described in $3 + 2$ five-dimensional superspace, with the amplitude of the modulation in the fifth dimension becoming nonzero at the phase transition.

As shown in Fig. 3, incommensurate n-alkane/urea crystals exhibit two distinct high symmetry hexagonal phases (in

dark green and light green). For each of the shortest guests (n = 7–12), there are no Bragg peaks associated with the guest periodicity, and the diffraction signature of the guest substructure occurs only as diffuse planes perpendicular to the channel axis. Here, the guests have only one-dimensional paracrystalline order along the channel and no long-range order between guests in adjacent channels. The space group assignment can then be attributed solely to the host subsystem and is found to be hexagonal $P6_122$ or its enantiomorph $P6_522$ (dark green in Fig. 3).

A different structural solution is found for longer guests ($n \geqslant 13$). Except for the commensurate $3+0$ structure of n-eicosane/urea ($n = 20$), these materials are $3+1$ incommensurate composites at 260 K, exhibiting Bragg peaks at host, guest, and satellite positions. Such incommensurate composites are described by the following rank-4 superspace basis:

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

in which $\boldsymbol{a}^*$ and $\boldsymbol{b}^*$ are the conventional reciprocal unit cell vectors, shared by both substructures, while $\boldsymbol{c}_h{}^*$ and $\boldsymbol{c}_g{}^*$ are those of the host and guest, respectively. In this four-dimensional basis, Bragg peaks may be crudely separated into four classes: peaks from the commensurate ($\boldsymbol{a}^*$, $\boldsymbol{b}^*$) plane are indexed (h k 0 0) and are called common Bragg peaks; host peaks are indexed (h k l 0); guest peaks are indexed (h k 0 m), and, finally, satellite peaks, which characterize the intermodulation of one substructure with the other, are indexed as (h k l m) with l and $m \neq 0$. Intensities of host and guest peaks may contain contributions from both substructures; that is, host peak intensity does not necessarily arise exclusively from scattering by the host, and guest peaks may contain contributions from the host substructure. These crystals are described by a rank-4 superspace group $P6_122(00\gamma)$ (light green in Fig. 3). The suffix (00γ) means that the guest periodicity along $\boldsymbol{c}$ is $c_g = c_h/\gamma$ and that $\boldsymbol{c}_h{}^*$ and $\boldsymbol{c}_g{}^*$ are parallel. In real space this implies that the mean value of the offset between neighboring chains in adjacent channels, as defined in Fig. 1, is $\Delta_g = 0$.

Upon cooling from room temperature, three main features are revealed concerning the phase transitions in these composite crystals. The first corresponds to a transition to monoclinic symmetry. This is observed in compounds with short-chain guests, which present a larger translational degree of freedom along the channels (n = 7, 8, 11, 12). We note that one of them ($n = 11$) locks in to a commensurate structure and is then described by a monoclinic three-dimensional space group, thus exhibiting a decrease in the dimension of the crystallographic space. Others create monoclinic intermodulated composites described by four-dimensional monoclinic superspace groups [13,38]. The second set of compounds present phase transitions that maintain the four dimensions of crystallographic superspace and correspond to transitions from the hexagonal superspace group $P6_122(00\gamma)$ to the orthorhombic $P2_12_12_1(00\gamma)$. More surprising is the third set, which presents an increase in the dimension of the crystallographic superspace from 4 to 5 (n = 15, 16, 18, 19, 21, 24). As developed above, these phase transitions are described by group/subgroup relations with the appearance of a supplementary modulation $Ae^{i\phi}$ along the aperiodic channel

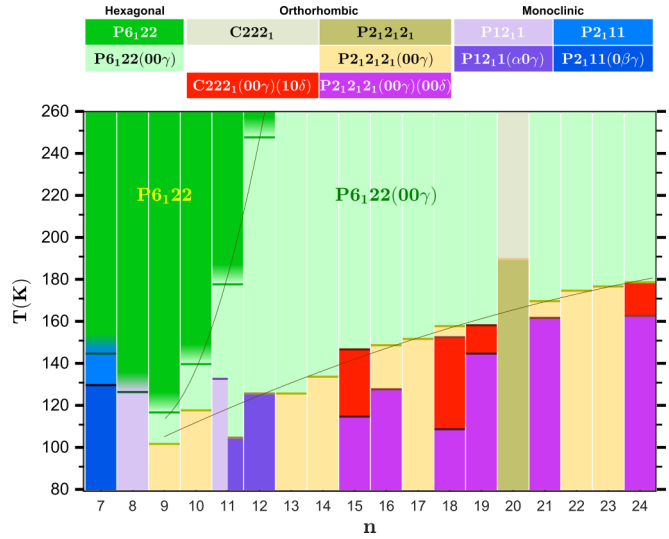


FIG. 4. Phase transitions in n-alkane/urea inclusion compounds, showing the sequence of structural phases in crystallographic superspace as a function of the number of carbon atoms in the guest molecules versus temperature. Superspace groups with maximal symmetry allowed by the systematic absences are indicated. Curved lines are a guide for the eyes. The top line separates the order-disorder transitions for the guest molecules between a one-dimensional quasiliquid with no long-range guest order perpendicular to the channel (dark green, $P6_122$) and ordered guest exhibiting Bragg peaks [light green, $P6_122(00\gamma)$]. The bottom line indicates the ferroelastic phase transitions from hexagonal to orthorhombic or monoclinic. Color coding for the phases is the same as in Fig. 3.

direction within the four-dimensional superspace [39–43]. In this five-dimensional crystal, there is a supplementary reciprocal unit cell vector along the direction of the aperiodic modulation, $\boldsymbol{c}_m{}^*$, and the basis is

$$\boldsymbol{Q}_{hklmn} = h\boldsymbol{a}^* + k\boldsymbol{b}^* + l\boldsymbol{c}_h{}^* + m\boldsymbol{c}_g{}^* + n\boldsymbol{c}_m{}^*. \quad (2)$$

As already discussed in the literature [40–44,49–53], this supplementary modulation doubles the unit cell within five-dimensional superspace. Two cases are encountered: a C-centered superspace group $C222_1(00\gamma)(10\delta)$ and the lower symmetry $P2_12_12_1(00\gamma)(00\delta)$. The main point is that all of the phase transitions shown in Fig. 3 correspond to group/subgroup phase transitions using superspace crystallography when applied to crystals that are aperiodic by construction. This corresponds to an extension of the group/subgroup Landau theory previously applied to periodic crystals that either remain periodic or become incommensurately modulated.

Figure 4 maps these sequences of phases present in n-alkane/urea inclusion compounds between 260 and 80 K (using the same color coding for the various phases as in Fig. 3). The figure shows two general trends, represented by the curved lines, both of which decrease in temperature toward shorter guests. These trends can be attributed to the shorter alkane molecules being more mobile within the crystal. The top-left line separates the order-disorder transitions for the guest molecules between a one-dimensional quasiliquid in

$P6_122$ and a phase with ordering of the guest molecules that exhibit Bragg peaks in $P6_122(00\gamma)$. Bottom line indicates the ferroelastic phase transitions [54] from hexagonal $P6_122(00\gamma)$ to orthorhombic or monoclinic symmetry (where ferroelastic refers to the appearance of a spontaneous strain tensor, here, a distortion away from hexagonal metric symmetry, upon cooling). Note that these trends are reversed for the shortest guests $n = 7$ and 8, their phase transition temperatures being higher than expected. Without results for even shorter guest lengths (because crystals with $n < 7$ are so unstable), it is difficult to say whether this reversal is the beginning of a different regime of host-guest interactions, or simply that $n = 7$ and 8 are outliers. The particularities of their phase transitions are discussed below.

In most cases, within experimental error, the phase transition temperatures were the same on cooling and heating. However, hysteresis was observed for *n*-octadecane/urea and *n*-tetracosane/urea in the transitions between the rank-5 *C*-centered and rank-5 primitive phases. The phase transition temperatures on cooling are shown in Fig. 4. On heating, the phase transition temperatures are 122 K for $n = 18$ (higher by 13 K), and 175 K for $n = 24$ (higher by 12 K).

A. Transitions within superspace

For guest alkane molecules with $n \geqslant 9$, the ferroelastic phase transitions are much more diverse than shown in previous analyses as a function of the guest length [30–35]. The description in terms of symmetry breaking within crystallographic superspace reported here present a significant departure from the prior literature, revealing a multiplicity of possible structural solutions and several different sequences of phases. Several compounds exhibit original sequences of phases that go from rank 4 to rank 5 upon cooling. For example, in *n*-hexadecane/urea the sequence is from rank-4 $P6_122(00\gamma)$, to rank-4 $P2_12_12_1(00\gamma)$, to rank five $P2_12_12_1(00\gamma)(00\delta)$ [39,49,50].

More intriguingly, three compounds ($n = 15$, 19, 24) show a transition from rank-4 $P6_122(00\gamma)$ to a *C*-centered rank-5 $C222_1(00\gamma)(10\delta)$ structure, where (10δ) signifies that the phase of the supplementary modulation alternates by $c_m/2$ between adjacent channels along the $\boldsymbol{a}$ axis (or for the alternate setting, with (01δ), along the $\boldsymbol{b}$ axis [45]). The crystallographic signature of this phase is the appearance of a supplementary modulation, characterized by $h + k =$ odd Bragg peaks indexed as $(h\ k\ l\ m\ n)$ with $h + k + n =$ even. Here, common, host, and supplementary intermodulation peaks are all systematically absent for $h + k + n =$ odd, due, in part, to the *C*-centered host structure. The crystallographic superspace groups of five dimensions have been discussed in Ref. [55] and tabulated in Ref. [56]. According to Ref. [56], the superspace group of rank 5 that fulfills the given condition $(h\ k\ l\ m\ n) : h + k + n$ even is number 20.2.24.2: $C222_1(00\gamma)(10\delta)$. Note, however, that guest peaks $(h\ k\ 0\ m\ 0)$ with $h + k =$ odd are present in this phase, indicating that the guest structure is primitive with orthorhombic metric symmetry. (This is the opposite of what was observed for phase III in *n*-heptane/urea, where the guest substructure was *C* centered and the host substructure was primitive [36].) The systematic absence of only $h + k =$ odd common peaks for the guest sublattice therefore gives its maximal space group as either $Pm2_1n$ or $P2_1mn$ (both having equivalent systematic absences). These space groups, however, require the guest molecules to be disordered equally, and symmetrically about the mirror plane. More generally, space group $P11n$, or a structure with guests in neighboring channels being related by a translation of $\boldsymbol{a_o}/2 + \boldsymbol{b_o}/2$, would satisfy the observed systematic absences with no requirement for specific guest disorder. In any of these four cases, the mean planes of the guest backbones are necessarily parallel in neighboring channels [ferro ordering, cf. Fig. 1(b)]. The presence of guest peaks with $h + k =$ odd was not evident at the time of prior publications [40,41,43–45], but reexamination of the data shows that these phases are even more complex than previously thought, highlighting the breadth of structural solutions available in aperiodic composites.

Upon further cooling, all three of these compounds ($n = 15$, 19, 24) lose the centering of the five-dimensional supercell to give the five-dimensional superspace group $P2_12_12_1(00\gamma)(00\delta)$. The value of the supplementary modulation misfit parameter δ is found to be the same in both phases and is independent of temperature. The most heavily studied compound that exhibits this sequence of phases is *n*-nonadecane/urea [41,42,44,45].

Our studies of pretransitional diffuse scattering and phase behavior in *n*-octadecane/urea show how competing order parameters give rise to an unusual sequence of phase transitions. On cooling, critical scattering for a rank-4 $P2_12_12_1(00\delta)$ phase and a rank-5 $C222_1(00\gamma)(10\delta)$ phase grow concurrently. The $P2_12_12_1(00\gamma)$ phase grows more steeply and dominates in a narrow temperature range before $C222_1(00\gamma)(10\delta)$ becomes the dominant long-range order on further cooling. Finally, the crystal transitions to rank-5 $P2_12_12_1(00\gamma)(00\delta)$ at the lowest temperatures [40]. We note that in each phase of *n*-octadecane/urea, the (0 0 0 1 0) guest reflection is present, indicating that the guest structure does not have a 2_1 screw axis along $\boldsymbol{c}$. (This is analogous to all known *n*-alkane/urea inclusion compounds with host superspace group $P6_122(00\gamma)$, where the guest structure exhibits violations of the 6_1 screw axis along the channel [17].) If the common peaks in the lowest temperature phase of *n*-octadecane/urea contain contributions from both host and guest substructures, then the maximal space group for the guest in this phase is $P2_12_12$.

The problem of the deviation from systematic extinctions in *n*-alkane/urea compounds was already raised many years ago [57]. The authors reported a Bragg peak that was forbidden along the $\boldsymbol{c}^*$ direction according to the assigned space group. From appropriate crystallographic measurements, they were able to attribute part of it to "Umweganregung" diffraction, the Renninger effect. However, the higher mobility of the terminal methyl groups of the *n*-alkane molecules was also considered as a possible explanation for the deviation from perfect symmetry. Further studies should be done to elucidate this delicate problem.

From these observations, we can postulate that the varying strength of interaction between the host and guest substructures as a function of temperature is at the core of the phase transitions through the $C222_1(00\gamma)(10\delta)$ phase. In this phase, the choices of maximal space group for the guest are $Pm2_1n$,

$P2_1mn$, or $P11n$, as discussed above. Crucially, these guest space groups are polar but achiral, in contrast with the nonpolar, chiral structure of the host. The dissimilarity of these two structures is a plausible cause of frustration, the effect of which is dependent on the level of host-guest interactions at that temperature. For example, in the $C222_1(00\gamma)(10\delta)$ phase, the host-guest interactions could be sufficiently weak to allow both types of structure to coexist, but at lower temperatures the interaction should be stronger, such that the host imposes its symmetry on the guest, whose maximal $P2_12_12$ space group now shares the nonpolar and chiral 222 point symmetry of the $P2_12_12_1(00\gamma)(00\delta)$ host.

B. Transitions with lock-in

Upon cooling to 133 K, *n*-undecane/urea exhibits a thermal lock-in to a commensurate structure [47]. Further studies on large facilities (ESRF, beamline ID23) revealed additional original behavior (to be published); the misfit parameter changes discontinuously from an irrational value with $\gamma = 0.675$ to the commensurate value of $\gamma = 2/3$ at the phase transition. In this transition, the rank of the space group decreases from four to three and goes from $P6_122(00\gamma)$ to the monoclinic space group $P2_1$. Some regions of the crystal remain incommensurate, and at a lower temperature they become monoclinic with superspace group $P2_111(0\beta\gamma)$, the same space group as the low temperature phase of *n*-dodecane/urea (as shown below).

Concerning *n*-octane/urea, the superspace description of its structure at room temperature has been published [58]. *n*-Octane/urea presents a single and direct transition from $P6_122$, in which the one-dimensional quasi-liquid state of the guests gives only diffuse scattering [46], to a commensurate rank-3 space group $P12_11$ exhibiting Bragg scattering from the guest [47]. Additional measurements have been performed on large facilities (APS, beamline 14 BM-C and ALS, beamline 8.2.2.) (to be published); they give a reliable value for the mean guest periodicity ($\gamma = 0.886$) above the phase transition at 121 K. At the transition, this system undergoes a thermal lock-in, this time to a commensurate structure with $\gamma = 7/8$ (0.875). Surprisingly, the low-temperature monoclinic phase remains metrically hexagonal; therefore, unlike other alkane/urea inclusion compounds, this system does not undergo a ferroelastic phase transition at the temperatures studied. This phase transition seems to be sample and cooling-rate dependent, with some crystals exhibiting mixtures of commensurate and incommensurate phases while others remain incommensurate.

In aperiodic crystals, lock-in requires a relative change of the periodicities of the sub-systems. In both *n*-octane/urea and *n*-undecane/urea, the host repeat c_h does not change during lock-in, so a change in γ equates only to a change of the guest repeat length ($c_g = c_h/\gamma$). Although the individual change in c_g is quite small, when added together over the length scales of a domain sufficiently large to give Bragg diffraction, this requires large-scale cooperative translation of the guests along the channels [59] on the order of tens of angströms. As a result, even for a small change in c_g the driving forces have to be significant. Hence, lock-in is quite rare across the *n*-alkane/urea series, despite several of them having γ close to a commensurate ratio. Note that in both of these cases, a decrease of the misfit parameter is observed upon lock-in, meaning the guest repeat length increases. In this way, thermal lock-in reveals the opposite effect of lock-in observed for *n*-hexadecane/urea under hydrostatic pressure, where there is an increase in γ, due to a decrease in c_g (see Fig. 2) in Ref. [60]. In contrast with these aperiodic composites, the incommensurate to commensurate phase transition in incommensurately modulated crystals involves only small displacements of individual atoms from their mean positions within the periodic unit cell [61]. This delicate balance of frustrated forces in incommensurately modulated crystals is generally overcome upon cooling and often leads to low-temperature commensurate phases [1].

C. Transitions to intermodulated aperiodic monoclinic composites

The ferroelastic phase transition in *n*-heptane/urea ($n = 7$) is unusual [13,38]. In the first place, it occurs at 145 K, a much higher temperature than expected based on the trends represented by the curved lines in Fig. 4. Both above and below this phase transition, the guest structure remains as a quasiliquid, and this phase transition is simply associated with the host structure, which moves from rank-3 hexagonal $P6_122$ to rank-3 monoclinic $P2_111$. Upon further cooling to 130 K, the system undergoes a phase transition to an intermodulated aperiodic monoclinic composite in which the guest exhibits long-range order, and the dimensionality of the crystal increases from rank 3 to rank 4. For this phase, the superspace group is $P2_111(0\beta\gamma)$ and the guest molecules exhibit an offset relative to those in neighboring channels ($\Delta_g \neq 0$), as shown in Fig. 5 from Ref. [38]. The misfit parameters $\alpha = 2\Delta_g/c_g$ and $\beta = 2\Delta_g/c_g$ are the projected components of the reciprocal $\boldsymbol{c}^*$ vector on $\boldsymbol{a}^*$ and $\boldsymbol{b}^*$ for *n*-dodecane/urea and *n*-heptane/urea, respectively. For *n*-heptane/urea, the misfit parameter β decreases continuously from 0.49 at the 130 K phase transition to 0.467 at 80 K [13]. Since $\Delta_g = (\beta c_g)/2$ this means that at different temperatures, the guests in neighboring channels have different offsets relative to each other [see Fig. 1(a)]. This corresponds to a gradual sliding of guest molecules along the channel while maintaining their periodicity along the channel (γ).

The low-temperature phase of *n*-dodecane/urea ($n = 12$) is similar to that of *n*-heptane/urea, also having $\Delta_g \neq 0$, but this time the high-temperature phase above it is rank 4, meaning the guests already have long-range order in all directions [38]. When cooled below 123 K, the space group goes from $P6_122(00\gamma)$, where $\Delta_g = 0$, to $P12_11(\alpha 0\gamma)$ where $\Delta_g = (\alpha c_g)/2$. Thus, the guest molecules abruptly translate along the channels to have a fixed displacement relative to those in neighboring channels, again without changing their periodicity along the channel (γ). (For a related example of abrupt changes in Δ_g, see Ref. [62].) As in the case of lock-in, when considered on the scale of a diffracting domain, both of these compounds exhibit large-scale cooperative guest motions: discontinuous displacement in *n*-dodecane/urea and sliding in *n*-heptane/urea. Note that the low-temperature space groups in *n*-dodecane/urea and *n*-heptane/urea differ in the directions of their displacement axes (perpendicular to

the 2_1 axis) and also in the magnitude of the offset Δ_g, as illustrated in Fig. 5 from Ref. [38].

IV. DISCUSSION

The description of the phase transitions in aperiodic composites such as *n*-alkane/urea is very complex. A theoretical analysis of the group-subgroup relationship within a crystallographic superspace was previously reported in the literature, conserving the rank 4 of the crystallographic superspace in these materials [17]. As pointed out above, the incommensurability is due to the irrational ratio of the lattice parameters of the host and guest subsystems. This is fundamentally different from the case of incommensurately modulated crystals in which a periodic high-symmetry phase can be used to define a mean Brillouin zone within an aperiodic phase. Phase transitions in incommensurately modulated crystals may be described as a perturbation of the high-symmetry periodic phase and Landau theory of phase transitions may be applied. In the case of aperiodic composites, no such simplifications are allowed, but semimicroscopic models such as the double chain model have been proposed [63–65]. The system consists of two parallel chains at a distance d. In the first chain atoms are at positions x_n and in the other at positions y_m. Intrachain couplings, $V_1(x)$ and $V_2(y)$, respectively, are considered either harmonic or Lennard-Jones potentials with minima for $x = a$ and $y = b$, respectively, whereas a Lennard-Jones potential $W(r)$ describes the interchain coupling $W(r) = \lambda[(\sigma/r)^{12} - 2(\sigma/r)^6]$, with $r^2 = (x-y)^2 + d^2$. The potential energy then reads [65]

$$V = \sum_n V_1(x_n - x_{n-1}) + \sum_m V_2(y_m - y_{m-1}) + \sum_{n,m} W(x_n - y_m). \tag{3}$$

Such a model is much too simple to describe the actual sequence of phases in *n*-alkane/urea aperiodic crystals, where many types of short- and long-range interactions and disorder exist. We mention it here only to elucidate some trends in the reported experimental results. For the high-symmetry phases encountered in *n*-alkane/urea systems with $n = 7$ to 12 ($P6_122$ space group for the host) and also for the intermediate phase in *n*-heptane/urea ($P2_111$ space group for the host), there are no observable intermodulations, indicating that λ is negligible. In each of these phases, the guests have their own independent ordering, which is restricted to long-range order only along the channel. When λ is different from zero, but sufficiently large, the two subsystems become modulated, each system having a modulation wave vector from the other subsystem. With chain lengths of $n = 13$ to 24 (except $n = 20$), this high-symmetry superspace group is rank 4 with hexagonal symmetry, $P6_122(00\gamma)$. A phase transition may appear if one of the vibrational phonon branches becomes unstable. In some cases, the rank of the crystallographic superspace is conserved in the process, as exhibited by the compounds that go through a ferroelastic phase transition from rank-4 hexagonal $P6_122(00\gamma)$ to rank-4 orthorhombic $P2_12_12_1(00\gamma)$. In other cases, the frequency of the soft mode goes to zero at a general point in reciprocal space [1], and a supplementary modulation appears, requiring an additional vector, $\boldsymbol{c_m}^*$, to index the diffraction pattern. This is the case for $n = 15$, 19 and 24, which present ferroelastic phase transitions leading to the rank-five *C*-centered superspace group $C222_1(00\gamma)(10\delta)$. Such phase transitions may result from the softening either of a phonon branch or of the branch associated with the sliding mode, a specific excitation of the internal space of the superspace [42]. Further dynamical studies of pretransitional phenomena in which collective excitations in these materials are measured are required before definitive conclusions concerning the origin of these transitions can be made. In one case, *n*-eicosane/urea, the interaction term λ is large enough to give a commensurate structure by construction at room temperature. For $n = 8$ and $n = 11$, the increase of the interaction term λ with decreasing temperature would explain the thermal lock-in reported in the two compounds.

V. CONCLUSION

In the present paper, we report the multiple and varied sequences of phases exhibited by a prototype aperiodic composite family, the *n*-alkane/urea inclusion compounds, as a function of temperature. This family of crystals presents an excellent opportunity to systematically study their phase transitions by incrementally varying the number of carbons in the guest molecules. Even though they are inherently very similar in overall construction, these crystals exhibit a large number of different phase transitions. Our results on alkane lengths from $n = 7$ to 24 show 11 different phases with 12 types of phase transitions. In addition, the space group dimensionality is observed to change between ranks 3, 4, and 5. This represents a more sophisticated analysis than previous synthesis articles [33,35], which gave a very basic picture of the phase transitions in terms of just two phases, without taking the aperiodicity into account.

In our pursuit of establishing the rules that govern superspace phase transitions, we conclude that the overarching behavior is that the group-subgroup relationship is preserved upon going through a phase transition, regardless of the change in rank. This is analogous to incommensurately modulated crystals and constitutes a key result for developing a general theory of superspace phase transitions for aperiodic composites. The findings presented here offer a framework for future investigations of other aperiodic composite crystals and at the same time demonstrate their versatility. Such behavior should be encountered in many different kinds of aperiodic materials, which are now recognized to be ubiquitous in nature.

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Correction: A missing closing bracket in an inline equation located above Equation (3) has been inserted.