Comment on “The true structural periodicities and superspace group descriptions of the prototypical incommensurate composite materials: Alkane/urea inclusion compounds” by Couzi M. et al.

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In their article, Couzi et al. report an analysis of certain phases of n-nonadecane/urea and n-hexadecane/urea within a crystallographic superspace [1]. From their X-ray diffraction on n-nonadecane/urea, the authors contest the validity of previous work published by our groups [2–5]. Surprisingly, their data are strikingly different from that reported recently using complementary techniques [2–4]. As elaborated here, the data reported by Couzi et al. are not from phase II of n-nonadecane/urea and cannot be used to discuss the sequence of phases in this compound. Phase II is clearly identified by the absence of common and host superstructure Bragg peaks (together with other extinctions). The existence of this phase was simply disregarded in the article published by Couzi et al., since they found no differences in the presence/absence conditions observed in their reconstructed diffraction profile at 147 K (which claim is from phase II) and at 100 K (phase III). (See figs. 2(a) and 3(a) of ref. [1].) Consequently, they have proposed the same space group for both phases II and III.

As shown in table 1, there are large discrepancies between their data for phase II and ours for the same phase (e.g., figs. 2C and 3B in ref. [36] of their paper, here ref. [3]). In this table, we use the standard definition of Bragg peak positions within five-dimensional (5D) crystallographic superspaces: \(Q_{hklmn} = h\alpha^* + k\beta^* + l\gamma^* + m\delta^* + n\epsilon^*, \) with \(n = 0 \) in the four-dimensional (4D) case.

It is for Couzi et al. to explain why they have failed to observe the absence/presence conditions that characterize phase II, in particular the common and host superstructure Bragg peaks, which are not in phase II and whose emergence with cooling signifies phase III. The trivial explanation is that they made both of their measurements on phase III. We cannot understand why these authors would choose 147 K for their study of phase II of n-nonadecane/urea, since earlier adiabatic calorimetry data (table 2a of ref. [59] of Couzi et al. [1]) had given 147.0(1) K as the phase transition temperature.

We have interpreted the systematic absence of common and host peaks in the superstructure layer lines of phase II of n-nonadecane/urea in terms of ferro-ordering of the host subsystem [2,4], in total disagreement with the anti-ferro shearing predicted by the superspace group \(P2_12_12_1(00\gamma)\) proposed by Couzi et al., who argue for a 4D superspace group on the basis of numerology alone: “... we have recognized that a simple relation actually exists between the values of the two misfit parameters \(\gamma\) and \(\delta\), specifically: \(-2 + 5\gamma = \delta\).” However, we gave this relation explicitly in fig. 2C of our 2008 paper [3]. So, of course, we first considered the simplest hypothesis of a 4D superspace group. However, in the superstructure layer lines listed in table 1 (and in others), Bragg satellite reflections can be interpreted only in terms of the presence

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condition of $h + k + n$ = even, using a 5D superspace. We concluded that phase II is characterized by the appearance of a supplementary modulation.

Couzi et al. devote a short section of their paper to n-hexadecane/urea, without any new experimental results. Our paper [5] described high-resolution data from a cold neutron triple-axis spectrometer as well as high-resolution X-ray data. A careful analysis of the sequence of phases in terms of calorimetric data and symmetry breaking was given according to Landau group/subgroup theory. Three very different structural phases were reported: phase I, hexagonal $P_6_32(00)\gamma$; phase II, a rank-4 orthorhombic structure with superspace group $P2_12_12_1(00)\gamma$ where only common, host, and guest Bragg peaks appear in the superstructure lines (in which $h + k = \text{odd}$); and a phase III below $T_{c2} = 127.8$ K. Phase III presents a diffraction image strikingly different from that reported for phase II. At $T_{c2}$, a dense set of Bragg satellite peaks appears around each of the common, host, and guest superstructure Bragg peaks of the parent phase II. Their appearance at $T_{c2}$ signals a symmetry change, and their growth during cooling allows one to measure the evolution of the order parameter according to Landau-type group/subgroup theory. The key point is that these satellites are evenly spaced in the vicinity of the “main” Bragg peaks with a periodicity $\delta = 0.058(2)$ in $c_{\text{host}}$ units. The maximal superspace group that we propose for phase III is $P2_12_12_1(00)\gamma)(000)\gamma$ [5]. Couzi et al. again propose the same space group $P2_12_12_1(00)\gamma$ for phases II and III.

According to the 5D superspace group that we proposed, the indexation of all of the satellite Bragg peaks is very simple, as shown in fig. 9 of ref. [5]; using five $hhklnm$ indices, the values of $n$ are simply $+1, +2, +3 \ldots$ around the common ($l = m = 0$), guest ($l = 0$ and $m = 1$), and host ($l = 1$ and $m = 0$) Bragg peaks. Assuming the 4D approximant ($c^*_n = 2c^*_{\text{host}} - 4c^*_{\text{guest}}$) proposed by Couzi et al. [1], the Bragg peaks for $n = +1, +2,$ and $+3$ next to each of the aforementioned main peaks are given by the following sets $(l, m)$: $(2, -4)$, $(4, -8)$, $(6, -12)$; $(2, -3)$, $(4, -7)$, $(6, -11)$; $(3, -4)$, $(5, -8)$, $(7, -12)$. The fundamental physical features that these Bragg satellites represent are lost within this 4D notation.

We stated that “…the periodicity of the supplementary modulation ($\lambda = c_n/\delta$) has a rather large value of 190 Å…Within the current precision of our data, it is impossible to discriminate between true aperiodicity and very high order periodicity.” [5]. In their article, Couzi et al. use our data to simply choose one of the two possibilities (high-order periodicity) without bringing the necessary higher-resolution data. Our approach, which ties the phase transition to a change in superspace group, explains the order parameter evolution according to the intensities of the new Bragg satellites that appear at $T_{c2}$, the origin of the $C_p$ signature that coincides with the emergence of those Bragg satellites, and the periodicity of the satellites surrounding their parent peaks.

We conclude that Couzi et al. have measured both of their datasets of n-nonadecane/urea on phase III. Because of this, they found no differences in the presence/absence conditions for phases II and III of this material and therefore cannot make valid conclusions on the sequence of phases. In n-nonadecane/urea and n-hexadecane/urea, the 5D description not only carries with it a physical picture that explains the additional Bragg peaks, it adheres to Landau group/subgroup theory of the characteristic features of these phase transitions.

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