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M. Abiyaala [a] , P. Duval [b] & A. Mimet [a]

[a] G.E.M.F., Département de Physique, Faculté des Sciences de Tétouan B.P., 2121, Tétouan, Maroc

[b] G.M.P, UMR CNRS 6634, Faculté des Sciences, 76134, Mont Saint Aignan, France

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Electron Microscopy Study of Hα → Qα Transition Phase in a Sodium Dodecylsulfate-Formamide (SDS-Formamide) System

M. ABIYAALA[a*], P. DUVAL[b] and A. MIMET[a]

[a]*G.E.M.F., Département de Physique, Faculté des Sciences de Tétouan, B.P. 2121, Tétouan (Maroc) and* [b]*G.M.P, UMR CNRS 6634, Faculté des Sciences, 76134 Mont Saint Aignan, France*

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The study of the SDS-Formamide system by freeze-fracture electron microscopy revealed in addition to hexagonal phase Hα and the cubic phase Qα the existence of a structure with flexible cylinders. This structure is located in the diagram of phases between hexagonal phase Hα (p6m) and cubic phase Qα (Ia3d) and is characterised by defects (dislocations, disinclinaisons, focal domains, flexion and torsion boundaries). The hexagonal phase thus appears under two morphological varieties: a variety with rigid cylinders on the side low in surfactant and a variety with flexible cylinders on the side rich in surfactant. Any fractures present a network with square meshes revealing thus the cubic Qα(Ia3d). We think that the structure with flexible cylinders observed by electron microscopy is a stage to wards the transition Hα→Qα whose we will have the results.

1. INTRODUCTION

the first work relating to a sodium dodecylsulfate (SDS)-water system was completed by Luzzati and his collaborators. The latter showed the formation of lyotropic phases in this system in X-ray diffraction and optical microscopy. They thus located in concentration and temperature the micellar, hexagonal and lamellate phases [1,2]. Other techniques such as the NMR [3], electric conductivity measurements [4] and the thermal analysis [5] contributed to the determination of SDS-water system diagram. Kekicheff [6,7,8] highlighted in precise way the

* For all correspondance send to: ABIYAALA, 4 Parc des deux Bois, 76130 Mont Saint Aignan, France E-Mail: Abiyaala@aramail.com

intermediate phases between hexagonal and lamellate phases there. However, there is not still complete phase diagram of the SDS-formamide system. But work in x-rays diffraction facts in our laboratory, along "solid+solution/lyotropic phases" balance line, on the binary non-aqueous system SDS-formamide, allowed the highlighting of lyotropic ordinate phases Hα, Qα and Lα [9,10].

The formamide is the polar solvent that presents the most analogy with water taking into account its character structured [11]. Certain work went up that ordered lyotropic phases can be formed in SDS-formamide system [9,10]. Indeed, the studies in x-ray diffraction carried out in our laboratory along "solid+solution/lyotropic phases" balance line show with increasing concentration in SDS the succession of the following lyotropic phases:

$$\underset{}{\text{Micelles}} \rightarrow \underset{(2D)}{H_\alpha(p6m)} \rightarrow \underset{(3D)}{Q_\alpha(Ia3d)} \rightarrow \underset{(1D)}{L_\alpha}$$

The transition between Hα and Lα phases is thus done by the intermediary of a cubic Ia3d group space phase Qα(3D).

The transitions between lyotropic phases were also interpreted starting from a competition between the electrostatic interactions, the hydration forces and the empilement chains energy. Certain theorists seek to include/understand the transitions between lyotropic phases, either on thermodynamic bases [12], or on geometrical bases. On this last basis is currently based an interface film crystallography [13]. The most significant work in electron microscopy relates to especially the cubic phase Qα, which is the object of study as well theorical as experimental. The goal of this work is to specify and confirm the complex structure of Qα [14,15]. Work by electron microscopy on the two-dimensional phases such as Hα is relatively restricted, except those carried out on lipidic systems within the framework of molecular biology [16]. Mc Grath and Kekicheff recently observed in optical microscopy the transition between the hexagonal phase and a lamellate phase freezing.

Our work by electron microscopy that we present here concerned the transition between Hα(p6m) and Qα(Ia3d) phase.

II. EXPERIMENTAL TECHNIQUES

II.1. Preparation of solutions

Our solutions surfactant-solvent are weighed and prepared in a tube closed with a perfect sealing so that the composition does not vary during the homogenisation. The tube is firstly cleaned and rinsed abundantly with the water distilled then

dried and placed during a few hours in a drying oven with 100 °C. To obtain spatially homogeneous mixtures several methods were used, the tube containing the mixture is placed in a drying oven with 80 °C, sufficient temperature to obtain a good mixture, this during a half hour. In order to accelerate the homogenisation process on a microscopic scale we used an ultrasound vat by maintaining the tube at the temperature. This operation was not simple for temperatures close to 80 °C.

II.2. Preparation of the samples

For their observation in electron microscopy, the samples were prepared by freeze-fracture method. Indeed, a solution film with about a few tens microns thickness is imprisoned between two fine copper cups 2,8 mms in diameter. The sandwiches thus formed are placed in a furnace and undergo an isothermal maintenance at the temperature wished during a given time, then are soaked directly starting from the furnace in a cooling bath. In our case, the nitrogen liquidates which is cooling insufficient for the lyotropic systems using water like solvent, proved sufficient to block any crystallization and even molecular displacements higher than approximately 2 nm [19]. The vitrified sandwiches are then fractured under ultra-high vacuum (a few 10–7 mm Hg). A platinum layer about 2 nm average thickness, reinforced by a 20 nm layer of carbon, and is deposited by evaporation on the fractures. After extraction and washing of the counterparts in adapted baths, those are examined under the electron microscope (JEOL 2000 FX II to 200 Kv). The measurement of the periodicities observed was taken in two ways:

a - by optical diffraction starting from the stereotypes: this traditional method allows the observation of diffractograms which one can adapt the enlargement. On the other hand, this process is very sensitive to the presence of other diffracting sources that the studied photograph, so that the diffractograms are sullied with a strong background noise.

b - by a small angles electron diffraction: we are probably the first to have to adapt this technique to this type of problems [20]. Its interest (although the coherence of the electron beam is well worse than that of an optical laser He-Ne) is not that it can be used during the observations and that it gives stereotypes cleaner than those obtained by optical diffractography. The order of magnitude of the periodicities given by our system leads however to diffraction spots very close to the central spot of a diagram, even at the height enlargement in diffraction of our microscope (625 mm Å).

III. RESULT

The sequence of the ordered lyotropic phases formed by SDS-formamide system was detected in our laboratory by x-ray diffraction. Indeed, the cubic phase Qα (Ia3d) that appears with a concentration of 75 % (to T > 79,8 °C) occupies a narrow field whereas the hexagonal phase Hα(p6m) occupies an area of concentration ranging between 42 % (with T > 57 °C) and 75 % (with T > 79,8 °C). Our work by freeze-fracture electron microscopy made possible to observe the Hα(p6m) and Qα (Ia3d) phases. In addition, our observations showed that with increasing concentration the cubic phase succeeds the hexagonal phase by transfomation of the cylinders from where the existence of two varieties of the hexagonal phase:

- side low in surfactant, a variety in which the cylinders of the hexagonal phase are rigid and are assembled in microdomains of great extent (approximately 1 μm). In this case the fractures can reveal these cylinders: they confirm the values found in x-rays for the diameter of these cylinders [9]. Sometimes, the fractures have particular textures and do not reveal the cylinders themselves. These textures can be interpreted within the framework of the hexagonal phase [17,18].
- side rich in surfactant, a variety in which the cylinders are flexible. Those, of diameter slightly higher than the precedents then are always revealed, but the aspect of the fractures is then tormented much more and one can highlight of many defects whose aspect points out the polygonal figures observed in optical microscopy in the lamellate phases. We think that these defects are precursory transfomation of the hexagonal phase.
- to stronger concentration into surfactant, the cubic phase Qa (Ia3d) comes to replace the flexible variety of the hexagonal phase. Indeed, Hα→Qα transition seems to be done by a change of Hα cylinders morphology.

III.1. Study of hexagonal phase Hα

The most frequent fracture plans reveal fields made of very long rectilinear fibers (their length can exceed the micrometer) and also spaced. The distance between fibers, measured either directly on the image, or starting from diffractions optical or electronic, is of approximately 4 nm, which corresponds well to the parameter *a*h measured by x-rays. These fracture plans correspond then to (10) plans, fibers correspond to Hα cylinders (Fig. 1). We showed in a former publication that these plans contain defects and that the fracture in the hexagonal phase can occur according to tilted plans [18].

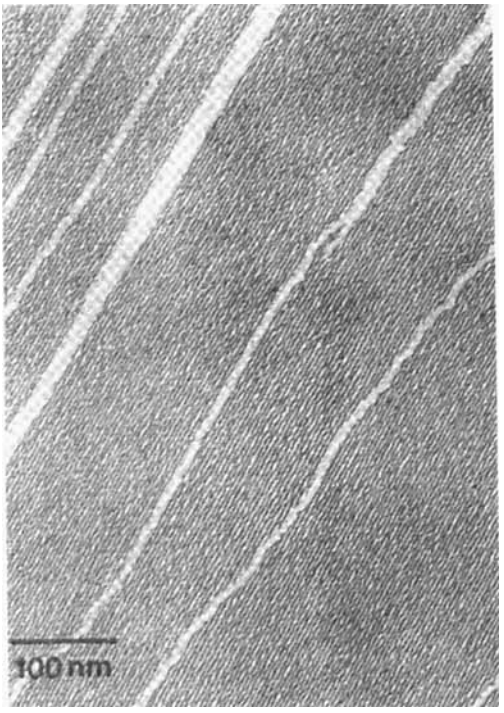

FIGURE 1 Fracture plan electron micrography corresponding to the hexagonal phase (10) plan. This phase constituted with rigid cylinders

The structure with flexible cylinders appears in a field of compositions richer in SDS than the phase with rigid cylinders. Spacing between cylinders observed by freeze-fracture method is variable but on average larger than that observed in the rigid phase (5 nm instead of 4 nm). It is characterized on micrographies by sinuous fibers forming of the fields in which the fibers remain parallel. The fields are much smaller than those of the rigid phase (120 to 300 nm instead of 1 with several microns) (Fig. 2).

In order to find an agreement with the areas of concentration observed in x-rays, it is necessary to admit, in our samples, a slip about 15 % of composition on the side of the strong concentrations in SDS. Thereafter, we will distinguish between the nominal composition from the samples (that to which those were prepared), and the supposed real composition, higher of 15 % than the nominal composition.

We found Hα rigid phase in samples of nominal composition ranging between 25 and 50 % in SDS. In addition, within the limit of our values precision, the

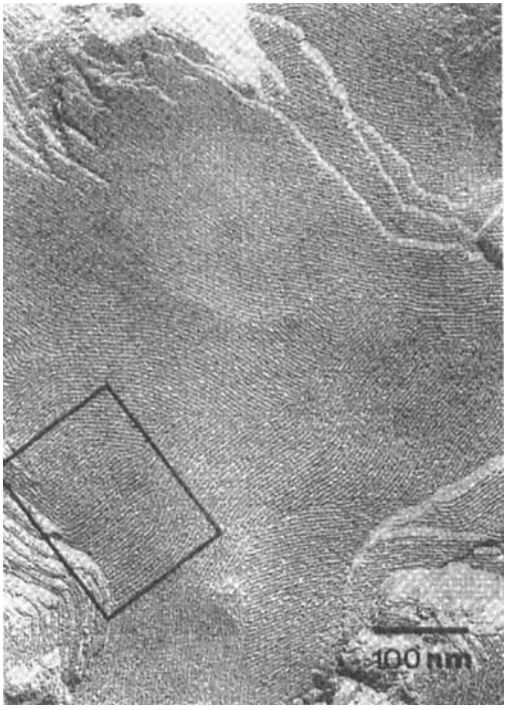

FIGURE 2 Flexible phase electron micrography shows Sinuous cylinders fields; the framed zone shows that the cylinders are curved in the passing of a wall

parameter *a*h of this phase remains constant in all this interval ($ah \approx 4$ nm). However, the flexible variety appears according to our observations with the nominal composition of 40 % and coexists, with the top of this composition with Hα rigid phase in the same sample. Our observations let think that the flexible phase comes to replace the rigid phase. As we specified above the periodicity observed on micrographies of the flexible phase is definitely higher than that of the rigid phase, and especially, it is variable (of 4,5 nm with 6 nm) (Fig. 3) and this inside a same sample. However, on average it grows with the concentration. We showed in a former work that the variety with flexible cylinders contained also many defects [18].

III.2. Study of cubic phase Qα

The cubic phase Qα(Ia3d) already was the subject of a study in x-rays in our laboratory by × Auvray. This phase whose parameter is $ac = 7{,}96$ nm and varies lit-

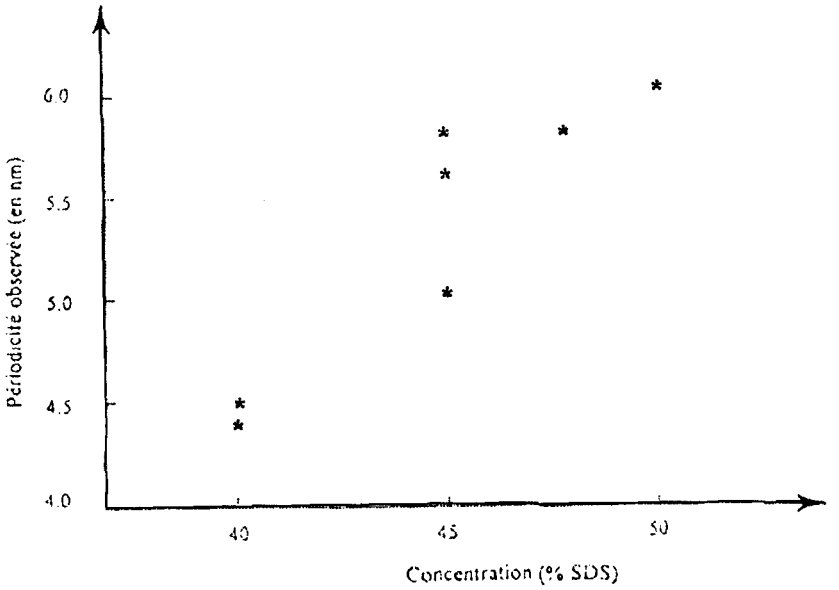

FIGURE 3 Variation of the periodicity measured in the structure with flexible cylinders according to the concentration

tle with the concentration, is characterized in x-rays by the reticular distances in the reports/ratios $\sqrt{2}$, $\sqrt{8}$, $\sqrt{14}$, $\sqrt{16}$, $\sqrt{20}$, $\sqrt{22}$, $\sqrt{24}$ and $\sqrt{26}$. These reticular distances correspond to the indices of Miller 211, 220, 321, 400, 420, 332, 422 and 431 (Fig. 4) [9,10]. The freeze-fracture examination of samples (SDS/FA) of nominal composition 50 % in SDS revealed the existence of fractures giving place to diagrams of diffraction having the symmetry of the square (Fig. 5).

The parameter of the squares is of 4 nm. We checked that, if this symmetry is possible for Hα a phase fracture, it would lead to a parameter equal to $ah\ \sqrt{3}/\sqrt{2}$. may be, 4,9 nm. It is not thus certainly about Hα phase detected by x-ray-diffraction. On the other hand, the periodicity is, with the experimental errors close half of the parameter *ac* found in x-rays for the Qα. Phase. This observation, which is not inevitably contradictory with x-rays measurements will be commented on and discussed there after. We also found other fractures that probably correspond to the phase Qα the preceding one. The difficulty of their interpretation is related to the fact that these fractures are generally not plane. However, we identified a fracture that we think of being close to a plan (110) [17].

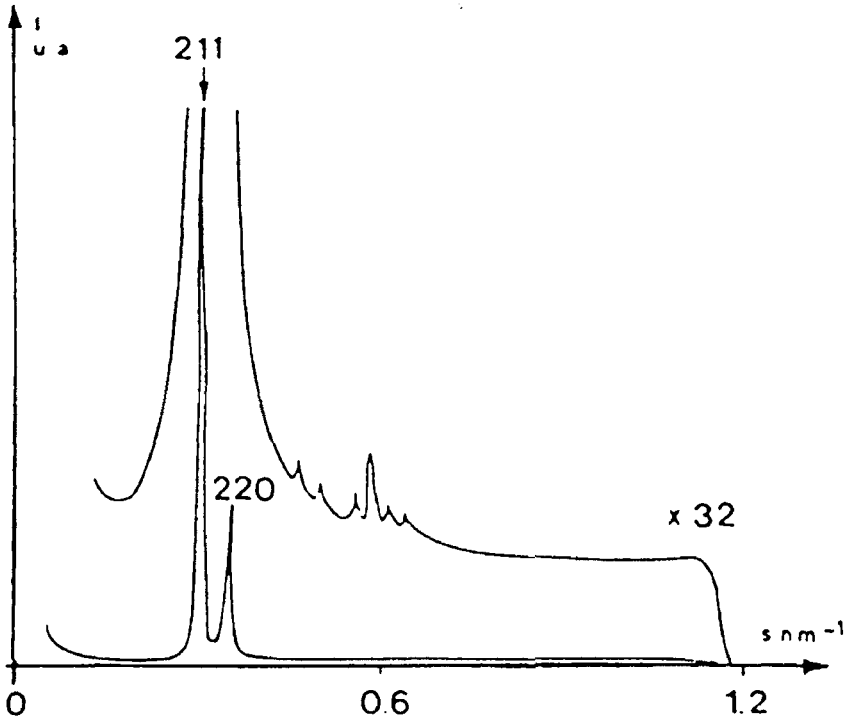

FIGURE 4 X-ray diffraction spectrum of the cubic phase Qα(Ia3d) [9,10]

IV. DISCUSSION

We clearly observed rigid phase Hα detected in diffraction of x-rays in SDS-formamide system. However the flexible phase that we observed by freeze-fracture electron microscopy was not detected in x-rays. According to us the absence in x-rays of peak corresponding to the parameter measured by freeze-fracture on the flexible phase can, at least partly to be explained by the presence in this phase of small fields and many defects, and especially by the variation of it parameter inside the same sample. All these effects contribute to a widening and a depression of x-rays peaks. It is noted, in this case, that the fractures occur generally parallel to the axis of fibers, that those are flexible or not (they can occur according to oblique plans [18]. These fibers themselves are generally directed parallel to the supports of the sample. It is in this orientation of the fractures that those appear best solved, probably because the fixation platinum sites are dense in this orientation, so that the mobility of the platinum grain is very reduced. This sup-

poses that it is admitted implicitly that the fracture circumvents the solvent-amphiphilic interface.

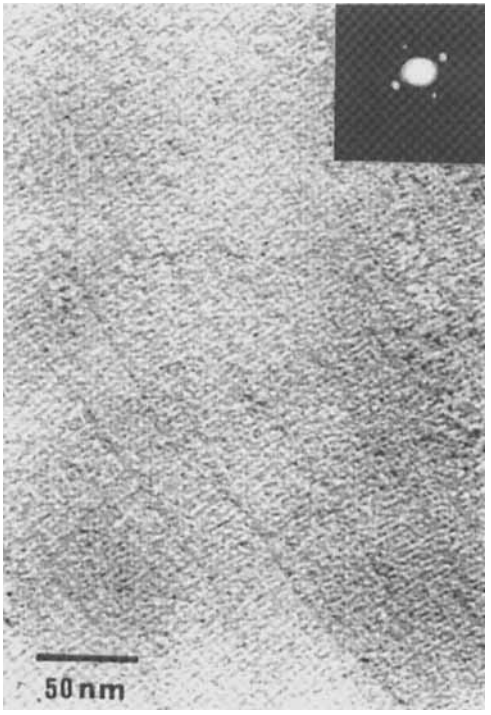

FIGURE 5 (100) plan electron micrography of cubic phase Qα(Ia3d) revealed by the fracture. A small angle electron diffraction highlighted a square network

We observed fractures presenting a network to square meshes, but with cell parameter half of that observed by x-rays. This is not inevitably contradictory with the x-rays results, insofar as by x-ray diffraction are introduced conditions of extinction which can be removed if one examines only one plane section of the structure, or even a section of which the thickness is a fraction of the elementary meshe. We must thus examine this possibility.

Figure 6 represents two plans (100) superimposed Ia3d structure of our system, respectively of dimension 1/8 and 3/8. On this diagram, the surfactant labyrinths skeletons illustrated by small segments (in black for those of dimension 1/8, and hatched for those of dimension 3/8) connected by zigzag if they belong to the same labyrinth. The obstruction reality of SDS in the plans (100) is illustrated by cylinders (finished by hemispheres) surrounding each segment. The following possibilities then are noted:

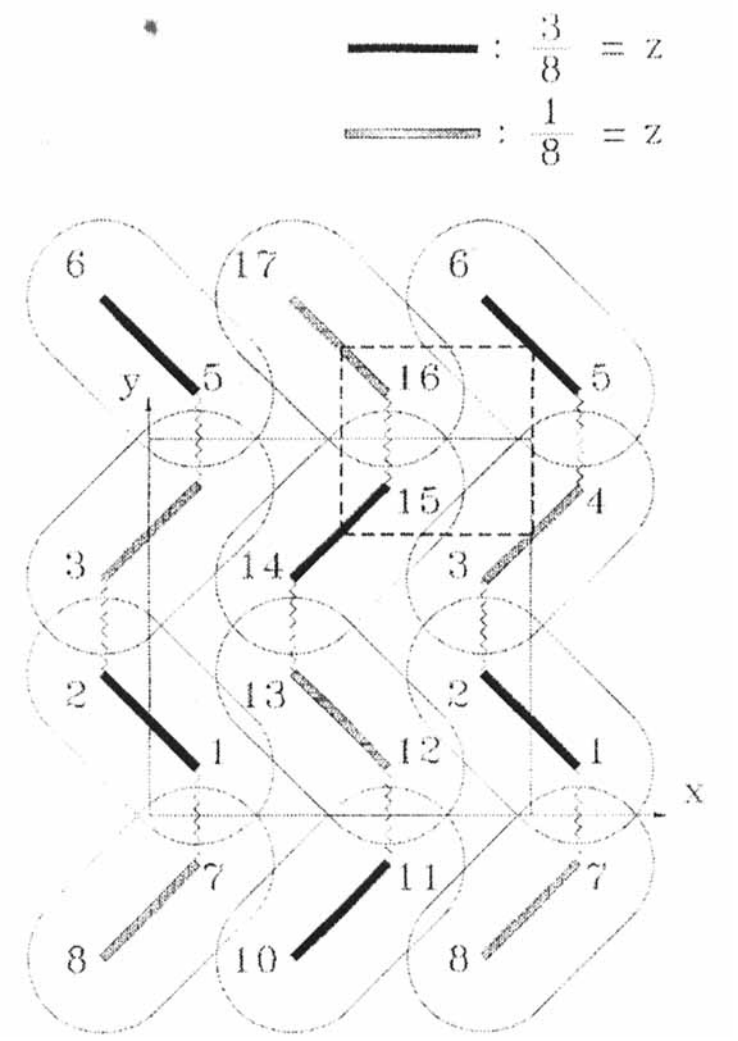

FIGURE 6 Two (100) plans superposition of the Ia3d structure

- If the fracture is perfectly plane and very resolvent, it will révèlera the cylinders of the plan with their orientation, and the periodicity observed will be then that of the meshe *a*c.
- If the fracture, always plane A an insufficient side resolution (≈ 3 nm) information on the orientation of the cylinders of the plan is lost. With the place of

those, one will observe spots of random orientation and the periodicity observed will be nothing any more but $ac\sqrt{2}/2$.

– If moreover, the fracture is not plane any more but presents a relief highlighting fractions of plan of dimension 1/8 and others of dimension 3/8, the periodicity observed will be only $ac/2$, corresponding to the square in dotted drawing. This means in-depth loss of resolution about $ac/4$, so 2 nm. It is reasonable to think that the fractures we obtained correspond to this last case, which is of course to confirm by new measurements.

V. CONCLUSION

The examination by freeze-fracture electron microscopy method made it possible to highlight Hα→Qα transition in SDS-formamide system. This confirms the results obtained by x-ray diffraction. In the case of our system, Hα (2D)→Qα (3D) transition is brutal, since there is no intermediate phase. It is probably necessary to pass by a stage in which occurs a fast decrease of the constants of the interfaces mechanic rigidities, in Hα phase. The most obvious demonstration for this phenomenon is the fibers curve possibility. But we think that the phase becomes not only flexible, but also malleable, cylinders being able to appellate themselves, without total change of the parameter *ah*. This can explain the periodicity disparity of fibers observed by freeze-fracture method in a given sample, as well as the increase in this apparent parameter, Hα phase becoming increasingly malleable with the approach of the transition. This can also explain the permanent presence by x-rays of the peak corresponding to the parameter $ah = 4$ nm, and the progressive disappearance of a higher nature peaks when the transition is approached.

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