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Local ordering in lyotropic cholesteric liquid crystals studied by X-ray scattering

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Résumé. — Nous avons réalisé des expériences de diffraction X sur des phases nématiques-calamitiques lyotropes et cholestériques-calamitiques lyotropes induites par un dopage de sulfate de brucine et de d-octanol. Les spectres de diffraction de la phase cholestérique déroulée sont comparés aux spectres de la phase nématique orientée usuelle. Ils montrent une conservation globale de la structure pseudo-lamellaire en phase cholestérique, avec toutefois des déformations locales de cette structure pseudo-lamellaire dans le cas des échantillons dopés au sulfate de brucine.

Abstract. — X-ray diffraction experiments with lyotropic calamitic-nematic phases and induced lyotropic calamitic-cholesteric phases doped with brucine sulfate and d-octanol are performed. The diffraction pattern of the usual oriented nematic phase is compared with the patterns of the untwisted cholesteric phase. The analysis of the patterns indicate that even in the cholesteric phase the pseudo-lamellar structure is maintained. The different features observed in the diffraction patterns of the nematic and cholesteric phases doped with the brucine sulfate are explained in terms of local deformations of the pseudo-lamellar structure.

Introduction.

Lyotropic cholesteric liquid crystals [1-3] may be obtained by adding chiral molecules to lyotropic nematic mesophases. These chiral molecules, such as brucine sulphate, d(2)2 octanol or cholesterol, induce a cholesteric arrangement of the amphiphilic micelles. Three types of lyotropic cholesteric mesophases have been identified: ChD-discotic cholesteric [3, 4]; ChBX-biaxial cholesteric [5] and ChC-calamitic cholesteric [3, 4]. The subscription D, BX and C indicate only that the cholesteric phases are obtained from the discotic (ND), biaxial (NBX) or calamitic (NC) nematic phases [6, 7] respectively, by adding chiral molecules. In the presence of a strong enough magnetic field (H), the ChD and ChBX orient with the cholesteric planes perpendicular to H and the ChC phase is untwisted. The untwisted effect of the field on the ChC phase may be interpreted as a cholesteric (Ch) to nematic (N_C) phase transformation [8], where the pitch diverges for a critical field, starting from a finite value. We name N_C the nematic phase obtained from the untwisting of a cholesteric phase.

A puzzling question that came from the induced cholesteric systems is how the chiral molecules modify the local ordering of the nematics to form a long range cholesteric structure. Especially how the pseudo-lamellar ordering observed in nematics [7] is perturbed by the presence of the optical active agent.

In this paper we present a X-ray diffraction study of the N_C phases obtained from the ChC phase untwisted by the magnetic field. The lyotropic systems studied are the potassium laurate (KL) and the sodium decil sulfate (SDS) doped with the chiral molecules d-Octanol (DOC) and brucine sulfate hepta-hydrated (BS) respectively. The location of the DOC and the BS molecules is expected to be different [2] in these cholesteric mixtures: the amphiphilic molecules of DOC are expected to be located in the micelles (as the decanol or the potassium laurate); the BS molecules in the presence of water partially ionizes and are probably...
located [2] in the water, in the electric double layer, outside the micelles. The diffraction patterns of the N\textsuperscript{c} phase are compared with the usual N\textsubscript{c} patterns.

**Experimental section.**

**MATERIALS.** — Sodium decylsulphate (SdS), 1-decanol (DeOH), the brucine sulphate heptahydrated (BS), the d-2-Octanol (DOC) and the \(d, f\)-2-Octanol (DLOC) are of commercial origin (Merck p.p.e. > 99 \%), (Fluka p.p.e.> 99 \%) (Flukapurum), Aldrich respectively. The potassium laurate (KL) was prepared in the laboratory (Orsay).

**COMPOSITION OF THE MESOPHASES.** — The lyotropic mesophases were prepared following the classical procedure [9]. Their concentrations in weight percent and their phase sequence as a function of the temperature are :

(a) the nematic phase - S1

SdS ......... 39.02
DeOH ........... 7.50
H\textsubscript{2}O ........... 53.48

\(15^\circ C \rightarrow 21^\circ C \rightarrow 45^\circ C\)

N\textsubscript{D} \(\rightarrow\) N\textsubscript{BX} \(\rightarrow\) N\textsubscript{C} \(\rightarrow\) POL

where POL denotes a polyphasic domain.

(b) The cholesteric phase - S2

SdS ........... 38.81
DeOH ........... 7.46
H\textsubscript{2}O ........... 53.19
BS ........... 0.54

\(17.9^\circ C \rightarrow 21^\circ C \rightarrow 47^\circ C\)

CH\textsubscript{D} \(\rightarrow\) CH\textsubscript{BX} \(\rightarrow\) CH\textsubscript{C} \(\rightarrow\) POL.

(c) The nematic phase - S3

KL .......... 26.88
DeOH ........... 4.49
H\textsubscript{2}O ........... 66.91
DLOC .......... 1.72

\(<0^\circ C \rightarrow 34^\circ C\)

ISOTROPIC \(\rightarrow\) N\textsubscript{C} \(\rightarrow\) ISOTROPIC.

(d) The cholesteric phase - S4

KL .......... 26.29
DeOH ........... 4.44
DOC ........... 1.77
H\textsubscript{2}O ........... 67.50

\(1^\circ C \rightarrow 30^\circ C\)

ISOTROPIC \(\leftarrow\) Ch\textsubscript{C} \(\rightarrow\) ISOTROPIC.

The molar concentration of quiral molecules per amphiphilic molecules \(M_s\) is defined as follows :

\[ M_s = \frac{[\text{quiral molecule}]}{[\text{soap}]+[\text{alcohol}]} \]

Sample S2 and S4 have \(M_0^{0.5} = 2.7 \times 10^{-3}\) and \(M_0^{0.9} = 9.9 \times 10^{-2}\) respectively. The cholesteric pitch is about 100 \(\mu\text{m}\) for both S2 and S4 samples.

A small quantity (about 0.05 wt \%) of a water-base ferrofluid [10] from Ferrofluids Corp. was added to the lyotropic mixtures to help the alignement under weak magnetic field (typically 100 G). This addition of ferrofluid does not change the temperature transitions and the general features of the X-ray diffraction patterns as has been checked.

**X-RAY DIFFRACTION.** — Samples are sealed in Lindemann glass capillaries of 1.5 mm diameter placed in the vertical direction in a temperature controlled stage (stability of \(\pm 0.2^\circ C\)). X-ray diffraction patterns were obtained at fixed temperatures : 24.4 \(^\circ C\) for the samples S1 and S2 ; 24.0 \(^\circ C\) for the samples S3 and S4. The axis of the capillary is perpendicular to both the magnetic field (3 kG) and the X-ray beam, in a transmission geometry. X-ray diffraction patterns are obtained by the photographic method using the synchrotron X-ray monochromatic radiation (Ge crystal, wavelength, \(\lambda = 1.62 \text{\AA}\) of Orsay (Laboratoire pour l'Utilisation du Rayonnement Electromagnétique - LURE). The mean experimental resolution is \(\Delta q = 4 \times 10^{-3} \text{\AA}^{-1}\) (where the scattering vector modulus is \(s = 2 \sin \phi/\lambda\) ; \(2 \phi\) is the scattering angle and \(q = 2 \pi s\)).

**LABORATORY REFERENCES AXES.** — The magnetic field defines the axis X of the laboratory frame. The capillary axis is along the axis Y and the X-ray beam is along the axis Z.

**Results and discussion.**

1. **COMMON FEATURES IN THE STRUCTURE OF THE N\textsubscript{C} AND N\textsuperscript{c} PHASES.** — The X-ray diffraction patterns of the oriented nematic N\textsubscript{C} phases (samples S1 and S3) and the N\textsuperscript{c} phases (samples S2 and S4) in the presence of the magnetic field present the same general features: their reciprocal space structure may be schematized as a hollow cylinder parallel to H with intense edges [7]. A typical two-dimensional densitometer map of the diffraction pattern obtained with the Ch\textsubscript{C} phase (sample S2) untwisted by the field is shown in figure 1 [11]. One can observe in the diffraction pattern the first (a-band: hereafter we will use this name for all the strong first order bands along the Y-axis, for both the N\textsubscript{c} and N\textsuperscript{c} diffraction patterns) and the second order [12] bands along the Y-axis, indicating the existence of a pseudo-lamellar ordering along this direction, and a more diffuse band along the X-axis (this band is not clearly visible in Fig. 1 because this diffraction pattern cannot be over exposed — this band can be seen in Ref. [4]). From the relative width of the a-bands, we can estimate the positional correlation in the direction of...
the Y-axis. Using Scherrer's expression [13] we find the positional order to extend along this direction to about 200 Å (≈ 5 lamellar distances) in all the samples. The measurements of the scattering vector modulus along the Y-axis and the X-axis show that these periodicities are: $s_Y^{-1} = (41.0 \pm 0.2)$ Å and $s_X^{-1} = (60 \pm 1)$ Å$^{-1}$ respectively in both the S1 and S2 samples; $s_Y^{-1} = (50.0 \pm 0.5)$ Å and $s_X^{-1} = (110 \pm 1)$ Å in both the S3 and S4 samples.

The existence of the first and second order bands along the Y-axis and the same periodicities in the nematic and cholesteric samples indicate that the pseudo-lamellar ordering previously observed in the nematic structure [7], is maintained even after the chiral molecule doping in the $N_C^*$ phase.

2. DIFFERENCES BETWEEN THE STRUCTURES OF THE $N_C$ AND THE $N_C^*$ PHASES. — Even if the general features of the diffraction patterns of the oriented $N_C$ and $N_C^*$ phases are the same, a difference in the shape of the strong first order band (a-band of Fig. 1) in the case of the BS doping can be detected. To analyse the shape of this diffraction band we measured the diffracted intensity $I$ in the plane $X-Y$ from the 2D densitometer maps. Figure 2 shows a sketch of the pattern with the local axes $X-Y$ and the angle $\theta$. $\rho$ is the position of the diffracted intensity maximum as a function of $\theta$ ($\rho_0$ corresponds to $\theta = 0^\circ$). The diffracted intensity of the a-band is

![Fig. 2. Sketch of the X-ray diffraction pattern of a nematic $N_c$ phase with the local axes $X-Y$ and the angle $\theta$. $\rho$ is the position of the local intensity maximum as a function of $\theta$ ($\rho_0$ corresponds to $\theta = 0^\circ$).]
measured in arbitrary units along the Y-axis (Fig. 3a) and as a function of $\theta$ (Fig. 3b) for both the oriented N$_c$ and N$_c^*$ phases (BS doping) (the maximum intensities are normalized). Within our accuracy, no difference has been detected between the X-ray patterns of the N$_C$ (sample S3) and N$_c^*$ (sample S4) phases, doped with the octanol.

Fig. 3. — The normalized intensity of the a-band in arbitrary units: (a) along the axis Y; (b) as a function of $\theta$. $Y_0$ is a normalization constant. N$_c$ phase (●) and N$_c^*$ phase (+).

In order to analyse the a-band, we first focus our attention upon the crest line, i.e., for a given value of $\theta$, we determine the position $\rho$ of the diffracted intensity maximum. Analysing the dependence of $I(\theta, \rho_0)$ as a function of $\theta$ one can estimate the orientational order parameter $S$. In both N$_C$ phases — samples S1 and S3 — and in the N$_c^*$ phase — sample S4 (DOC-doping) — we obtained $S = 0.85$. The N$_c^*$ oriented phase (DOC-doping) can be described as a non chiral N$_c$ phase with the same liquid order and particularly the same orientational ordering. In other words, the substitution of $\ell$-octanol does not affect the local ordering of the micelles.

For the BS doped sample the description of the ordering is less obvious. In a liquid containing identical micelles (or molecules), the diffracted intensity is a function of [13] the form factor of the micelles and the intermicellar interference function. If the form factor of the micelles and the interference function were exactly the same in both the N$_C$ and N$_c^*$ phases, one would expect that the maximum intensities along the a-band arc (for different values of $\theta$, Fig. 2) to be located at the same scattering angle $2 \phi$ ($\tan 2 \phi = \rho/D$, where $D$ is the distance between the sample and the film). Comparing the N$_C$ [7] and the N$_c^*$ (Fig. 1) diffraction patterns it is observed that for increasing values of $\theta$, the maximum intensities of the a-band in the N$_c^*$ sample, are at decreasing values of $2 \phi$ (i.e. $\rho$). At $\theta \sim 40^\circ$, the maximum intensity of the a-band (N$_c^*$ sample) is shifted towards large spacing distances in the direct space of about 10% of the original pseudo-lamellar spacing distance $sY_1$. Figure 4 shows the relative shift of the maximum intensity of the a-band $\delta \rho = \rho_0 - \rho$, as a function of $\theta$. The dots correspond to sample S2 and the crosses ($\times$) to samples S1 (N$_c$), S3 (N$_c$) and S4 (N$_c^*$-octanol doping).

Fig. 4. — Relative shift of the maximum diffracted intensity of the a-band ($\delta \rho = 1 - \frac{\rho}{\rho_0}$) as a function of $\theta$. The dots (●) correspond to sample S2 (N$_c^*$-brucine doping) and the crosses ($\times$) to samples S1 (N$_c$), S3 (N$_c$) and S4 (N$_c^*$-octanol doping).

For the BS doped sample the description of the ordering is less obvious. In a liquid containing identical micelles (or molecules), the diffracted intensity is a function of [13] the form factor of the micelles and the intermicellar interference function. If the form factor of the micelles and the interference function were exactly the same in both the N$_C$ and N$_c^*$ phases, one would expect that the maximum intensities along the a-band arc (for different values of $\theta$, Fig. 2) to be located at the same scattering angle $2 \phi$ ($\tan 2 \phi = \rho/D$, where $D$ is the distance between the sample and the film). Comparing the N$_C$ [7] and the N$_c^*$ (Fig. 1) diffraction patterns it is observed that for increasing values of $\theta$, the maximum intensities of the a-band in the N$_c^*$ sample, are at decreasing values of $2 \phi$ (i.e. $\rho$). At $\theta \sim 40^\circ$, the maximum intensity of the a-band (N$_c^*$ sample) is shifted towards large spacing distances in the direct space of about 10% of the original pseudo-lamellar spacing distance $sY_1$. Figure 4 shows the relative shift of the maximum intensity of the a-band $\delta \rho = \rho_0 - \rho$, as a function of $\theta$. The dots correspond to sample S2 and the crosses ($\delta \rho = 0$) to samples S1, S3 and S4. The width at half-height of the a-band at $\theta = 40^\circ$ is about three times larger than the width along the Y-axis, corresponding [13] to a positional correlation distance of about 50 Å. Our results indicate that the BS doping promotes a bending of the first-order diffraction a-band. Figure 5 shows a sketch of the deformation of the first-order diffraction band, induced by the BS (the proportions are not maintained in this sketch, the effect is amplified to be more visible). A possible deformation of the broad and diffuse band along the X-axis is not observed within our accuracy and experimental resolution.

The small value of the positional correlation distance for $\theta = 40^\circ$ (20% bigger than the spacing distance along the Y-axis) indicates that the local...
deformations of the pseudo-lamellar structure responsible for the bending of the a-band are non correlated.

In nematic liquid crystals it is assumed that the interference function is that of an assembly of parallel aggregates and that the orientational disorder does not disturb the interference function. In fact, this assumption is supported by the fact that the maximum intensity \( I \) corresponds always to \( \rho = \rho_0 \) (see Fig. 4, nematic samples). In the case of the BS doped sample let us first neglect the influence of the form factor of the micelles since in lyotropic nematics the localisation of the scattered intensity is mainly due to the interference function. The central part of the a-band \( (\theta \approx 0^\circ) \) (BS doping) is similar to the a-band for the undoped sample \( (S1) \). Therefore the structure of the \( N_c^\xi \) phase \( (S2) \) along the Y-axis resembles very much the \( N_c \) structure \( (S1) \). The outer part of the a-band \( (\theta > 20^\circ) \) corresponds to less ordered zones, where the pseudo-lamellar ordering is disturbed, with larger mean micellar spacing distances. If we assume that the magnetic field does not disturb the local ordering at a scale which corresponds to the X-ray diffraction experiment (coherence length \( \sim 300 \) Å), we have evidenced the presence of disordered zones in the pseudo-lamellar structure, induced by the BS doping.

Taking into account the possibility of a non uniform distribution of BS in the sample (already evoked), these large space distances could exist in the regions of the pseudo-lamellar structure highly perturbed by the presence of the BS. In these regions the order parameter is smaller than those typical of the \( N_c \) phase. This effect is more visible at large \( \theta \) because at small \( \theta \) the intensity of the a-band (originated by the almost unperturbed pseudo-lamellar ordering) is very high.

In a previous paper \([14]\) it was pointed out that in the pseudo-lamellar structure of lyotropic nematics there is a large number of edge dislocations. These edge dislocations in fact are needed to account for the good fluidity of the nematic phases, in spite of their lamellar structure. These numerous aperiodic objects are responsible for the diffuse X-ray scattering observed along the axis-Y, around the a-band in both \( N_c \) and \( N_c^\xi \) phases.

Taking into account that the brucine molecules ionize in the presence of water \([2]\), we expect that the brucine ions are preferentially located in the hydrophilic regions of the \( N_c^\xi \) structure. The retention of the same \( s^{-1}_y \) and width of the a-band along the Y-axis is consistent with this assumption. If the BS were placed in the hydrophobic region of the micelles, the available volume of the paraffinic chains of the amphiphilic molecules would be significantly reduced to keep the same \( s^{-1}_y \). A possible origin of the bending of the a-band to larger spacing distances for \( \theta > 20^\circ \) (see Fig. 4) is the existence of edge dislocations swollen by the BS ions (the BS dimensions are \( 6.5 \times 10 \times 16 \) Å). Considering that the brucine sulphate is completely ionized \([2]\), sample \( S2 \) has about one brucine ion per micelle \([15, 16]\). As the structure of the \( N_c \) (or \( N_c^\xi \)) is pseudo-lamellar and not lamellar, the swollen regions are not necessarily compensated by compressed regions, which could supress this excess of bending of the a-band i.e., could make \( \delta \rho = 0 \). The presence of the brucine in the edge dislocations could thus induce a local micellar deformation which increases the spacing distances for increasing values of \( \theta \).

The swelling of edge dislocations is not the only possibility for the BS molecules to make a local deformation of the structure. The same thing could also happen if the BS molecules were included in the pseudo-lamellar structure near the micelle edge. This could also produce micellar deformations increasing the spacing distances at large \( \theta \), but keeping \( s^{-1}_y \) constant.

Comparing the values of the molar concentration \( M_o \) for both \( S2 \) and \( S4 \) samples (Experimental section) we observe that about 40 times more octanol than BS is needed to produce the same cholesteric pitch. This fact indicate that BS is more efficient to induce the cholesteric structure in a previous nematic pseudo-lamellar structure. The local deformation the pseudo-lamellar structure (originated by the swelling of edge dislocations and/or by the deformations of the micelles near their edges) is observed in our experiment, only in cholesteric samples doped with BS and not in cholesteric samples doped with octanol. Considering that the cholesteric structure in a lyotropic mesophase is achieved by the twist of the original nematic pseudo-lamellar structure (by means of the doping with a chiral agent), two different processes seem to exist:

- if the chiral molecule is an amphiphile, it can be integrated to the micelles inducing the cholesteric twist of the pseudo-lamellar structure, without introducing strong local deformations of the original nematic structure;
- if the chiral molecule is not an amphiphile, it is probably not directly incorporated to the micelles and the twist of the original pseudo-lamellar structure, to give a cholesteric ordering, is achieved with a great number of strong (detected in the diffraction pattern) local deformations in the pseudo-lamellar structure. The presence of the big BS molecule (its volume is about 1/3 of the typical micellar volume \([14]\)) between the micelles could act as strange bodies in the pseudo-lamellar structure.

Conclusions.

In conclusion, we observe that the pseudo-lamellar ordering characteristic of the lyotropic nematic struc-
ture, is maintained along the Y-axis in the cholesteric \( N_e \) phases (BS or octanol doping). In the case of the octanol doping, where the quiral molecules are incorporated inside the micelles, both the \( N_C \) and \( N_e \) phases present the same microscopic structures. On the other hand, the presence of large chiral molecules (BS) in the pseudo-lamellar structure, probably not directly incorporated to the micelles, modifies the reciprocal image of the \( N_e \) phase compared to that of the usual \( N_C \). The reciprocal image of the \( N_e \) phase in this case could be explained by non correlated local perturbations of the pseudo-lamellar structure.

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References

[11] The typical diffraction patterns of oriented \( N_C \) phase were published elsewhere; see reference [7].
[12] The second order band is not clearly visible in figure 1 because the diffraction pattern necessary for the 2D microdensitometer analysis cannot have the first order band over exposed. We have observed the second order band in patterns with typical exposure times of about 15 min.
[16] The estimated aggregation number of a micelle is about 200. See reference [15]