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Pseudo-lamellar ordering in uniaxial and biaxial lyotropic nematics : a synchrotron X-ray diffraction experiment

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Résumé. — Des mesures sont réalisées aux rayons X du synchrotron de LURE sur les phases lyotropes nématiques, uniaxes (discotiques et calamitiques) et biaxes, d'un mélange de laurate de potassium, 1-décanol et D₂O. Dans les trois phases, on observe le premier et le second ordre d'une bande de diffraction caractéristique d'une structure pseudo-lamellaire. Les clichés de diffraction X sont interprétés en termes de fluctuations orientationnelles de volumes de corrélations intrinsèquement biaxes. On en déduit que les phases calamitiques et discotiques ne sont pas composées de micelles cylindriques (ou en forme de disques), mais d'agrégats de forme statistiquement biaxe, semblable dans les trois phases nématiques. Seul l'ordre à longue distance change aux transitions nématiques uniaxes-biaxes.

Abstract. — Synchrotron X-ray measurements are performed in both uniaxial (discotic and calamitic) and biaxial nematic lyomesophases of the mixture K-laurate, 1-decanol and D₂O. A first-order band and a second-order band with spacing ratio 1 : 2 characteristic of a pseudo-lamellar structure are observed in the three nematic phases. The X-ray diffraction results are interpreted in terms of the orientational fluctuations of intrinsically biaxial correlation volumes. It is argued that the calamitic and discotic phases are not built up of cylindrical-like and disk-like micelles, but of aggregates of statistically biaxial shape, similar in the three nematic phases. The only change at the uniaxial-biaxial nematic transitions is the long-range order.

1. Introduction.

Under proper temperature-concentration conditions, mixtures of amphiphilic molecules and water may give lyotropic nematic phases [1]. From symmetry considerations [2], three types of nematics are expected, two uniaxial [1] and one biaxial [3]. X-ray [4, 5] and neutron [6] diffraction structural studies have been performed on both uniaxial phases. Depending on whether the director (\mathbf{n}) orients parallel or perpendicular to the magnetic field (\mathbf{H}), these uniaxial phases have been classified [6] as calamitic (N_C) and discotic (N_D), respectively. The form of the amphiphilic aggregates, averaged in the laboratory frame, was obtained from the maximum positions on the

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diffraction patterns [6]. In this analysis, the micellar shapes were found to be amphiphilic oblate and prolate ellipsoids in the N_D and N_C phases, respectively [5].

In this Letter we report what we believe to be the first X-ray structural study of the biaxial nematic phase (N_{BX}). From the data analysis, we argue in particular, that the N_C and N_D phases are not built up of cylindrical-like and disk-like « micelles », but of aggregates of statistically similar biaxial shape, piled up in a locally lamellar structure.

2. Experimental.

The nematic lyomesophase is prepared according to conventional procedures [1] with the following composition in weight % : potassium laurate (synthesized and recrystallized in the laboratory) — 26.50; 1-decanol (> 99 % purity from Fluka) — 6.68 and D_2O — 66.82. A small quantity of ferrofluid-FF (< 10^{-4} by weight) is added in order to help the alignment in the magnetic field [7]. This addition of FF does not modify the temperature transitions and the diffraction patterns within our experimental accuracy, as we have independently checked in the N_C phase. As the temperature is increased, the successive phases identified by conoscopic measurements [8] are : Isotropic (9.5 °C) N_D (13.2 °C) N_{BX} (23.2 °C) N_C (40 °C) Isotropic [9].

The sample is sealed in a Lindemann glass capillary with 1.5 mm diameter placed in a temperature controlled device (accuracy ± 0.1 °C), in the vertical direction, perpendicular to the X-ray beam, in a transmission geometry. A magnetic field of 3 kG and ~ 500 G (permanent magnet) is applied perpendicular or parallel to the X-ray beam, respectively. X-ray diffraction patterns are obtained by photographic method using a synchrotron X-ray monochromatic radiation (Ge crystal, wavelength $\lambda = 1.62$ Å) of Orsay (Laboratoire pour l'Utilisation du Rayonnement Electromagnétique — LURE). The exposure times are about 10 min and the mean experimental resolution in 2θ scattering angle is 0.04° (in fact this resolution does not vary drastically with the direction of the scattering vector in the small angles which are of interest in these experiments [10]) H defines the l -axis of the laboratory frame; the 3-axis coincides with the capillary axis (X-ray beam along the 1- or 2-axes).

The orientation of the sample has been carefully achieved in the three nematic phases. In the N_C phase, the director n simply orients parallel to H (1-axis). In the N_D phase, the capillary is rotated around its axis the 3-axis), in presence of H (along the 1-axis), following the classical NMR orienting procedure [1], which orients the director n along the 3-axis. Because the relaxation time of the orientation of our samples is typically 15 min, it is enough to apply the orienting procedure every 5 min to produce and to keep a good alignment of the sample. In N_{BX} , the monodomain is obtained by just oscillating the capillary by 45° around its axis and restoring it into its initial position. Note that interruptions of the exposure are needed for longer exposure times. The high intensity X-ray beam of the synchrotron source, which allows short exposure times, is very helpful to apply strictly the orienting procedure and, thus, to warrant the perfect orientation of the samples during the experiments.

3. Results.

3.1 GENERAL FEATURES. — The X-ray diffraction patterns of the uniaxial and biaxial phases are presented in figure 1 : the X-ray beam, directed along the 1- or 2-axes is parallel (or equivalently perpendicular) to the magnetic field H in the N_D phase (Fig. 1a), perpendicular to H in the N_C phase (Fig. 1b) and respectively parallel and perpendicular to H in the biaxial phase (Figs. 1c and 1d) [11]. Due to the infinite fold axis (director n) of the uniaxial phases, the measurement of the diffracted intensity may be reduced to one meridian plane of the reciprocal space. The whole three dimensional reciprocal structure is then generated by the rotation of the diffraction pattern around the director. In our experimental conditions, the directors in the N_D and N_C phases are along the 3- and 1-axes respectively. From figures 1a and 1b, we see therefore that the reciprocal

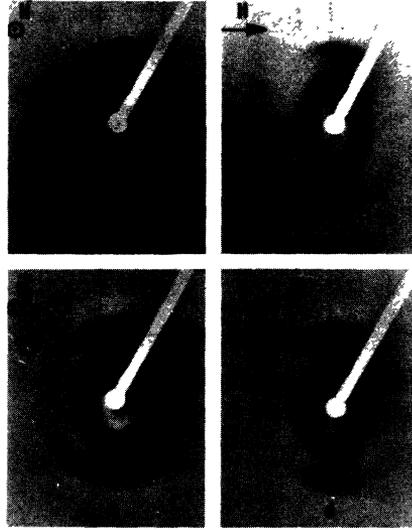


Fig. 1. — Synchrotron X-ray patterns of oriented K-laurate, 1-decanol, D_2O nematic lyomesophases. The capillary is set up in the vertical direction in the plane of the figure. (a) Discotic phase with the director (\mathbf{n}) along the vertical direction. $T = 12$ °C. Note that, for symmetry reasons, the X-ray pattern is the same when \mathbf{H} is in the plane of the figure, perpendicular to \mathbf{n} . (b) Calamitic phase with \mathbf{n} parallel to the magnetic field (\mathbf{H}) in the plane of the figure. $T = 24$ °C. (c) and (d) Biaxial nematic phase with \mathbf{H} parallel and perpendicular to the beam respectively. The sharp band d in figure 2 near the beam stopper more visible in (c) is due to the $\lambda/3$ radiation. $T = 20$ °C.

structure of the uniaxial phases may be schematized as a hollow cylinder parallel to \mathbf{n} with intense ends in the N_D phase [5], and intense edges in the N_C phase. The biaxial phase has only three perpendicular two-fold axes, and at least two cuts of the reciprocal space are needed to give its reciprocal structure. Figure 1c and 1d, which represent cuts of the reciprocal space by the planes containing the 3-, 2-axes and the 3-, 1-axes, respectively show that the 3D image in the reciprocal space is a hollow barrel of section flattened in the direction of \mathbf{H} , intermediate between the two uniaxial reciprocal images. By comparing the patterns of the uniaxial phases with those previously published [4, 5] we observe new features, common to all our uniaxial and biaxial X-ray patterns. We see essentially a second-order band (band b in the scheme of Fig. 2) with a spacing-ratio of 1/2 associated to the first-order band (a-band) along the 3-axis direction. It is to be noted that these characteristic features are observed in all the numerous (~ 10) nematic samples of various concentrations that we have prepared in the phase diagram of Saupe [3].

3.2 ANALYSIS OF THE X-RAY DIFFRACTION PATTERNS ALONG THE 3-AXIS.

3.2.1 Orientational fluctuations. — Liquid crystals [12] have, in addition to their short-range (positional and orientational) ordering, a long-range orientational order. The associated fluctuations of orientation smear the X-ray pattern from the short-range positional ordering, giving typical band-arcs (band a in Fig. 1). These, in turn, allow a measurement of the amplitude ϕ of the orientational oscillations about the 3-axis which yields a determination of the order parameter S in the uniaxial nematic phases $\left[S = \frac{1}{2} \langle 3 \cos^2 \phi - 1 \rangle \right]$. From the analysis of figures 1a and

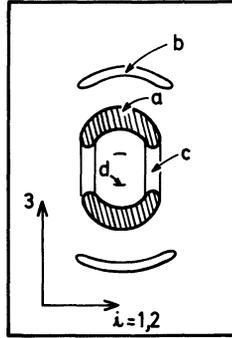


Fig. 2. — Sketch of the diffraction patterns presented in figure 1 with a denomination of the different diffraction bands.

1b [13], S is found to be 0.85 in the N_D phase and 0.90 in the N_C phase, close to the biaxial transitions. Moreover, the high degree of orientational order is confirmed by the rectilinear shape of the c-band. In the middle of the biaxial temperature range (Figs. 1c and 1d), the oscillations referred to the 3-axis are of the same order of magnitude as in the uniaxial phases, but they have in reality, different amplitudes in the 3-1-plane and in the 3-2-plane because of the biaxial symmetry. Near the $N_{BX} - N_C$ phase transition, the orientational fluctuations in the 3-2-plane have a larger amplitude, until they become full rotations over the director (the 1-axis) of the N_C phase.

3.2.2 Pseudo lamellar structure. — The second-order band (b) which is observed (Fig. 1) in the three nematic phases, including the N_C phase up to the N_C -Isotropic transition, is remarkable. In the usual picture of the N_C phase as composed of cylinder-like micelles [5], a second-order band relatively broad corresponding to a six-fold coordination would have been expected at a ratio of about $\frac{1}{\sqrt{3}}$. Within our present sensitivity we only see a sharp band with a $\frac{1}{2}$ spacing ratio. This indicates a 1D periodicity of the micelles along the 3-axis. The measurement of the scattering vector modulus $\left(s = \frac{2 \sin \theta}{\lambda}\right)$ along the 3-axis shows that this periodicity is $s_3^{-1} = 48.7 \pm 0.8 \text{ \AA}$, constant across the whole N_D , N_{BX} , N_C range (Fig. 3). From the relative width of the a-band (Fig. 1) [13], we can estimate the positional correlation in the direction of the 3-axis. Using Scherrer's expression [14] we find the positional order to extend along this direction on about 400 \AA ($\simeq 8$ lamellar distances), in good agreement with previous and X-ray measurements in the N_C phase of a different mixture [15], and constant in the three nematic phases. Note that this 1D-periodicity is also correlated in the directions perpendicular to the 3-axis, as indicates the narrow arc-shape of the a-band, very reminiscent of the thermotropic smectic A. Finally, the three nematic phases are found to exhibit the same pseudo-lamellar structure on short-range scales.

3.3 DIFFRACTION MAXIMA ALONG THE 1- AND 2-AXES. — The positions of the diffraction maxima are also measured along the 1- and 2-axes (c-band of Fig. 2). The data s_1^{-1} and s_2^{-1} , (and s_3^{-1}) are plotted *versus* temperature in figure 3. In the uniaxial phases, because of symmetry, two out of the three s_i^{-1} become undistinguishable. In figure 3, we note that s_1^{-1} varies slowly with temperature ($\sim 4\%$ from the N_D to the N_C phase), and that s_3^{-1} is constant. This indicates in the usual naive real-space picture that the dimensions of the micelles, i.e. their « diameters » and « lengths », [19] are just interchanged in the N_D and N_C phases.

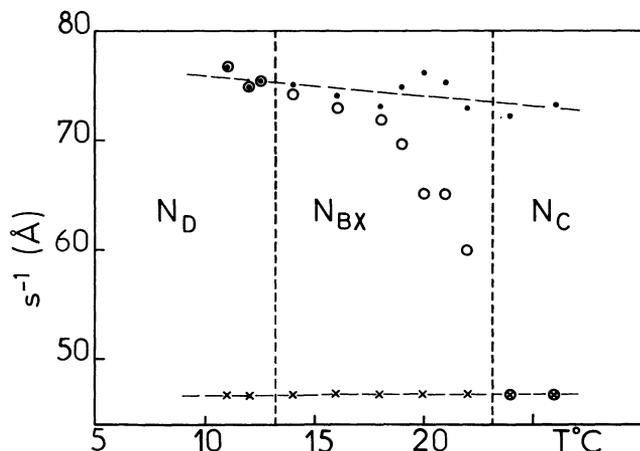


Fig. 3. — Synchrotron X-ray measurements of s_1^{-1} (●), s_2^{-1} (○) and s_3^{-1} (×) as functions of temperature in the three nematic phases. The variations of s_1^{-1} and s_3^{-1} with temperature are visualized by broken lines. The experimental error in the measurements of s_i^{-1} from the microdensitometer profile of the diffraction patterns is about (0.8 Å). The transition temperatures (dashed lines) are determined independently by measuring the optical anisotropies [8].

4. Discussion.

The observation of the same local structure in the three N_D , N_{BX} , N_C phases is not really a surprise. The theory of second-order phase transitions shows that local ordering, on scales smaller than the correlation length ξ , should be the same on both sides of the transition, and identical to that of the ordered phase [16]. This remark applies to the uniaxial-biaxial nematic phase transition which is found to be a mean-field second-order transition [8]. The correlation length ξ has recently been estimated from a Rayleigh scattering experiment [17]. The bare correlation length ξ_0 for the $N_D - N_{BX}$ transition, is found ~ 100 Å. This indicates that $\xi \left(= \xi_0 \left| \frac{T - T_c}{T_c} \right|^{-1/2} \right)$ is larger than ~ 500 Å over the whole nematic range, at least an order of magnitude larger than the micellar size. The local order should therefore be similar in the three nematic phases, and identical to that of the ordered phase, i.e. biaxial. In the N_C phase, such a biaxial local ordering seems to be confirmed from recent neutron measurements [18]. One can now use this idea to reconstruct the observed diffraction patterns. Let us consider the reciprocal-space image of a cluster of 1D positional order (of size ~ 400 Å, smaller than ξ), similar in the three nematic phases, and biaxial. In a coarse approximation, it is an elongated cylinder C^* with an elliptic section, resembling the reciprocal image of the N_{BX} phase. It has sharp and intense spots at the ends (due to the well-defined pseudo-lamellar ordering) and more diffuse edges. The reciprocal structure of the different nematic phases can be obtained by averaging the cylinder C^* over the orientational fluctuations characteristic of these phases. In the N_D phase, the orientational fluctuations consist mainly in rotations over the 3-axis. The reciprocal structure of the N_D phase is then a circular cylinder, similar to C^* , which may be interpreted in the real space, as produced by average disk-like micelles of spacing distances equal to s_3^{-1} and s_1^{-1} along and between their symmetry axis (3-axis) respectively. In the N_C phase, the reciprocal structure is obtained by averaging the same cylinder C^* over rotations around the 1-axis. This is now a thick disk which seems, in the real space, to be due to average cylindrical micelles of spacing distances equal to s_1^{-1} and s_3^{-1} along and between their symmetry axis (1-axis), respectively. This reconstruction explains that the dimensions of the

average micelle, i.e. the « diameter » and the « length » [19], are just interchanged in the N_D and N_C phases, as found experimentally (Fig. 3). The interpretation of the X-ray measurements in the biaxial phase can also be obtained by averaging the reciprocal cylinder C^* over the orientational fluctuations (of small amplitude now). These fluctuations which are described by the biaxial order parameter $q_{\alpha\beta}$ [12], introduce similarities between the temperature variations of the s_i 's and the optical indices n_i [8]. In particular, they drive s_2 in the N_{BX} phase from its value ($= s_1$) in the N_D phase to its value ($= s_3$) in the N_C phase [20].

5. Conclusions.

Using the Synchrotron X-ray radiation, we have obtained the reciprocal structure of the nematic discotic, biaxial, and calamitic phases in the ternary mixture of potassium laurate, decanol and D_2O . We have observed the same local pseudo-lamellar ordering in the three nematic lyomesophases. Using this local biaxial ordering, one can reconstruct the observed X-ray diffraction patterns in the three nematic phases, by averaging over the symmetry allowed rotations and oscillations around the directors of the phases. Going back to real space, if one supposes that these phases are built of individual micelles, one can give the image that the micelles keep a well-defined thickness (related to the amphiphilic double-layer), and, on a local average, the same lateral elliptic shape. The statistics which governs the biaxial shape and the size of the micelles is actually unknown (a mixture of disk-like and cylinder-like micelles may not be excluded). The important point is that this statistics (e.g. mixture of disks and cylinders) must remain very similar in the three nematic phases, with only a smooth temperature variation which could trigger the nematic phase transitions.

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