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Biaxial Nematic Lyomesophase Studied by X-Ray Diffraction†

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Biaxial nematic lyomesophases of potassium laurate/l.decanol/D_2O have been studied by X-ray diffraction technique using conventional and synchrotron source radiation. The procedure used for orienting the biaxial phase is described, together with the use of ferrofluid. The X-ray diffraction patterns showed biaxial symmetry in reciprocal space.

INTRODUCTION

Under appropriate temperature-concentration conditions, mixtures of amphiphilic compounds with water[1] produce nematic lyomesophases composed of micellar aggregates. From symmetry considerations,[2] two uniaxial phases and one biaxial phase are expected. Depending on whether the director ($\vec{n}$) orients parallel or perpendicular to the magnetic field ($\vec{H}$), these uniaxial phases have been classified[3] as calamitic (N_C) and discotic (N_D) respectively. The form of the micellar aggregates, averaged in the laboratory frame, was obtained from the positions of the maxima in the X-ray diffraction patterns:[4] oblate and prolate ellipsoids for the N_D and N_C phases respectively. The first experimental evidence of a biaxial nematic lyomesophase

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(N_{BX}) was obtained by Yu and Saupe[5] using NMR and conoscopic measurements in a ternary system of potassium laurate (KL)-Decanol(DeOH)—D_2O.

In order to improve the orientation of the uniaxial lyomesophases Liébert and Martinet[6] have added small quantities of ferrofluid to these phases.

In this paper we discuss the experimental procedure used to obtain a well oriented monodomain of the N_{BX} phase in capillaries for X-ray diffraction experiments. We compare also, the diffraction results obtained for samples with and without ferrofluid.

EXPERIMENTAL

The nematic lyomesophases (S 1 and S 2) were prepared according to conventional procedures[1] with the compositions (in weight %): S 1 (KL - 25.5; DeOH - 6.4; D_2O- 68.1) and S 2 (KL - 26.50; DeOH - 6.68; D_2O - 66.82; ferrofluid[7] $\sim 10^{-4}$). The potassium laurate was synthesized and recrystallized in this laboratory from commercial lauric acid (Fluka pp. a > 99%), the l-Decanol was obtained from Fluka (p.p.a. > 99%) and the D_2O was obtained from the CEA Saclay. As the temperature was increased, the successive phases identified by conoscopic measurements[8] were: S 1 (Isotropic (10°C) N_D (17.2°C) N_{BX} (19.5°C) N_C (40°C) Isotropic) and S 2 (Isotropic (9.5°C) N_D (13.20°C) N_{BX} (23.2°C) N_C (40°C) Isotropic).

The samples were sealed in glass capillaries of 1.5 mm diameter, and were placed in a temperature controlled device (accuracy of 0.1°C) with vertical orientation (transmission geometry), with their axes perpendicular to the X-ray beam. X-ray diffraction patterns were obtained by a photographic method. The magnetic field defined axis 1 of the laboratory frame and the axis 3 coincides with the capillary axis. The capillary is free to rotate around axis 3.

A critical point in structural studies by X-ray or neutron diffraction experiments is to keep the sample well oriented for at least the duration of the measurements. In a first approach, a Laue camera (sample S 1 without ferrofluid) was used together with a conventional sample orienting procedure[4] which assumed that the nematic orientation was preserved during the exposure time, even in the absence of a strong magnetic field. In order to check this hypothesis of a slow disorientation, sample S 2 (with ferrofluid) was investigated with synchrotron radiation. In this case, short exposure times could be used, low magnetic fields, which were sufficient to allow the ferrofluid

to cause the orientation of the sample,[9] could be applied perpendicular or parallel to the beam.

Laue Camera

A monochromatic Laue camera[10] with Cu K_α radiation ($\lambda = 1.54$Å) and a sample to film distance of 120 mm was used. A static magnetic field of 15 KG could be applied perpendicularly to the X-ray beam. The exposure times were about 8 hours.

The classical procedure to break the orientational degeneracy in N_D phases was established some years ago by NMR studies.[1] It consists basically of combining a static magnetic field with the continuous rotation of the sample around an axis perpendicular to $\vec{H}$. In our case, we rotated the capillary (N_D phase), around axis 3 ($\vec{H}$ applied along the axis 1) by 90° every 10 minutes (for about 1 hour) before the exposure. After this the sample was well oriented (checked by the X-ray diffraction patterns), the temperature was raised to give the N_{BX} phase in the presence of $\vec{H}$. Under these experimental conditions (A) we obtained the diffraction pattern in the plane of the 1-3 axes. To obtain the pattern in the 2-3 plane we cooled the sample in the N_D phase and repeated the orientational procedure. When a well oriented N_D phase was obtained we heated the sample up to the N_{BX} phase, switched off the field and rotated the sample by 90° (experimental condition B).

Synchrotron radiation

The X-ray beam used was from the DCI synchrotron ring at LURE (Laboratoire pour l'Utilisation du Rayonnement Electromagnétique-Orsay) and was reflected by a Ge(111) bent single crystal. The chosen wave length was 1.62 Å and a 0.3 mm collimator was used. The sample to film distance was of 203 mm and the experimental resolution of 2×10^{-3} Å^{-1}. A magnetic field of 3 KG and ~ 500 G (permanent magnet) was applied perpendicular (condition A) or parallel (condition C) to the X-ray beam, respectively. The exposure times were about 10 minutes.

The same procedure as above was used for orienting the sample (S 2). An oriented N_D phase was obtained in the presence of $\vec{H}$ by successive rotations of the capillary around the axis 3 (90° every 3 minutes) for about 15 minutes. Then, the temperature of the sample was raised to give the N_{BX} phase in the presence of $\vec{H}$. The sample was then oscillated by 45° about its initial position every 3 minutes.

Each time the orientational procedure was applied the exposure was stopped.

RESULTS AND DISCUSSION

The effect of the ferrofluid

We have observed, by conoscopic measurements[8] that, to within our experimental accuracy, the addition of a small quantity of ferrofluid does not modify the transition temperatures, the nature of the different phases or the value of the birefringence of the nematic lyomesophases which we have studied. We have also verified that the ferrofluid does not modified the X-ray patterns of the N_C phase[11]

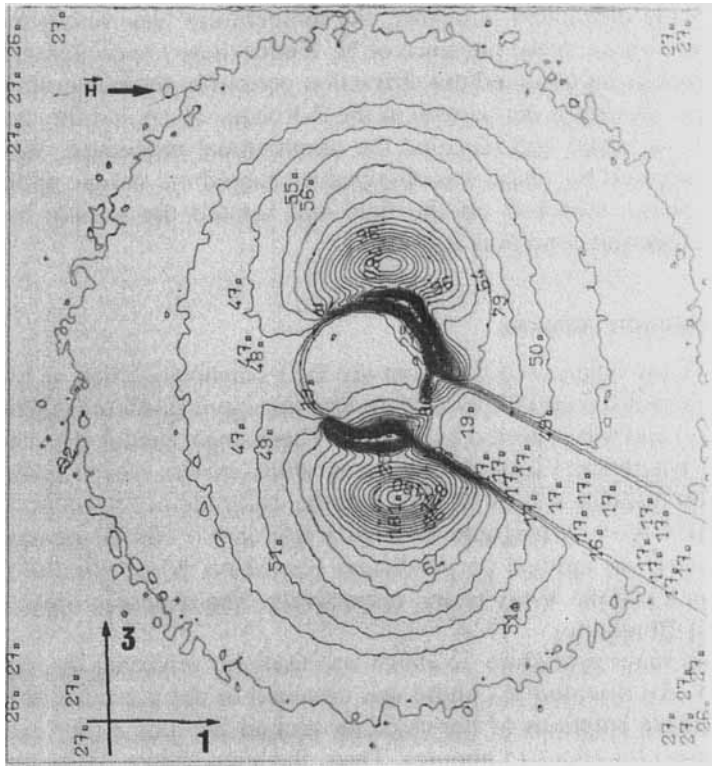

FIGURE 1 X-ray diffraction pattern of the N_{BX} phase of S 1; Laue camera; experimental condition A. Plane of the axes 1-3. The capillary vertical in the plane of the figure. Magnetic field along axis 1, perpendicular to the beam.

(the positions and widths of the measured bands being unchanged). All of these observations show that the addition of ferrofluid in small quantities to this lyotropic system, is a powerful tool to orient the nematic phases in weak magnetic fields without producing appreciable modifications of the physical properties.

X-Ray diffraction results N_{Bx} phase

Figures 1 and 2 show the densitometer maps of the patterns obtained with the Laue camera (sample S 1) in the conditions A and B respectively. In the configuration A, (Figure 1) the diffraction pattern presents two intense spots along the axis 3 at $s_3^{-1} = 50 \pm 1$ Å (s is the modulus of the scattering vector), joined by streaks along the axis 1 at $s_1^{-1} = 55 \pm 1$ Å. In the configuration B (Figure 2) we observed two weak spots along the axis 3 at $s_3^{-1} = 49 \pm 1$ Å and streaks along the axis 2 at $s_2^{-1} = 51 \pm 1$ Å. The values of s^{-1} (Figure 2) were similar to within the experimental accuracy. This suggested that the sample was partially disoriented and is consistent moreover with the abnormally long crescents observed in Figure 2 (orientational

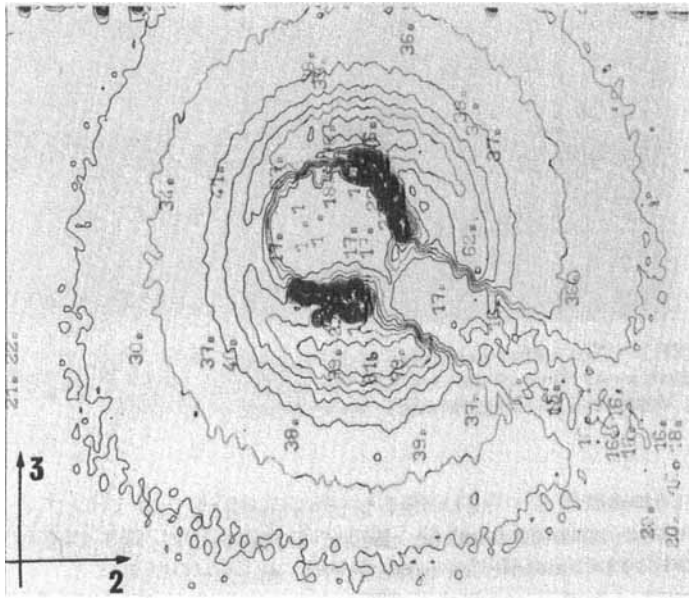

FIGURE 2 X-ray diffraction pattern of the N_{Bx} phase of S 1; Laue camera; experimental condition B. Plane of the axes 2-3. The capillary is vertical in the plane of the figure. Residual orientation (H = 0).

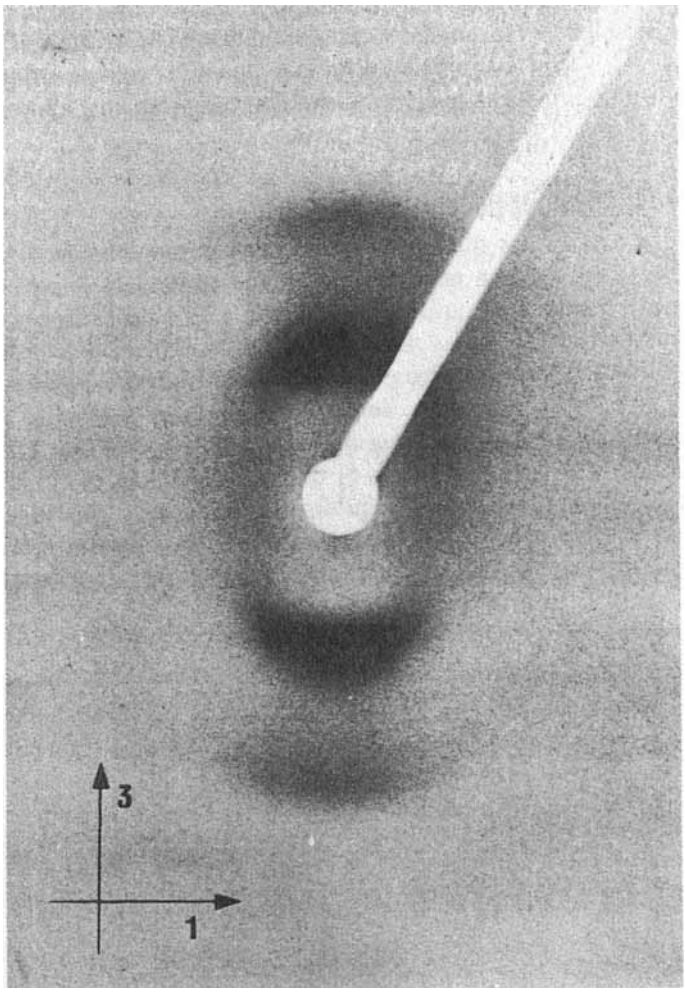

FIGURE 3 X-ray diffraction pattern of the N_{Bx} phase of S 2; synchrotron radiation; configuration A. Plane of the axes 1-3. The capillary is vertical in the plane of the figure. Magnetic field along the axis 1, perpendicular to the beam.

order parameter S ~ 0.3) which is incompatible with the usual values of S in the oriented nematic phases.[12] Therefore, this experimental method is not suitable for quantitative measurements.

Figures 3 and 4 show the diffraction patterns obtained with synchrotron radiation (samples S 2) in geometries A and C respectively. In the configuration A (Figure 3) the pattern contains two intense

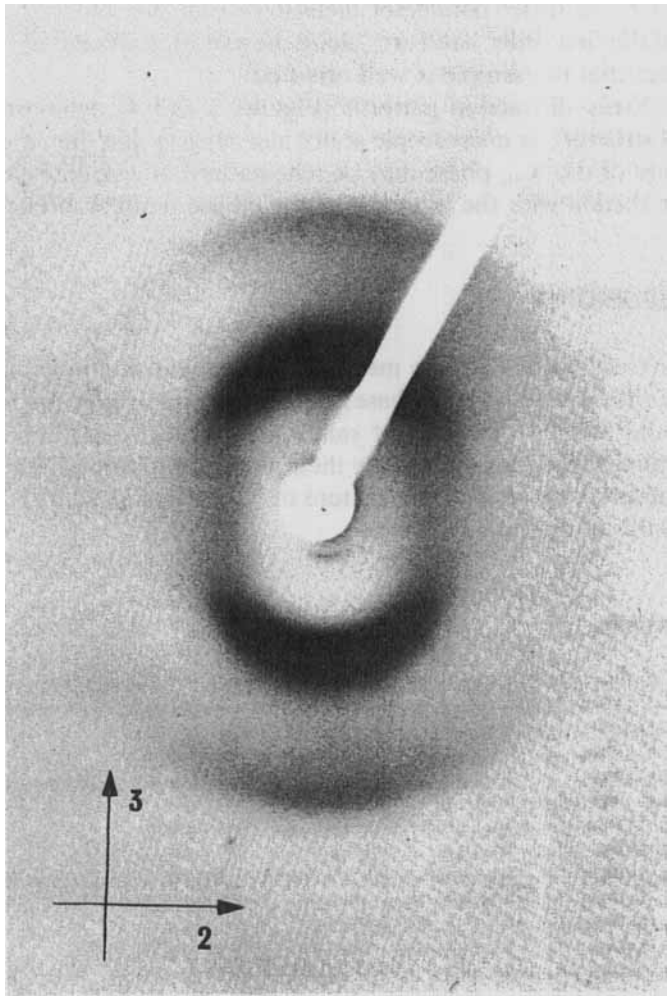

FIGURE 4 X-ray diffraction pattern of the N_{BX} phase of S 2; synchrotron radiation; configuration C. Plane 2-3. The capillary is vertical in the plane of the figure. Magnetic field along axis 1, parallel to the beam. The sharp band along the 3 axis near the beam stop is due to the $\lambda/3$ radiation.

spots along axis 3 at $s_3^{-1} = 48.6 \pm 0.8$ Å joined by streaks along the axis 1 at $s_1^{-1} = 76.1 \pm 0.8$ Å. In the configuration C (Figure 4) we observed two spots along axis 3 at $s_3^{-1} = 48.6 \pm 0.8$ Å joined by streaks along axis 2 at $s_2^{-1} = 65.2 \pm 0.8$ Å. A second order band along the axis 3 is also visible in both patterns at $s^{-1} = 24.6 \pm 0.8$ Å. A detailed analysis of this second order band is made elsewhere.[13]

Note that the order parameter measured from the intensity profile around the first order band arc (along the axis 3) is about 0.85, which indicates that the sample is well oriented.

The X-ray diffraction patterns (Figures 3 and 4) demonstrate a biaxial structure at microscopic scales and suggest that the reciprocal structure of the N_{BX} phase may be schematized as a hollow barrel of elliptic section with the long axis of the ellipse parallel to $\vec{H}$.

CONCLUSIONS

We have established an easy method for obtaining monodomain samples of the biaxial nematic phase, which seems necessary for reliable structural studies. Addition of small quantities of ferrofluid to the lyotropic system does not modify their physical properties and allows us to observe the reciprocal structure of N_{BX} which presents a biaxial symmetry at microscopic scales.

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