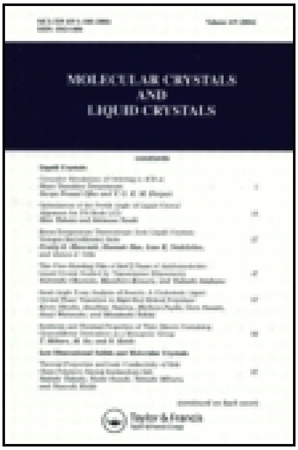


Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl17

X-Ray Study of Modulated Smectic A Phase

B. I. Ostrovskii [a] & M. A. Saidachmetov [a]

[a] Institute of Crystallography USSR Acad. Sci., Leninsky prospekt 59, Moscow, 117333, USSR

Version of record first published: 22 Sep 2006.

Mol. Cryst. Liq. Cryst. 1990, Vol. 192, pp. 19–24
Reprints available directly from the publisher
Photocopying permitted by license only

Printed in the United States of America

X-RAY STUDY OF MODULATED SMECTIC A PHASE

B.I.OSTROVSKII and M.A.SAIDACHMETOV

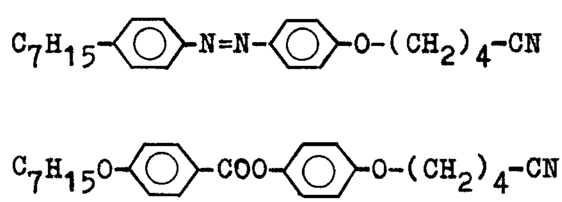
Institute of Crystallography USSR Acad.Sci., Leninsky prospekt 59,Moscow, 117333 USSR

Abstract X-ray diffraction has been used to study the lamellar ordering in mixture of mesogenic compounds in which polar cyano end group is decoupled from aromatic core through non-polarizable methylene chain. The smectic $\tilde{A}$ phase with bilayer density wave modulated in the plane of the layers has been found. The spatial period of modulated structure depends on the composition of a mixture.

INTRODUCTION

A smectic A phase is characterized by the one-dimensional translational order in an orientationally ordered fluid. When the constituent molecules possess strongly polar end groups , a rich variety of lamellar packings occurs[1,2]. Apart from the ordinary smectic A_1 phase with spatial period d approximately equal to the molecular length l, there are bilayered smectics A_d , whose spatial period is incommensurate with the molecular length and smectics A_2 with the period d = 2l. In addition, there exist a smectic $\tilde{A}$ phase with the bilayer density wave modulated along the direction perpendicular to the director $\vec{n}$[3] and a smectic A_{ic} phase with two collinear modulations of incommensurate wavelengths simultaneously condensed[4]. The incommensurate layering has been also found for terminally non-polar compounds with complicated steric interaction[5].

Here we present the results of X-ray diffraction study of lamellar ordering for a novel class of terminally polar liquid crystals. In these compounds the polar cyano end group is sterically and electrically decoupled from the rigid and polarizable aromatic core through a flexible and non-polarizable methylene $(CH_2)_4$ chain, Figure 1. As a result the longitudinal dipole moment of a molecule is localized in the region of the CN group. The mesogenic compounds with such properties have been known to form either monolayer (A_1) or bilayer (A_2) smectic A phases[1,6]. Our X-ray measurements



(1)

(2)

FIGURE 1 Molecular structures of 7CBAB (1) and 7OBECBP (2) liquid crystals.

give evidence that the low temperature liquid crystalline phase in 7CBAB-7OBECBP mixture is a smectic $\tilde{A}$ with the bilayer density wave modulated in the plane of the layers.

EXPERIMENTAL RESULTS AND INTERPRETATION

The phase diagram for the 7CBAB-7OBECBP mixture is shown in Figure 2. The 7OBECBP forms only monotropic nematic phase at the temperatures lower than t=68°C. In contrast to 7OBECBP 7CBAB shows the phase sequence with rather rich smectic polymorphism: $Cr \overset{67^\circ}{\longleftrightarrow} \tilde{A} \overset{77^\circ}{\longleftrightarrow} A_1 \overset{86^\circ}{\longleftrightarrow} I$. Smectic $\tilde{A}$ phases for 7CBAB-7OBECBP mixture are easily supercooled down to t= 40° where crystallisation occurs. Our X-ray study was performed using a standard photo-

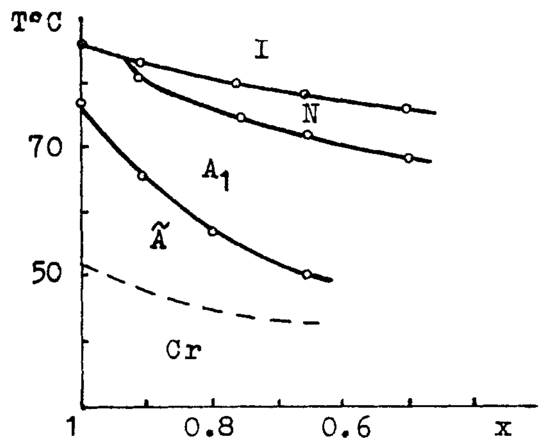


FIGURE 2 Phase diagram for 7CBAB-7OBECBP mixture, x is a concentration of 7CBAB in mixture.

technique and a diffractometer with a linear, position sensitive detector and a CuK_α radiation source. Details of the X-ray experiment have been reported earlier[7,8]. The orientation of liquid crystal was induced either by an A.C. electric field of strength 1 $kV.cm^{-1}$ and frequency 3 kHz or by a 1T magnetic field.

The X-ray patterns in the wide scattering angles region show broad, liquid-like peak centered at $q \simeq 1,5 Å^{-1}$ corresponding to average intermolecular distance of $\simeq 5Å$ in the smectic planes. Thus the smectic phases studied in our experiment have to be referred to smectic A ones.

Several degrees above the $A_1 \leftrightarrow \tilde{A}$ transition, the scattering from 7CBAB-7OBECBP mixture shows a Bragg-like peak at wave vector $\vec{q}_1 = (0,0,q_{\parallel 1})$ corresponding to monolayer ordering and two diffuse spots with wave vectors $\vec{q}_{\tilde{A}} = (q_{\perp o},0,q_{\parallel 2})$ corresponding to fluctuations of smectic $\tilde{A}$ antiphase structure in which the bilayer density wave is modulated in the plane of the layers ($q_{\parallel 1} = 2q_{\parallel 2} = 0.230 \mathring{A}^{-1}$, $q_{\perp o} = 0.027 \mathring{A}^{-1}$, $x=1$). Because the $\tilde{A}$ modulated lauering is degenerate in the smectic planes, the smectic $\tilde{A}$ fluctuations in the smectic A_1 phase manifest themself as a ring of scattering at $\vec{q}_{\tilde{A}} = (q_{\perp o}\cos\varphi , q_{\perp o}\sin\varphi , q_{\parallel 2})$, $0 \leq \varphi \leq 2\pi$, in reciprocal space. Its intersection with the Ewald sphere leads to the appearance of reflections (2) in the diffraction pattern, Figure 3. The interlayer distances for monolayer ($d_1 = 2\pi/q_{\parallel 1}$) and bilayer ($d_2 = 2\pi/q_{\parallel 2}$) ordering are practically independent on temperature and concentration in mixture. In contrast to d_1 and d_2, the period of the transverse modulation in the $\tilde{A}$ phase $L_\perp = 2\pi/q_{\perp o}$ depends on the concentration x of 7CBAB in a mixture. Its value changes from $L_\perp = 240 \mathring{A}$ at $x = 1$ to $L_\perp = 80 \mathring{A}$ at $x = 0.65$.

The $A_1 \leftrightarrow \tilde{A}$ phase transition line is signaled by the growth and sharpening of a scattering peak at $\vec{q}_{\tilde{A}}$. Below the $A_1 \leftrightarrow \tilde{A}$ transition the $\vec{q}_{\tilde{A}}$ scattering is resolution limited in the longitudinal direction and mosaic limited im the transverse direction. The detailed analysis of the critical behaviour in the vicinity of $A_1 \leftrightarrow \tilde{A}$ phase transition will be the subject of a special paper *.

CONCLUSIONS

The smectic $\tilde{A}$ phase with bilayer density wave modulated in the plane of the layers has been found for the mix-

---

* The high resolution X-ray scattering measurements of the critical fluctuations at the $A_1 \leftrightarrow \tilde{A}$ transition for 7CBAB-7OBECBP mixture were made recently in AMOLF (Amsterdam) in collaboration with W.de Jeu and W.Bouwman.

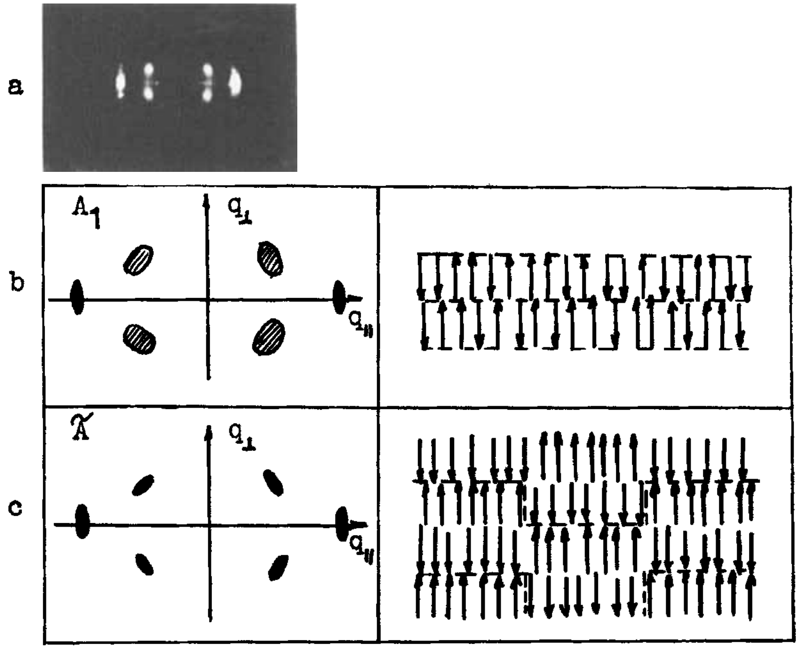


FIGURE 3 X-ray diffraction pattern for an oriented smectic $\tilde{A}$ liquid crystal, x =0.8, t =49°C (a). Real and reciprocal space pictures of smectic A_1 (b) and smectic $\tilde{A}$ (c) structures.

ture of terminally polar mesogenic compounds. The spatial period of modulated structure has been shown to depend on the composition of a mixture. It will be interesting to compare the smectic $\tilde{A}$ phase with classical incommensurate systems with displacive modulations. In most incommensurate systems such as metals with charge -density waves or certain dielectrics the main basis of the reciprocal lattice vectors $\vec{q}_0$ being pertubed by the weak sinusoidal potential with wave vector $\vec{q}_m$, results in a diffraction pattern with a small number of modulation peaks (satellits) at the $\vec{q}_o + \vec{q}_m$ points.[9] In the oposite case of the strong modulation, sharp, defect walls or antiphase boundaries appear resulting in a large number of higher harmonics in the diffraction pattern. Our X-ray study shows that the second variant of displacive modulation occurs for 7CBAB-7OBECBP mixture. The smectic phase consists of large regions of the bilayer A_2 phase periodically separated by defect walls or phase solitons where the phase of the modulation wave jumps by π, Figure 3. The absence of higher harmonics in the diffraction patterns from the $\tilde{A}$ structure **does not indicate** the weakness of transverse modulation, but is the consequence of the smoothness of smectic A phase revealing in sinusoidal shape of A_2 density wave.

We are indebted to P.Adomenas for synthesizing the liquid crystals. The authors are grateful to E.M.Averyanov, L.M.Blinov, W.Bouwman, V.E.Dmitrienko, W.de Jeu, E.I.Kats, V.V.Lebedev, A.R.Muratov, M.A.Osipov, E.I.Ryumtzev and E.M.Terent'yev for fruitful discussions.

REFERENCES

1. F.Hardouin, A.M.Levelut, M.F.Achard, G.Sigaud, J.Chim.Phys.,80, 53 (1983).
2. J.Prost, P.Barois, J.Chim.Phys.,80, 65 (1983).
3. F.Hardouin, Physica,140A ,359 (1986).
4. B.R.Ratna, R.Shashidhar and V.N.Raja, Phys.Rev.Lett. 55 , 1476 (1985).
5. S.Diele, G.Pelzl, W.Weissflog and D.Demus, Liq.Cryst. 3 ,1047 (1988).
6. F.Barbarin, M.Dugay, A.Poovesan, D.Guillon and A.Scoulios, J.Physique ,49 ,1583 (1988).
7. Yu.M.Lvov, B.I.Ostrovskii, L.A.Feigin, Soviet Phys. Crystallogr.,32, 671 (1987).
8. B.I.Ostrovskii, A.I.Pavluchenko, V.F.Petrov and M.A.Saidachmetov, Liq.Cryst, 5 , 513 (1989).
9. Incommensurate phases in Dielectrics ,edited by R.Blinc and A.P.Levanyuk (Elsevier, New York,1986).