1786199

INSTITUTO DE FÍSICA

preprint

IFUSP/P-224

STUDY OF ORIENTATIONAL EFFECTS IN A TYPE II LYOMESOPHASE

by

L.Q. Amaral

Instituto de Física, Universidade de São Paulo
CP 20516, CEP 05508, São Paulo, Brasil

B.I.F.-USP

UNIVERSIDADE DE SÃO PAULO
INSTITUTO DE FÍSICA
Caixa Postal - 20.516
Cidade Universitária
São Paulo - BRASIL

IFUSP/P 224

STUDY OF ORIENTATIONAL EFFECTS IN A TYPE II LYOMESOPHASE*

by

L.Q. Amaral

Instituto de Física, Universidade de São Paulo

CP 20516, CEP 05508, São Paulo, Brasil

* Paper to be presented orally at the Eight International Liquid Crystal Conference, to be held at Kyoto, Japan, from 30 June to 4 July 1980, and afterwards published in the Conference Proceedings, in a special volume of Molecular Crystals and Liquid Crystals.

JUNE/1980

STUDY OF ORIENTATIONAL EFFECTS IN A TYPE II LYOMESOPHASE

L.Q. Amaral

Instituto de Física, Universidade de São Paulo
CP 20516, CEP 05508, São Paulo, Brasil

ABSTRACT

A model of platelets for the structure of a type II lyomesophase SDS (Na decyl sulfate/water/decanol/Na sulfate) was previously proposed from small angle X-ray diffraction (SAX) in magnetically oriented samples; it was also shown that SAX results are strongly dependent on the orientational effects due to the surface of the container.

This paper reports orientational effects measured by SAX due to different interfaces SDS-container and SDS-air as well as effects due to electric and magnetic fields. The diffraction pattern consists of an inner difuse band (B) at ca. 120 Å and a sharper outer ring (S) at 38 Å whose broadeness and relative intensities vary strongly with sample container and degree of orientation. A remarkable strenghthening and sharpening of S is observed by surface orientation and by electrical orientation. Results are consistent with the hypothesis that under the influence of orientational forces the platelets aggregate forming macromicelles composed of several amphiphilic bilayers slightly swoolen while the water is seggregated.

I. INTRODUCTION

Lyomesophases that orient in presence of magnetic fields $\vec{H}$ and can be used as orientation matrix for NMR studies have been known for more than a decade[1,2]. These particular lyomesophases have been classified[3,4] as types I and II depending on the phase director orientation being parallel or perpendicular to $\vec{H}$; the two types can be identifyed by the ^2H NMR spectra.

We have reported previously[5-8] the study of a type II lyomesophase formed by a quaternary system (Na decyl sulfate/ decanol/ Na sulfate/water) by small angle X-ray diffraction (SAX). Results on samples conditioned in glass capillaries of 2 mm diameter have been obtained on unoriented samples (S_o) and on samples previously subjected to the action of a magnetic field $\vec{H}$ perpendicular to the capillary axis, with the X-ray beam parallel ($S_{\parallel}$) and perpendicular ($S_{\perp}$) to $\vec{H}$. SAX results[5-7] show a difuse inner halo at 80-140 Å and a sharp outer ring at 38 Å, that reduce to spots in the equator for $S_{\parallel}$; no diffraction maxima were produced for $S_{\perp}$.

To explain the observed diffraction patterns a model of finite planar micelles surrounded by water was proposed[6,7]. These planar micelles consist of an amphiphilic bilayer, in the form of platelets, probably disk-shaped, that align in presence of magnetic fields, with their plane parallel to $\vec{H}$. The observed results evidenced that further orientational restrictions were imposed by the container, and the platelets tend to remain in a plane that contains $\vec{H}$ and the capillary axis.

It was afterwards shown[8] that SAX results for this type II lyomesophase are strongly dependent on the container; the sharper outer ring at approximately the bilayer thickness is strenghtened by surface orientation when the sample is conditioned in quartz capillaries of 0.7 mm diameter, becoming a real Bragg

reflection; at the same time, no residual magnetic orientation could be obtained in this case. These results have been explained[8] with the hypothesis that under the influence of orientational forces the platelets aggregate forming macromicelles composed of several amphiphilic bilayers slightly swoolen while the water is segregated. However, from that study it was not clear whether the important parameter was the sample thickness or the container material; the nature of the surface orientation was also obscure.

In order to study further the orientational effects in this type II lyomesophase SAX measurements were now obtained in samples conditioned in different containers and also in samples subjected to the action of electric fields and of magnetic fields of different magnitudes.

II. EXPERIMENTAL

The quaternary lyomesophase SDS was prepared by the NMR laboratory of the Instituto de Química da USP according to procedures already described[6,7] and with the following composition: 37 wt% Na decyl sulfate, 5 wt% Na sulfate, 53 wt% water and 5 wt% decanol.

Samples were sealed in several types of containers:

C1 - Pyrex glass capillary with 2 mm diameter.

C2 - Container with mylar parallel walls and 1.4 mm sample thickness.

C3 - Lindemann glass capillary with 0.7 mm diameter.

C4 - Quartz capillary with 0.7 mm diameter.

Samples conditioned in capillaries were magnetically oriented in permanent magnets of 2 KG and 14 KG with $\vec{H}$ perpendicular to the capillary axis and the effect of residual magnetic orientation was studied by SAX. The effect of orientation by an external field $\vec{E}$ up to 12 KV/cm in the direction perpendicular

to the capillary axis was studied employing an insulated capacitor projected and constructed in our laboratory[9]. The device allows the obtention of diffractograms with $\vec{E}$ perpendicular to the X-ray beam ($S_{\perp}$). In the geometry $\vec{E}$ parallel to the X-ray beam ($S_{\parallel}$) only residual orientational effects are observed.

X-ray diffraction patterns were obtained at room temperature by photographing technique using a small angle Rigaku-Denki diffractometer with CuK_{α} radiation (Ni filtered) in a transmission geometry, with point focus and line focus. Some of the results were obtained with a Laue camera, with a 0.3 mm collimator and 10 cm sample to film distance.

III. RESULTS AND DISCUSSION

(A) Effect of container walls

SAX results obtained with the four containers and point focus are shown in figure 1 (a, b, c, d). The degree of orientation as well as the relative intensities of the sharper outer ring S and the difuse inner halo B and the broadness of S change considerably with the sample container, more than in type I lyomesophases[9]. The intensity of S is strongly dependent on sample thickness; increasing from C1 to C4; however results for C3 and C4, with same sample thickness, show the strong dependence on the container material as well. Quartz capillaries C4 gave the strongest surface orientation; S is very strong, reducing to well defined Bragg reflections in the equator, indicating reflecting planes parallel to the capillary axis. The preferred orientation along the equator indicates that the platelets tend to orient parallel to the capillary axis and perpendicular to the container walls. Mylar parallel walls (C2) show an intermediate degree of surface orientation: both bands are strong, but B is isotropic

while S is preferentially oriented in the equator.

B has been associated with the average distance between platelets in the water, while S corresponds roughly to the expected bilayer thickness[6-8]. The existence of this band has been associated[8] with formation of aggregates of platelets and seggregation of water. It seems therefore from our results that near the container surface this aggregation occurs while in the bulk sample the platelets are distributed in water. Isotropy in the bulk occurs only for thick samples without cylindrical symmetry.

(B) Effect of magnetic orientation

The effect of residual magnetic orientation could be observed only in samples without strong surface orientation. Container C1 gave results for $S_{\parallel}$ and $S_{\perp}$ that yield the model of platelets[6,7], while for C4 no residual magnetic orientation could be detected[8]. A compromise between orientation due to the container walls and to $\vec{H}$ was obtained with container C3. Figure 2 shows $S_{\parallel}$ and $S_{\perp}$ results obtained with C1 and C3 for line focus; corresponding results have also been obtained with point focus, but the photos with line focus are better suited for reproduction.

The diffraction figure changes with the sample diameter; for C1 , S is very weak while for C3 both B and S are strong. The orientation obtained in both cases indicate a director perpendicular to $\vec{H}$.

$S_{\parallel}$ for C1 container oriented in a stronger magnetic field of 14 KG resulted in the same diffraction pattern as for a 2 KG magnetic field; Figure 3 shows the result for point focus. However, the time of permanence in the magnet is an important factor: fully oriented samples are obtained after some days of exposure.

(C) Effect of electric field

The effect of orientation in presence of an electric field of 12 KV/cm perpendicular to the capillary axis has been studied for samples conditioned in C1 and C3 capillaries. For C1 the sample stayed for several days in the electric field and afterwards presented separation between the upper part and the down part, as seen under crossed polarizers. SAX measurements have been performed in both parts by moving the capillary height in relation to the X-ray beam. Figure 4(a-b) show $S_\perp$ results for the two parts. The down part presented relative intensities of B and S similar to those obtained by magnetic orientation, but in this case both bands are oriented along the vertical direction, indicating a director parallel to the capillary axis. The upper part presented a strenghtening of S, with the appearence of some Bragg points; orientation was also along the vertical direction. B splited in radial strikes in the direction of the Bragg points; this type of result is analogous to results obtained also by effect of electric fields in type I lyomesophases[9]. Results for $S_\perp$, in presence of $\vec{E}$, presented always a higher intensity than the residual geometry $S_\parallel$, but both were equal.

After switching off the electric field the electrical orientation was slowly lost and the directors moved cooperatively, so that the usual equatorial orientation was obtained. An intermediate position obtained after several days can be seen in Figure 4-c.

For the thinner C3 capillary (Figure 5) the effect of the electrical field consisted also in the strenghtening of S, that was transformed in Bragg points similar to those obtained for C4, oriented along the equator. Thus the effect of the quartz surface has been in a sense simulated by the applied electric field.

(D) Effect of air interface

The degree of order near the interface SDS-air was investigated by SAX and also by Laue transmission diffraction in samples conditioned in C3. In the Laue result the sample showed under crossed polaryzers a separation between upper and down parts, probably due to regions with different orientation. Figure 6 shows Laue results obtained just at the interface upper-down and in the down part, where the usual equatorial orientation was present. At the upper-down interface two different orientations are observed; the second, due to the region in contact with the air, was rotated towards the vertical meridian.

Figure 7 shows SAX result obtained near the SDS-air interface, also with orientation along the vertical. These results suggest that the separation observed in the capillary that stayed for long time in the electric field is also connected to the contact with the air interface.

The orientation in the air interface is probably related to transfer of water to the air.

IV. CONCLUSIONS

Orientation of the SDS type II lyomesophase due to surface effects are strongly dependent on sample thickness and container material; these orientational effects correspond to rather different diffraction results, expressed in the relative intensities of the bands B and S and in the broadness of S. It is not clear whether we are in presence of a phase transition and more systematic studies are in progress to determine whether the intensities change continuously as a function of sample thickness.

Surface orientation compete with magnetic orientation

and we continue this investigation to determine whether a Freedericks transition occurs in this case. The magnetic orientation is very sensible to the time spent in the magnet and relaxation times for magnetic orientation are excedingly long as compared to thermotropic nematic phases.

Results obtained in presence of electric fields indicate that surface effects may be of electrical nature, both for type II and type I lyomesophases[9].

Our results are consistent with the hyphotesis[8] that under the influence of orientational forces the platelets aggregate forming macromicelles composed of several amphiphilic bilayers slightly swoolen while the water is seggregated. The platelets tend to aggregate near the interfaces probably due to an interaction between the charged polar heads and ions on the container walls. The 38 Å peak corresponds to the first order reflection of the lamellar structures in the aggregates. This is in agreement with recent results obtained in the solid phase below 18°C, which show[10] the three first orders of a lamellar structure with repeat distance of 31.3 Å; electron microscopy results by freeze-etching technique now in progress[10] showed the presence of structures of about 2000 Å and confirmed the hypothesis of seggregation of water. Differential scanning analysis detected[10] the existence of three phase transitions between 0°C and room temperature, probably related to the phenomenon of water melting and seggregation.

We should also comment on the recent results obtained by Charvolin et al[11], who also studied the SDS system, but whith somewhat different concentrations, corresponding to both types I and II lyomesophases. Their experiment, obtained only with a conventional Laue camara, could detect only the outer ring S ; the inner band B occurs in the small angle region which is under the

direct beam in the Laue camera. They interpreted the 38 Å peak as the distance between micelles homogeneously distributed in water and attributed a value of 20 Å to the bilayer thickness. That this seems not to be the case has been already commented[8,9]. Regarding type II lyomesophases, it is not clear why they state that in the perpendicular configuration (with $\vec{H}$ present and perpendicular to the X-ray beam) they should have the X-ray beam perpendicular to the director of the mesophase. Their results on magnetically oriented samples are also different from ours since they obtain diffraction maxima along the vertical for a geometry equivalent to our $S_\perp$ configuration. It is difficult to analyse the discrepancy without knowing the exact salt concentration and the capillary diameter and material (both not mentioned in the paper).

ACKNOWLEDGEMENTS

I thank Dr. J.A. Vanin for the preparation of the mesophases and A.M. Figueiredo Neto for the colaboration in the measurements with electrical field; thanks are due also to both and to Dra. C.A. Pimentel and V.R. Paoli for many helpful discussions. Prof. L.W. Reeves helped with his incentive; FINEP and CNPq foundations gave us financial support.

REFERENCES

1 - K.D. Lawson and T.J. Flautt, J. Am. Chem. Soc. 89, 5489 (1967).

2 - P.J. Black, K.D. Lawson and T.J. Flautt, J. Chem. Phys. 50, 542 (1969).

3 - K. Radley, L.W. Reeves and A.S. Tracey, J. Phys. Chem. 80, 174 (1976).

4 - F. Fujiwara, L.W. Reeves, M. Suzuki and J.A. Vanin in Solution Chemistry of Surfactants, ed. K.L. Mittal (Plenum, New York, 1979) vol. 1, pp. 63-77.

5 - L.Q. Amaral, C.A. Pimentel and M.R. Tavares, Acta Crystallog. A34 (S4) S188 (1978).

6 - M.R. Tavares, Master Dissertation (University of São Paulo, Brasil, 1978).

7 - L.Q. Amaral, C.A. Pimentel, M.R. Tavares and J.A. Vanin, J. Chem. Phys. 71, 2940 (1979).

8 - L.Q. Amaral and M.R. Tavares, Mol. Cryst. & Liquid Cryst. Letters 56, 203 (1980).

9 - A.M. Figueiredo Neto and L.Q. Amaral, these Proceedings.

10- L.Q. Amaral, to be published.

11- J. Charvolin, A.M. Levelut and E.T. Samulski, J. Physique-Lettres 40, L-587 (1979).

FIGURE CAPTIONS

Fig. 1 - SAX results obtained with four different containers showing orientational effects due to the container:

(a) container C1 - pyrex glass capillary with 2 mm diameter.

(b) container C2 - mylar parallel walls and 1.4 mm sample thickness.

(c) container C3 - lindemann glass capillary with 0.7 mm diameter.

(d) container C4 - quartz capillary with 0.7 mm diameter.

Fig. 2 - SAX results on residual magnetic orientation:

(a) $S_{\parallel}$ ($\vec{H}$ parallel to the X-ray beam) with container C1.

(b) $S_{\parallel}$ with container C3.

(c) $S_{\perp}$ ($\vec{H}$ perpendicular to the X-ray beam) with container C1.

(d) $S_{\perp}$ with container C3.

Fig. 3 - SAX result on residual magnetic orientation: $S_{\parallel}$ with container C1.
Orientation in a magnetic field of 14 KG.

Fig. 4 - SAX results with electrical orientation; $S_{\perp}$ with container C1:

(a) down part of the sample.

(b) upper part of the sample.

(c) upper part, after some days of switching off the electric field.

Fig. 5 - SAX results for electrical orientation with container C3:

(a) unoriented sample S_o.

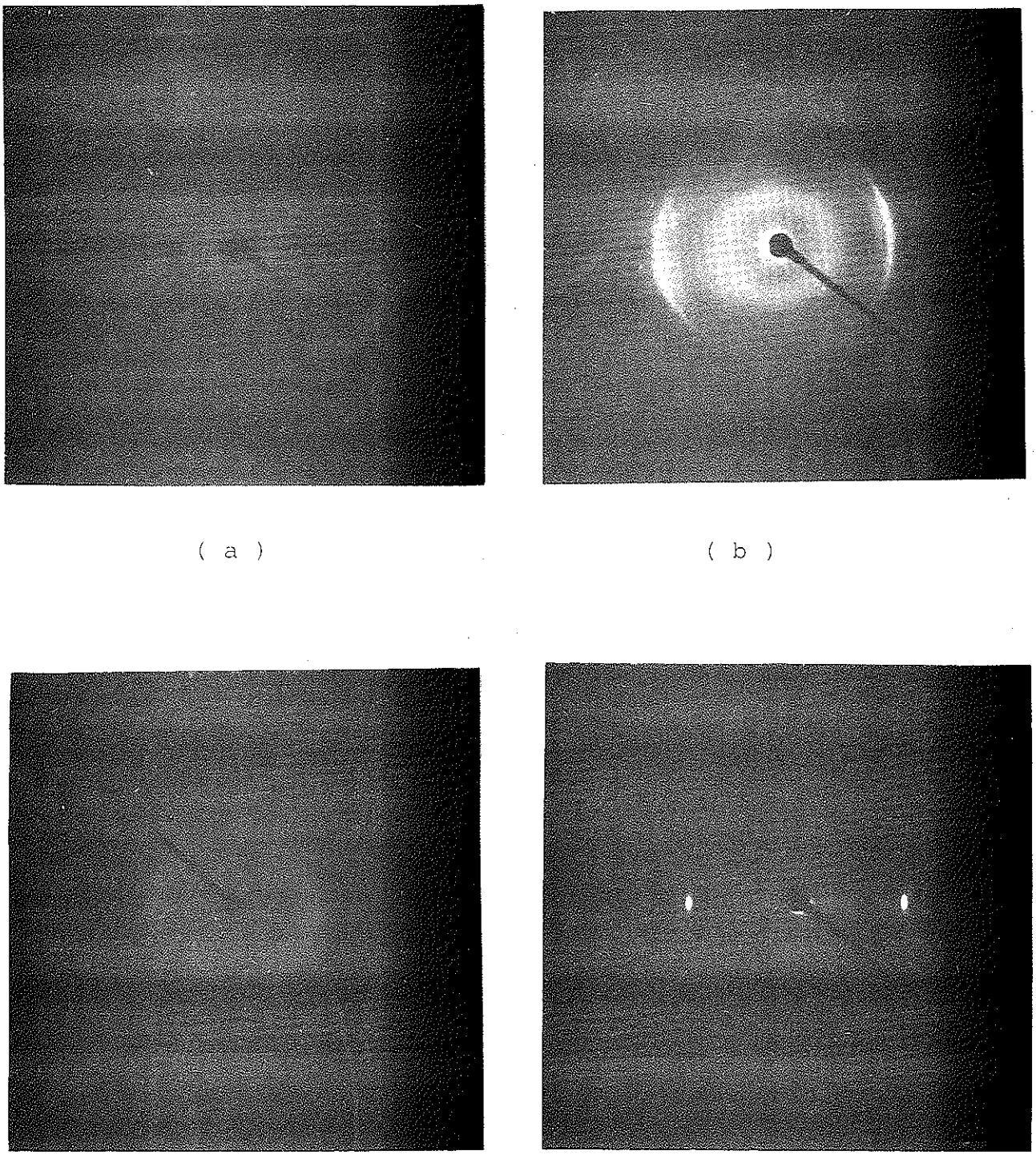
(b) residual electric orientation $S_{\parallel}$.

Fig. 6 - Laue results showing the effect of SDS-air interface; container C3.

(a) interface between upper and down parts of the sample.

(b) down part of the sample.

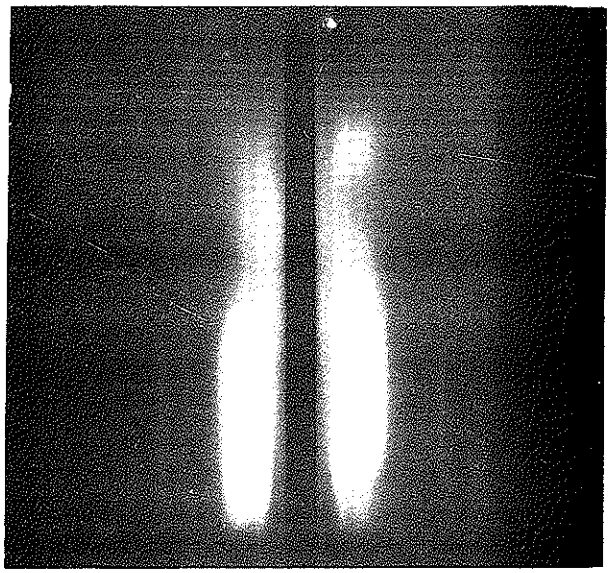
Fig. 7 - SAX result obtained near the SDS-air interface with container C3.



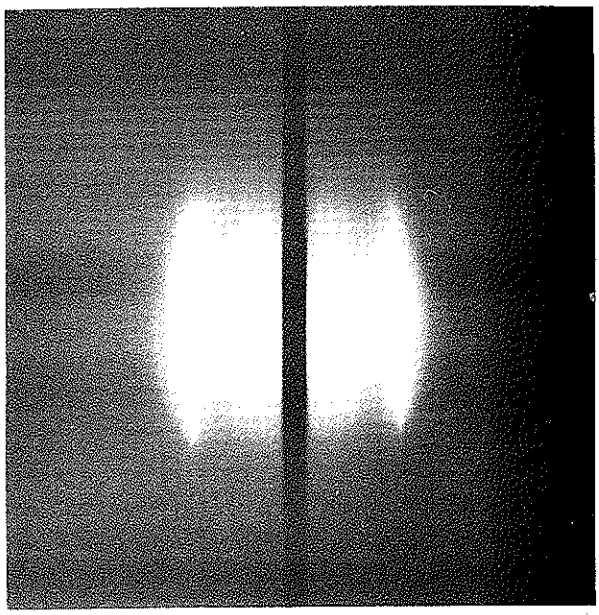
(a) (b)

(c) (d)

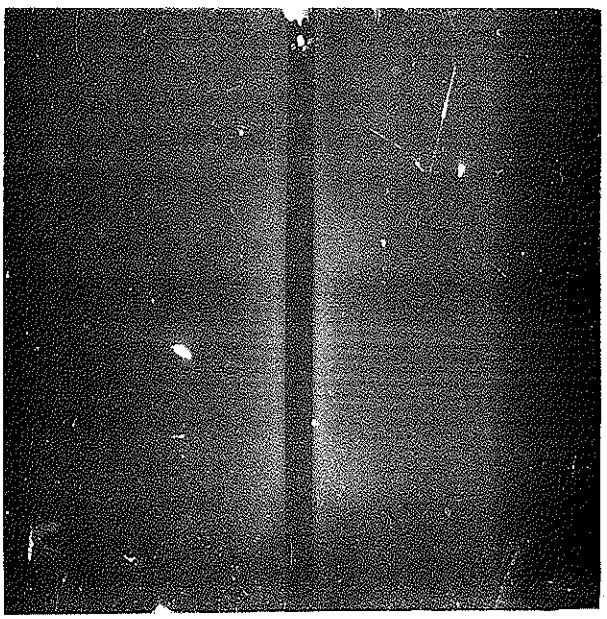
Fig. 1



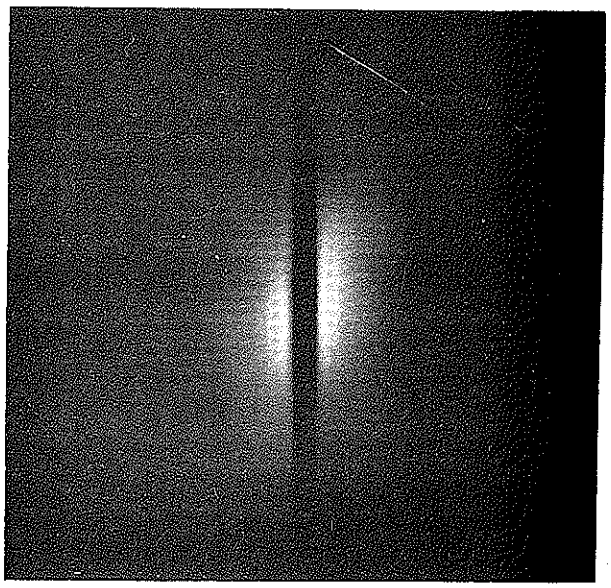
(a)



(b)



(c)



(d)

Fig. 2

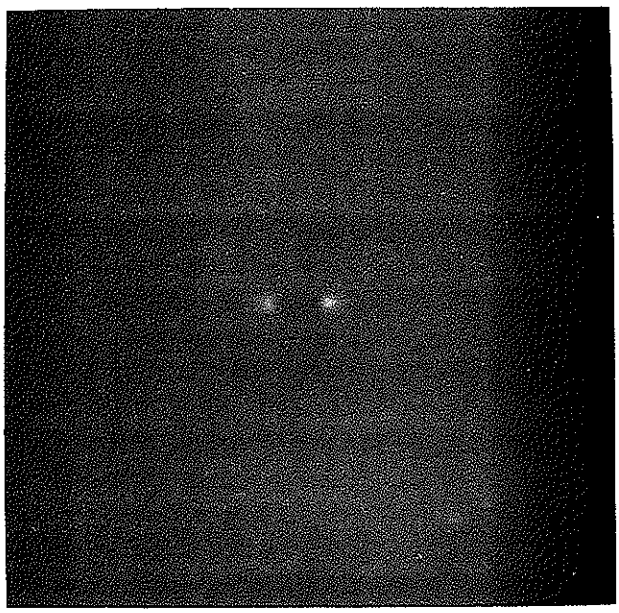
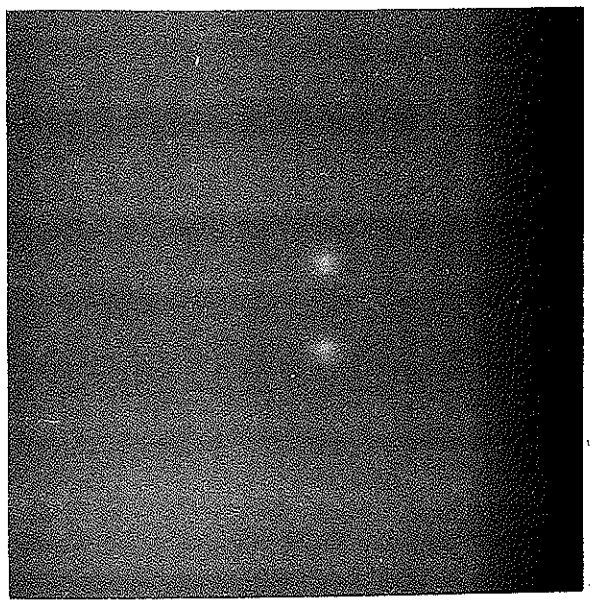
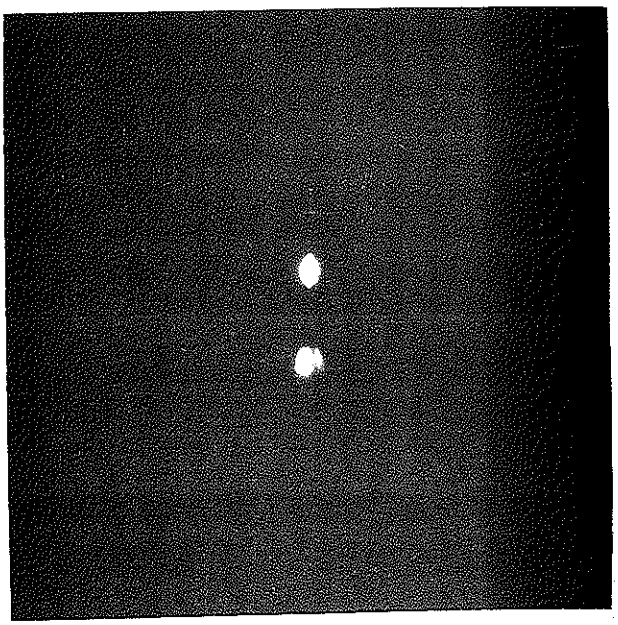


Fig. 3

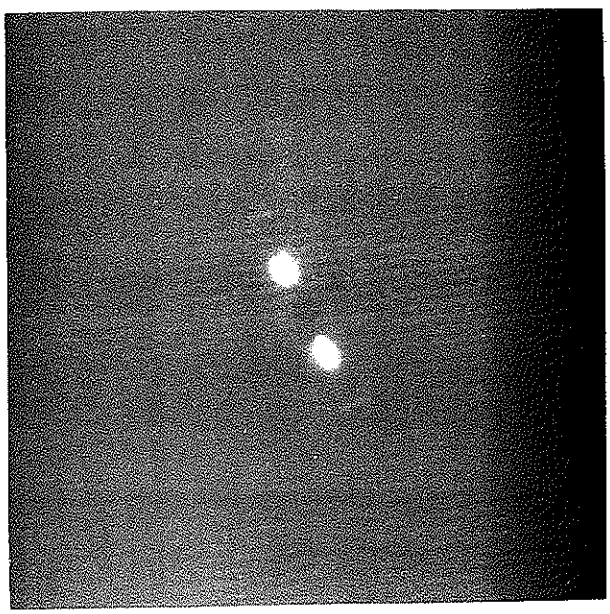


(a)

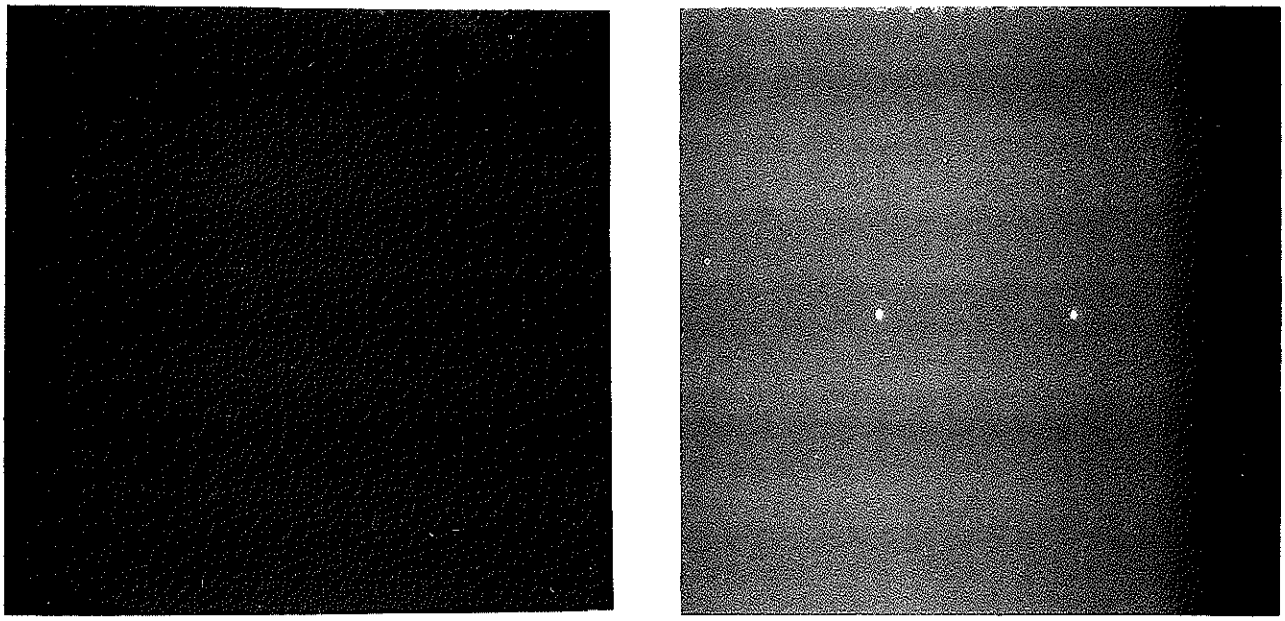
Fig. 4



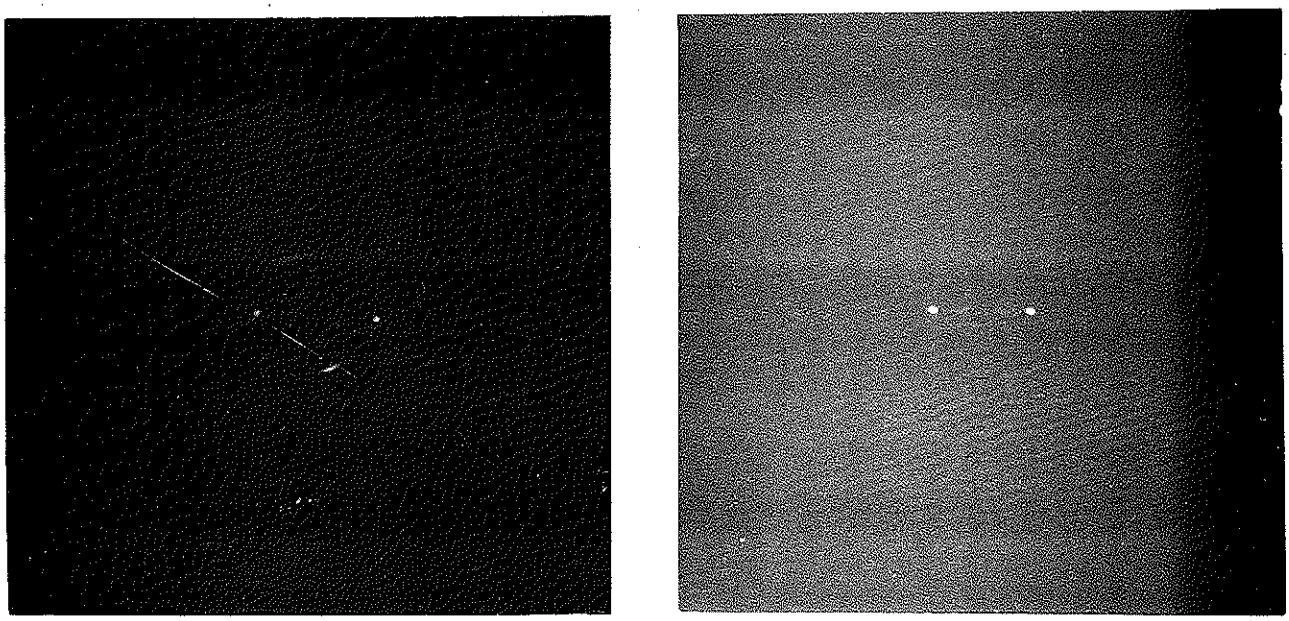
(b)



(c)



(a) Fig. 5 (b)



(a) Fig. 6 (b)

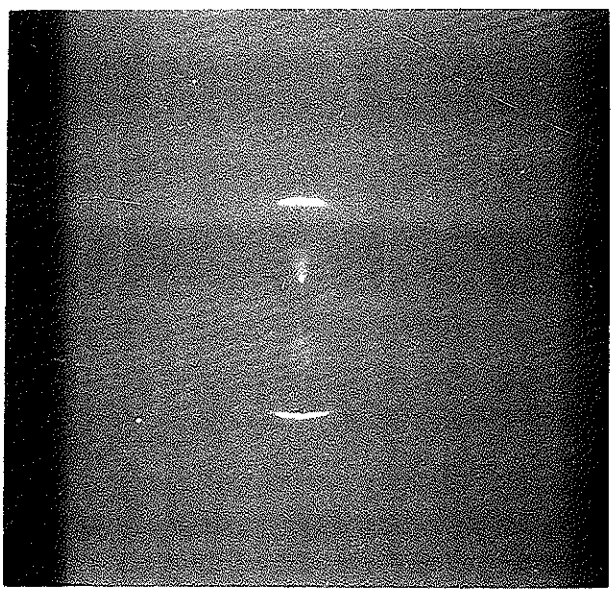


Fig. 7