INSTITUTO DE FÍSICA preprint

IFUSP/P-320

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LIQUID CRYSTAL OF POTASSIUM LAURATE/KCℓ/WATER

by

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FEB/1982

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ABSTRACT

Type I lyomesophase of potassium laurate was studied by X-ray diffraction techniques with temperature variation. The previously proposed structure of this mesophase is composed by aggregates of cylindrical micelles packed in an hexagonal array. A temperature region of phase coexistence between type I and hexagonal H_α phases (50-60°C) was determined. The lattice parameters of the two phases are 49.9 and 44Å respectively. The range of coexistence is located inside the observed by NMR studies (20-60°C) . A binary system of potassium laurate/water (H_α phase) studied by X-ray diffraction shows orientational and segregational effects. The container walls effects are important in the appearence of the coexistent H_α phase. Modification of the solvation water shell bounded to the micelles is probably responsible for the formation of the long range ordered structures and for the differences in lattice parameters.

I. INTRODUCTION

"Nematic" lyomesophases that spontaneously orient in presence of magnetic fields $\vec{H}$ have been classified as type I and II[1,2], depending on whether the phase director orients parallel or perpendicular to $\vec{H}$. The characterization of these mesophases as "nematics" was made by observation of its optical textures in a polarised microscope[3-6], which resemble nematic ones.

Amaral and co-workers[7-11] studied a type II lyomesophase by small angle X-ray scattering, proposing a model of finite planar micelles, in the form of platelets, not homogeneously distributed in water, forming lammelar aggregates.

Type I lyomesophases of potassium laurate (K laurate/KCℓ/H_2O) called LK and cesium decylsulfate (Cs decylsulfate/$CsNO_3/H_2O$) called CDS were studied [12] by X-ray diffraction and optical microscopy in several experimental conditions: different sample holders and samples in electric and magnetic fields at room temperature. A typical diffraction pattern obtained with LK in capillaries of 0,7 mm diameter has two bands at the s (absolute value of the scattering vector) position of $(40Å)^{-1}$ named outer band-OB and $(100Å)^{-1}$ named inner band-IB. The results obtained with magnetically oriented samples[12] confirm the previously proposed[2,3] model of cylindrical symmetry for the scatterers. The analysis of the diffraction patterns of LK samples, assuming non homogeneous distribution of amphiphilic in water , evidences the formation of aggregates of cylindrical micelles. In a previous paper[13], the model of aggregates was quantitatively developed; scattering curves were obtained with counter method and theoretical expressions for the diffracted intensity were adjusted to the experimental results for lyomesophase LK.

The micelles have cylindrical shape with radius of 17Å, length bigger than 500Å and are packed in an hexagonal lattice of parameter (49.9±0.5)Å. OB is associated to the 100 diffraction peak of the hexagonal array, for aggregates of about one hundred of micelles and IB is associated to the mean distances among smaller aggregates (about three or four micelles each). So, the "nematic" type I phase could be thought as composed by microdomains of the middle soap phase order (called H_α).

Fujiwara and Reeves[14] studied by nuclear magnetic resonance the LK (with deuterium instead of water) lyomesophase in the range of temperatures from 10 to 60°C. The analysis of the temperature dependence of D_2O deuterium quadrupole splittings evidences the existence of a region of coexistence of two phases (H_α and type I) in the range of

temperatures of 20 to 60°C. Above this, only the H_α phase was observed.

Preliminary X-ray diffraction studies with temperature variation were made[15] in mesophase LK, whose diffraction patterns presents bands (characteristic of type I phases) and Bragg's points (characteristic of H_α phase). In these paper, mesophase LK is studied by X-ray diffraction in the range of temperatures of 22 to 60°C with different sample holders. The binary mixture K laurate/H_2O (called LKb), wich forms a lyomesophase in the middle soap phase, is also studied.

II. EXPERIMENTAL

The mesophases LK and LKb were prepared [1,2] by the NMR Laboratory of the Instituto de Química da USP with the composition given in Table I.

Sample	K laurate (wt%)	H_2O(wt%)	KCℓ(wt%)
LK	34.49±0.06	62.6±0.1	2.94±0.01
LKb	38.00±0.06	62.0±0.1	-

TABLE I: Composition in weight % of the mesophases LK and LKb.

Samples were sealed in lindemann glass and quartz capillaries with 0.7mm diameter and pyrex capillaries with 2mm diameter, placed in vertical position, with their axis perpendicular to the X-ray beam in a transmission geometry. A small angle Rigaku-Denki diffractometer and a Laue camera, both with CuK_α radiation (Ni filtered) with point focus were used. The X-ray diffraction was detected by photographing technique.

The capillary with the sample stays in a furnace with a temperature controlling system. The device, designed and constructed in our laboratory, is attached to a goniometer head in a goniometer, allowing the sample

position to be freely adjusted. The sample is heated by a flux of hot air. The hot source consists of a stainless steel box where there is a 44Ω resistor composed by thin Ni-Cr wires. At the exit of the box there is a thermocouple connected to the electrical temperature controlling. The hot air leaving the box reaches two Cu capillaries positioned parallel to the sample, with small holes in their surfaces, pointing to it. The hot atmosphere is kept by a thin cylindrical mylar film with radius of 15 mm and height of 40 mm. Another thermocouple is positioned inside the mylar cylinder for the temperature reading. The air flux is maintained by a conventional compressor and the temperature could be controlled by it and by the voltage at the resistor. This device prevents the contact between the hot source and the sample and promotes a homogeneous heating along the capillary. Temperature gradients greater then 0.5°C along the capillary axis are therefore avoided, since they would be particularly incovenient in the case of liquid crystals. The temperature is controlled within 1°C in the range between room temperature to ~ 60°C.

At the sample position the X-ray beam had a diameter of 0.3 mm in small angle measurements and 0.5 mm in Laue camera measurements. All sample holders in both conditions received the beam in their central part. Exposure times varied between 24 and 48 hours (in small angle measurements) and between 6 and 8 hours (in Laue measurements), depending on sample holder.

III. RESULTS AND DISCUSSION

The photographing diffraction pattern obtained with sample LK at room temperature (~ 22°C) shows IB and OB (when 0.7 mm capillaries were used) and only IB (when 2 mm capillaries were used), both with preferred orientation along the horizontal equator [12] (Figure 1a,b). This result, as previously discussed[12], is characteristic of a sample with moderate degree of orientation of the aggregates caused by the glass surface.

For increasing temperatures in the range from 30°C to 50°C (0.7 mm capillaries), both bands lose the equatorial orientation and became isotropic (Figure 2a). This fact is probably connected to the increase of the thermal agitation of the system and breaking of the orientational interaction between the aggregates and the walls. Band positions did not change during this process.

At about 50°C there is a modification of the pattern in the OB region (Figure 2b): some Bragg points, characteristic of the diffraction in larger micellar aggregates, appear at $s = (38\text{Å})^{-1}$, wich identifyed to the 100 diffraction of the hexagonal array gives the lattice parameter of 44Å. IB did not change (Figure 2b) compared to the anterior condition (Figure 2a). For higher temperatures (50-60°C), the Bragg points on OB increased in number and intensity and IB is transformed into radial streaks, oriented in the directions where the Bragg points appear (Figure 2c), indicating that the axis of the aggregated micelles (small aggregates) lost the continously varying directions, fixing into discret ones. Part of the streaks intensity may be due to white radiation always present in Ni filtered beam, however, as discussed elsewhere[12], this contribution must not be dominant.

The diffraction pattern, in terms of the number, disposition and intensity of the Bragg points and streaks, are critically dependent of the heating process. Another pattern obtained with a quickly raise of the sample temperature till ~ 50°C (Figure 3) shows a distribution of Bragg points very close to a diffraction produced by a hexagonal network with the c axes parallel to the incident beam. This fact indicates that the hexagonally aggregated micelles orient with their axis perpendicular to the glass walls. In other case (Figure 4) (slowly heating) for smaller values of s it was observed a weak ring with characteristic distance $1/\sqrt{3}$ of Bragg points (at the Figure 4 this weak ring is not visible). An interesting result was obtained with LKb sample (H_α phase) in quartz capillary of 0.7 mm at room temperature (Figure 5). The diffraction pattern was different from the discussed by Luzzati and co-workers[15,16] (composed by concentric rings).

Our result composed by points, streaks and weak rings, evidences an orientational wall effect on the hexagonally packed micelles indicating that some of the microdomains had the c axes oriented perpendicular to the walls (with the appearance of the Bragg points closely disposed at an hexagon vertex-see for comparison Figure 3). The higher equator intensity indicates that some microdomains were oriented with the micellar axis parallel to the capillary axes. In the pattern it was possible to identify also the 110 and 200 diffractions, wich give the lattice parameter of (46.4±0.5)Å. This result evidences the surface orientational effect on the binary system (phase H_α), and is comparable to the LK high temperature results. Husson and co-workers[17] studied LKb H_α phase in the range of amphiphilic concentration of 60 wt% to 50 wt%, observing an increase in the lattice parameter as concentration decreases. Our value (at 38wt%) is comparable to the extrapolated from their results. The radius of a cylindrical micelle at 22°C is about 17Å [17], which related to the lattice parameter (46.4Å), gives a shell of solvation water (water bounded to the micelles) of about 6Å per micelle. Assuming[13,18] for the densities of K laurate and water the values of 1.2g/cm^3 and 1g/cm^3 respectively, and the hypotesis of homogeneous distribution of amphiphilic in water, the expected lattice parameter is about 50Å. This fact evidences that the process of water segregation caused by wall effect also acts in H_α phase.

Results obtained with LK samples in Laue geometry, where only the OB region is accessible, show the reversibility of the process. Figure 6a,b,c represent a sequence of exposures with different temperatures. In Figure 6a (room temperature) only OB is observed, characteristic[13] of a type I lyomesophase with aggregation numbers of about 100; in Figure 6b (at (54±1)°C) both OB and Bragg points are visible, characteristic of the long range order structures (i.e. phase H_α); in Figure 6c (room temperature), the initial condition is reached again. No thermal histeresis effect was observed during the cooling process.

Surface effect has a significant influence on

the appearence of the H_α phase. Results obtained with LK in capillaries of 2 mm in the considered range of temperature (22-60°C) show only IB at room temperature; at 60°C, besides IB there is a weak ring at an s value slightly larger than OB, but no Bragg points appear.

Macroscopically, there is an observable decrease in the fluidity of LK samples in 15 mm tubes (where the sample is preparated) with the temperature rise, which must be connected to the higher viscosity of H_α phase.

As discussed elsewhere[12], the container walls favours the appearence of the large aggregates of micelles in LK mesophase. Probably, the large H_α phase structures are formed with these seeds, by micellar aggregation and further compactation to a smaller lattice parameter (49.9Å for type I phase and 44Å for H_α). In 2 mm capillaries, where the wall effect is reduced[12], the formation of H_α could be difficulted; however, the appearence of the weak ring evidences that large aggregates are formed by a temperature effect. Also a translation of the phase coexistence temperature range may be caused by the influence of the walls.

In 0.7 mm capillaries, the range of detected phase coexistence from ~ 50-60°C is located inside the range given by NMR studies [14](20-60°C). Comparisom with NMR results must take into account the strong magnetic field present in that case. There are evidences that the magnetic field promotes the formation of larger aggregates[18]. The interplay of wall and magnetic field effects must be responsible for the differences observed in the phase coexistence phenomenon.

The observed compactation of the H_α phase in relation to the type I aggregates of micelles, revealed by the decrease in lattice parameter, cannot be holly explained by a contraction of carbon chains with temperature. The chain contraction with temperature may promote a modification of the lattice parameter of the aggregates of micelles in type I phase; however , the position of the broad OB is pratically unchanged at the pattern. Only counter technique could clarify this point. The modification

of the lattice parameter between the LKb H_α phase at room temperature and H_α coexistent phase at 55°C can be explained by chain contraction. The thermal linear dilatation coeficient[17] for the carbon chains is - 1.3×10^{-3} $^{o}C^{-1}$. The micellar radius of a micelle at 55°C obtained from the initial condition of radius of 17Å and 22°C is 16Å. This radius related to the lattice parameter of 44Å gives a shell of solvation water of about 6Å per micelle, as in the LKb result. This shell of solvation water is a little smaller than the observed in the aggregates of micelles in type I phase, where there is a 8Å thick shell per micelle[18]. The temperature probably promotes breaking of the solvation water bonds with its further segregation, besides the decrease of the micellar radius. Recent studies of the micellas interaction mechanism for the formation of the aggregates[18] reveals that the solvation water is fundamental for the system stability,which hydrated micelles tends to flocculate, i.e., the cylindrical micelles are packed together by attracting forces till the touch of the solvation water shells.

IV. CONCLUSIONS

A temperature region of phase coexistence was determined by X-ray diffraction technique in mesophase LK. This temperature region is located inside the one found by NMR studies[14]. Container walls effect are important in the appearence of H_α phase. The modification of the solvation water shell bounded to the micelles is probably responsible for the formation of the long range ordered structures.

Surface orientational effects are very intense not only on type I aggregates but also in H_α phase. Besides the orientational effects the walls act on this phase to promote segregation of unbonded water.

V. ACKNOWLEDGEMENTS

We thank Dra.V.R.Paoli and Mr.R.Gerigk for the skillful preparation of the lyomesophases and her and Dr. J.A.Vanin for many helpful discussions. FINEP and CNPq foundations gave us imprescindible finantial support.

FIGURE CAPTIONS

FIGURE 1: Small angle X-ray results with sample LK. The capillaries are in vertical direction in the plane of the figures. Temperature of about 22°C. (a) 0.7 mm thick; (b) 2 mm thick.

FIGURE 2: Small angle X-ray results with sample LK in 0.7 mm thick capillary in vertical direction (a) temperature of 45°C; (b) temperature of 50°C; (c) temperature of 55°C.

FIGURE 3: Small angle X-ray result with sample LK in 0.7 mm thick capillary in vertical direction. Quickly raise of the sample temperature(50°C).

FIGURE 4: Small angle X-ray result with sample LK in 0.7 mm thick capillary in vertical direction. Slowly heating.Temperature of 55°C.

FIGURE 5: Small angle X-ray result with sample LKb in 0.7 mm thick capillary in vertical direction. Temperature of 22°C.

FIGURE 6: Laue camera X-ray results with sample LK in 0.7 mm thick capillaries in vertical direction. (a) temperature of 22°C; (b) temperature of 54°C; (c) temperature of 22°C.

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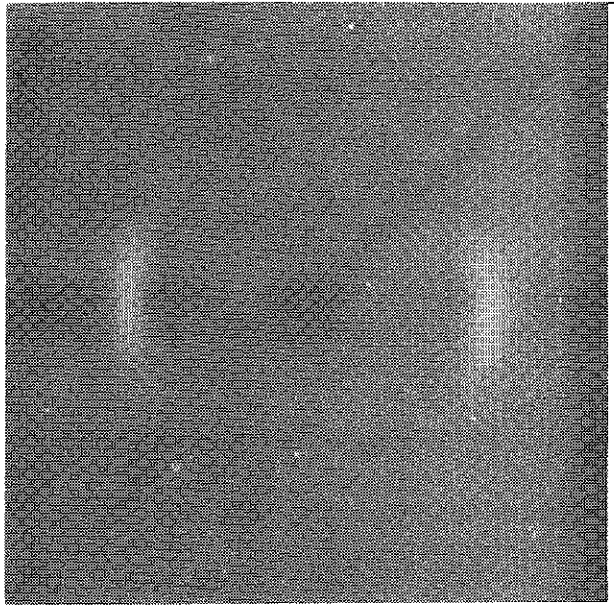


Fig. 1a

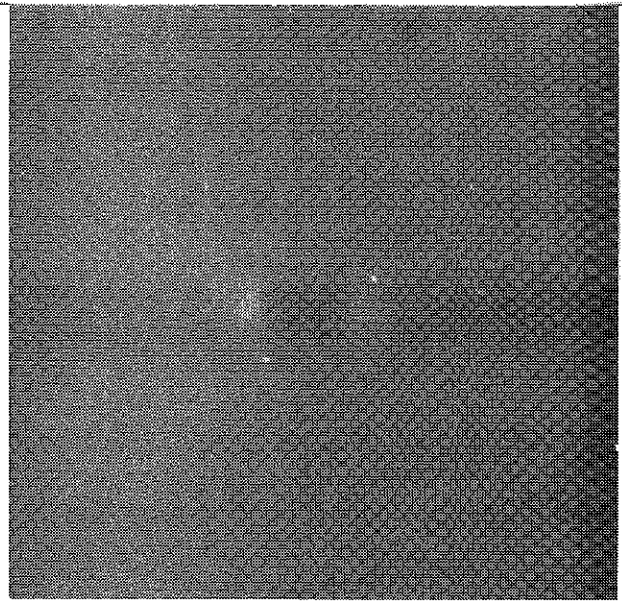


Fig. 1b

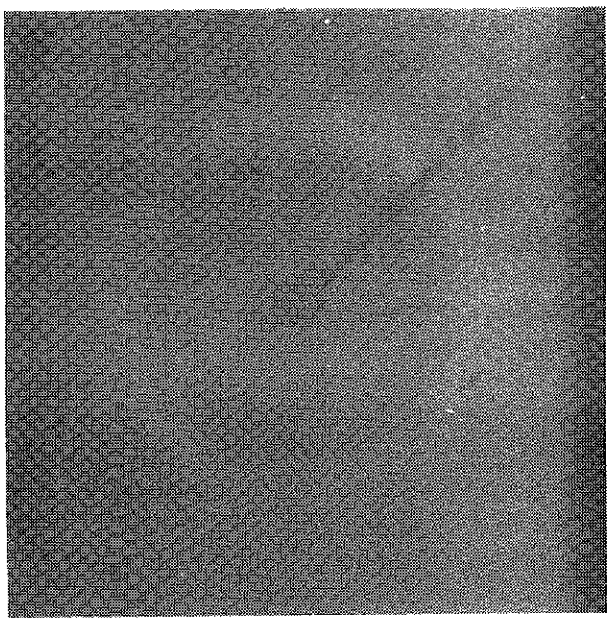
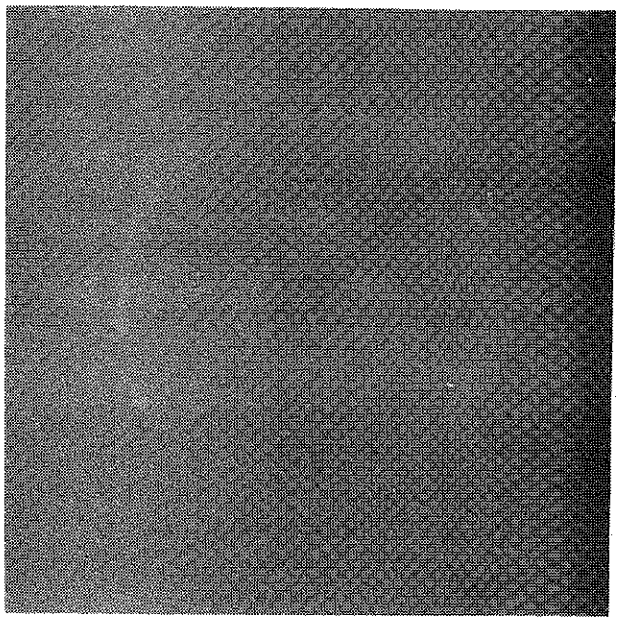


Fig. 2a



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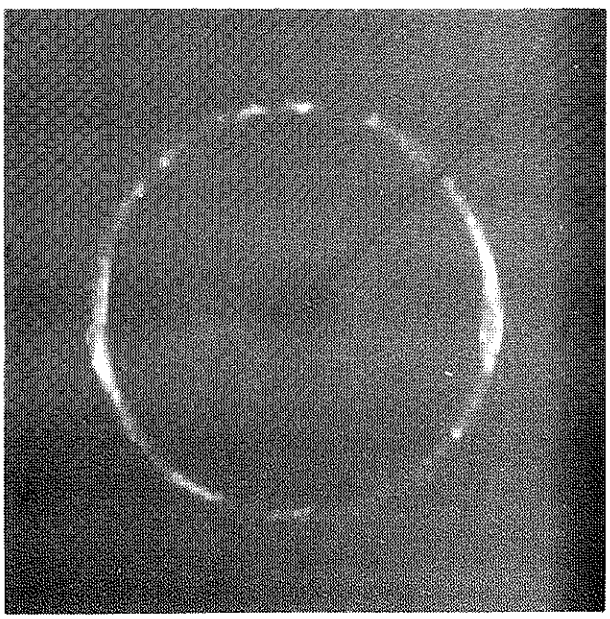

Fig. 2c

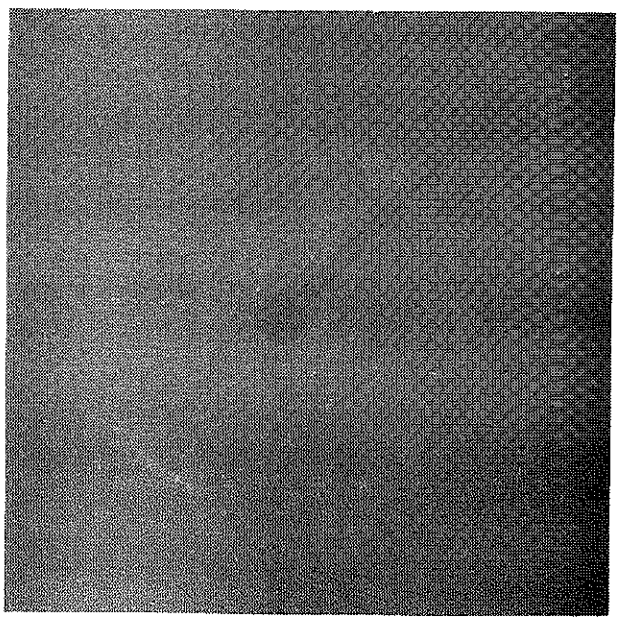

Fig. 3

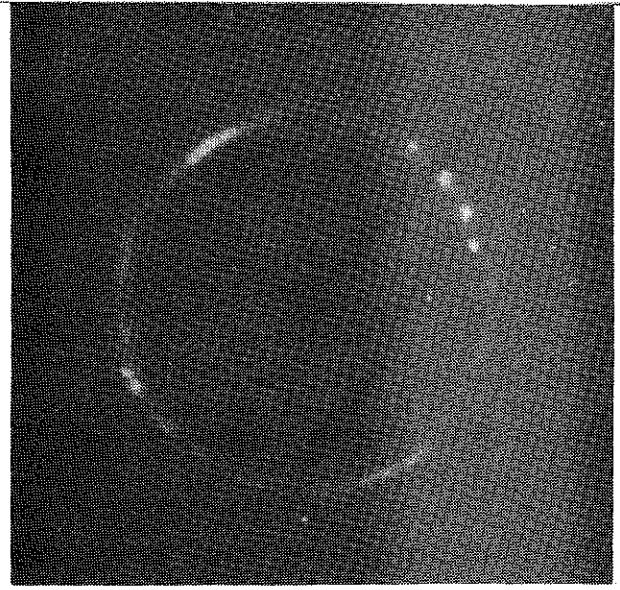

Fig. 4

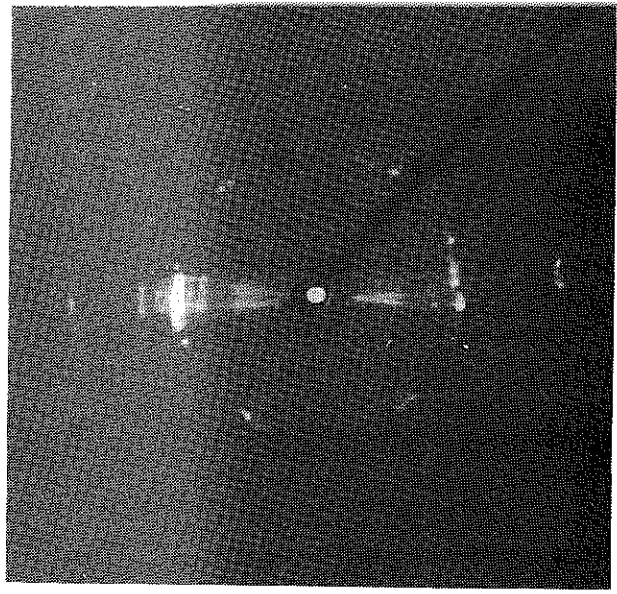

Fig. 5

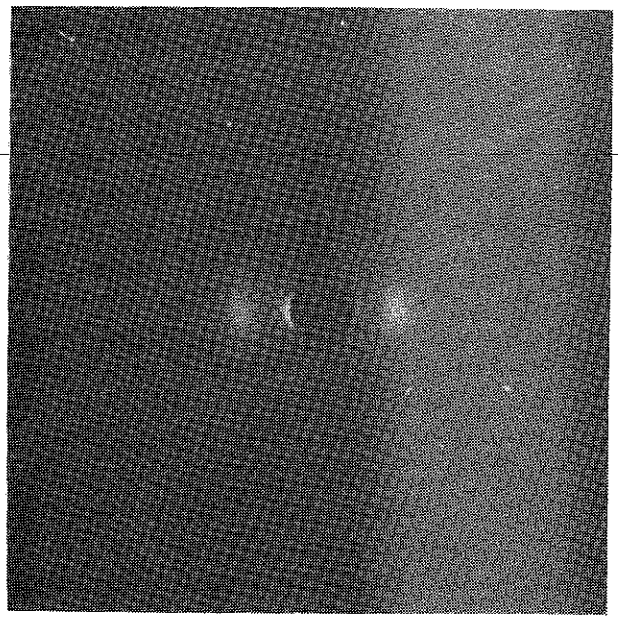

Fig. 6a

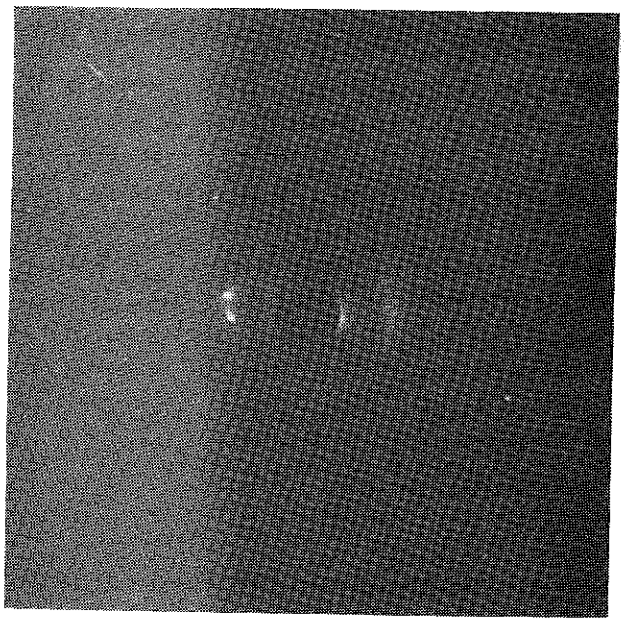

Fig. 6b

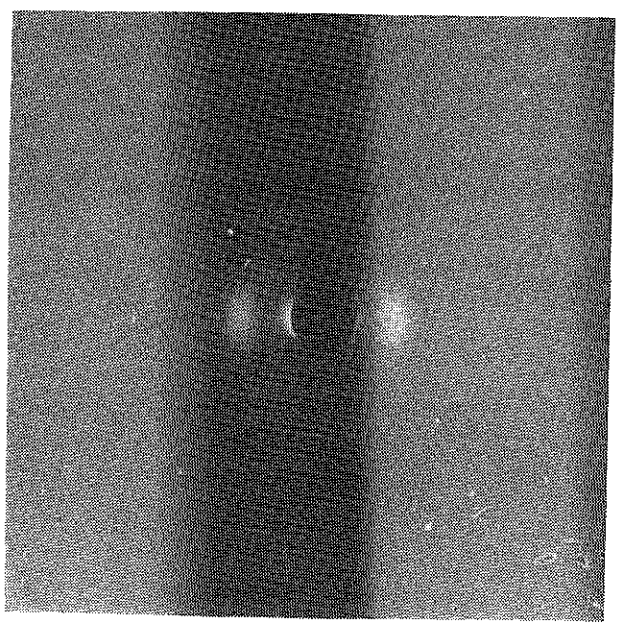

Fig. 6c