

CHAPTER - IV

EXPERIMENTAL VERIFICATION OF THE THEORY

INTRODUCTION :

We have so far discussed in detail the theory of light propagation along the optic axis of a cholesteric liquid crystal. In this chapter we give some experimental studies made in the light of the above theoretical investigation and examine how the experiments agree with the theoretical predictions. Before discussing the apparatus and methods used in the present investigation, we shall give a brief review of the experimental techniques used by the earlier workers.

Lehmann (1900) was the first person to suggest a technique for the measurement of large rotatory power of cholesteric liquid crystals. In his set up, the mesomorphic substance is placed underneath a plano convex lens resting on a piece of plane glass plate, so that its thickness increases towards the periphery of the lens. It is then inserted between a polarizer and an analyser of a polarizing microscope, which is set up for extinction and illuminated by monochromatic light (Fig. 1a). Concentric dark extinction rings are seen which resemble 'Newton's rings' (Fig. 1b). Each dark ring corresponds to light which has been rotated through $n \times 180$ where n is an integer. If ' r ' is the

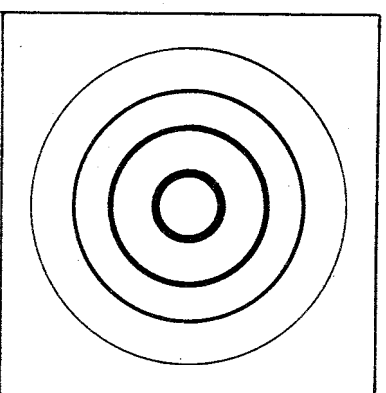
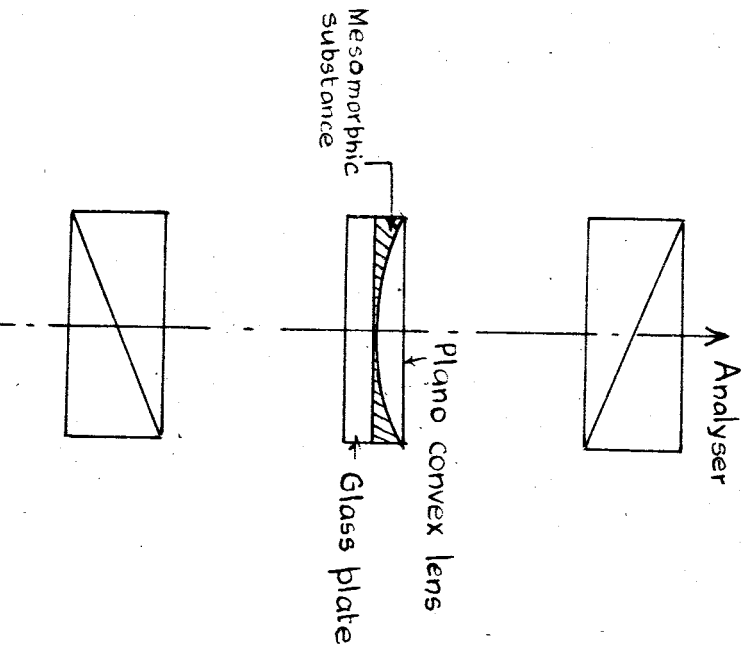


Fig. 1(b). Circular fringes observed

Fig. 1(a) Schematic diagram of the experimental setup of Lehmann.

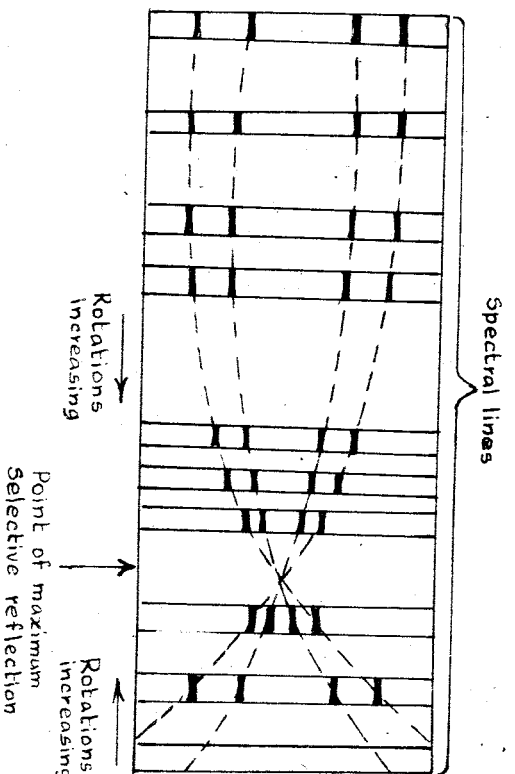


Fig. 2. Fringe patterns observed using the experimental setup of Stumpf.

radius of the n dark and ' R ' the radius of curvature of the surface of the lens in contact with the mesomorphic substance, then the thickness ' l ' of the substance which has caused a rotation of $N \times 180$ is approximately $4/98$. The rotation in degrees per millimetre will be given by measuring the radius of the consecutive dark rings by

$$l = \frac{2R(180)}{r_1^2 - r_2^2}$$

If a clockwise rotation of the analyser increases the width of the dark rings, the rotation of the mesomorphic substance is dextro and vice versa. In this technique the error in the evaluation of the thickness measurement has been automatically eliminated.

The modified method of this by Stumpf (1910, 1912) known as 'Stumpf spectro polarimetric technique' has been extensively used by a number of workers. This method, consists of focussing on the slit of a spectro-scope, an image of a diameter of the lens system described in Lehmann's method, the latter being illuminated either with white light or preferably with a source of illumination giving a number of intense lines. Each dark ring produces a dark band on either with white light on one side of the centre of each spectral line. The greater the rotation produced far

any particular wavelength the closer together will be the bands on the corresponding spectral line. The type of effect which may be observed in the region of a point of maximum reflection is shown in the Figures (2). The distances of the consecutive dark bands on any spectral line from the meridian line correspond to r_1 and r_2 of the above formula. Chate-
rain and Cano (1951, 1954, 1959) have made use of an essentially similar technique in their measurements of the rotatory dispersion of cholesteric liquid crystals. This set up has the slight disadvantages, that it is not usually possible to produce perfect single domain specimens of such large dimensions, because of the misorientation caused by surface effects, such as, curvature of the lens, etc.

Gaubert's method (1917) involves measuring the shift produced in the position of the black cross seen through the polarising microscope, with crossed polarizers when white light and monochromatic light are used for illumination respectively. The technique does not allow the measurements to be done over a wide range of spectrum.

Mathieu (1936) has used a visual polarimetric technique. The angle of rotation for any wavelength is measured by the difference in extinction readings

of the analyser with and without the specimen. The thickness of the specimen was measured by forming channelled spectra in air gap between the glass slides containing the specimen. In this method a single domain specimen can be formed quite easily between glass slides. Further, the measurements of reflection and circular dichroism were done by measuring the ellipticity of the transmitted light by the use of a Babinet's compensator. The measurements were made at different wave lengths by photographing the fringes produced by the Babinet's compensator through a spectrograph.

Recently Ferguson (1967) has studied the circular dichroism and rotatory dispersion of a mixture containing equal parts by weight of cholesteryl benzoate, cholesteryl acetate and cholesteryl palmitate by using an automatic recording dual beam instrument, the Cary Model Spectrophotometer. Circular dichroism was obtained by measuring the transmittance of the left and right circularly polarized light and using the formula

$$D = \frac{I_R - I_L}{I_R + I_L}$$

The phase difference (and hence the rotatory power) was directly obtained by measuring I_x and I_y the

intensities of the transmitted light, when the incident light is linearly polarized and the analyzer is placed parallel and perpendicular to the polarizer respectively and applying the formula

$$\delta = \cos^{-1} \frac{I_y - I_x}{(I_y + I_x)(1-D^2)}$$

where D is the circular dichroism.

We see from the studies of the earlier workers that most of the investigations are confined to a narrow region of the spectrum, and that detailed data on circular dichroism and rotatory power right through the reflection band are rather scanty. We shall now describe the experimental arrangements set up by the present writer and Chandrasekhar and Shashidara Prasad to make measurements over a wide range of the spectrum. The aim of these studies is to see if the theoretical predictions discussed in the previous chapter are verified by the experimental data.

Experimental Verification

Specimen Preparation : - To prepare a plane texture specimen it is necessary to align the molecules at the surface of the film. The substance was taken in between two glass slides and heated till it becomes a liquid, and then allowed to cool into the mesomorphic

range. Alignment was obtained by moving one cover slide over the other back and forth in a fixed direction till uniform colouration was seen. In this way fairly single domain cholesteric liquid crystal film were obtained. That the areas are optically homogeneous was tested by checking the uniformity and perfection of the extinction for wavelengths outside the region of reflection. Also measurements were made in the area having good orientation only, by covering the other parts by thin opaque foil. The specimen was maintained at a fixed temperature in the liquid crystalline range by mounting the cover slide at the centre of the electrical heater with a stabilized power supply. The temperature of the substance was determined by a pre-calibrated copper-constantan thermocouple.

Thickness Determination : Spacers were used so thickness of the specimen were accurately measured.

When spacers is not used, the method is to form interference fringes in air gaps between the glass slides. The light reflected from the inside surfaces of the slides was allowed to fall on the slit of a spectrograph. A 'channelled' spectrum was obtained the number of fringes between any two standard wavelengths (say 4358 Å and 5780 Å of Hg) were counted.

The procedure was repeated for various regions round about the specimen and the mean thickness was taken using the formula

$$t = n \lambda_0^2 / 2\mu (\lambda_1 - \lambda_2)$$

where n is the number of fringes observed between the wavelengths and of Hg spectrum. The thickness measurements were also made by an optical comparator which could read to an accuracy of 1 . The film thickness was usually of the order of a few microns. The accuracy was not better than ± 15 per cent.

Accuracy of the Experiment

The accuracy of the optical rotation measurements was checked by making several measurements of rotatory power of quartz at wavelengths from 4000 Å to 10,000 Å. It was found that the relative rotation could be determined to $\pm 4'$ of arc from 4000 to 10,000 Å. However the determination of absolute rotatory power of the liquid crystal was much less accurate, since the specimen film thickness could be determined only to ± 15 percent. Further the microscope slides themselves were not optically plane.

The temperature of the liquid crystal was maintained quite constant by the stabilized power supply and the high thermal capacity oil the heater and the experiment being conducted in an air conditioned room.

It was found that the fluctuation in temperature to be less than 0.1°C by the constancy of the observed emf at a particular temperature throughout the span of the experiment.

Set up for anomalous rotation and also away from the reflection band :

The experimental set up is shown in Fig. (3). A Hg vapour lamp or neon discharge lamp was used as a source (1). The quartz lens (2) was placed at a distance equal to its focal length from the source to render the light from the source parallel. The parallel light is then passed through a constant deviation spectrograph (3) a half shade (4) the liquid crystal specimen (5) and then the nicol (analyser)(6).

(1) When $\lambda \ll \lambda_0$, $\rho \rightarrow 1/\lambda^2$

Using the above set up, the rotation of a specimen of cholesteric chloride was found for various wavelengths away from the reflection band. The thickness of the specimen was 12.7μ . This thickness was got by using a Dupont Mylar spacers. The polarimetric arrangement was of a standard type (model No. 1013071), manufactured by Winkel-Zeiss, Göttingen). The light source was a Hg vapour lamp, and light of different wavelength was obtained by using a standard Hilger spectrograph.

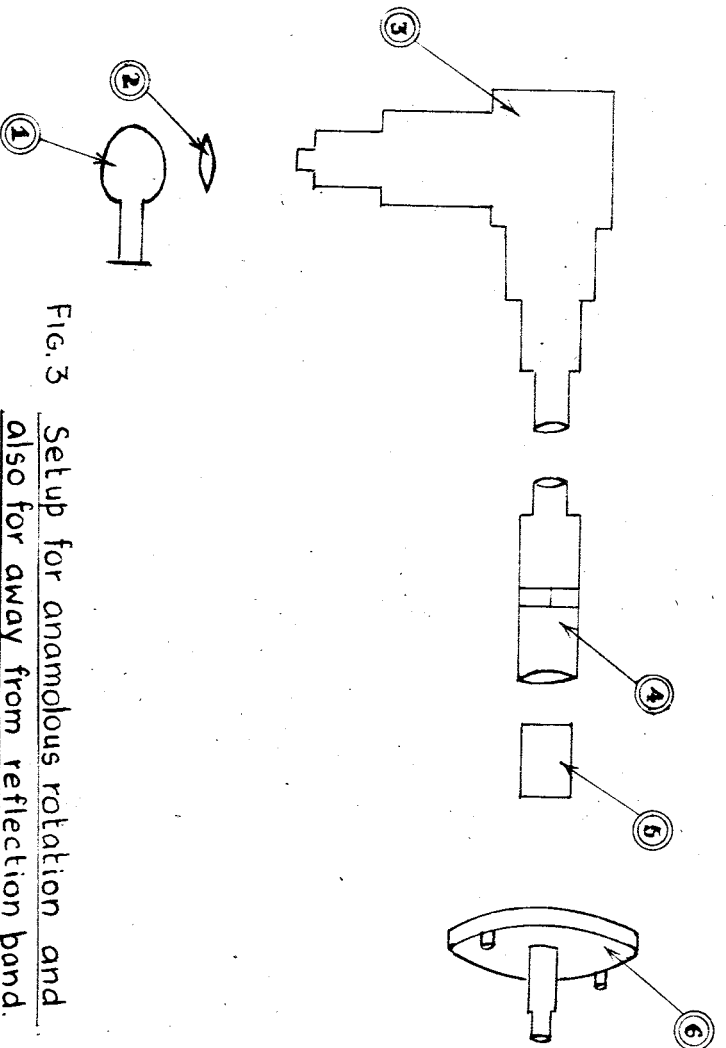


FIG. 3 Setup for anomalous rotation and also for away from reflection band.

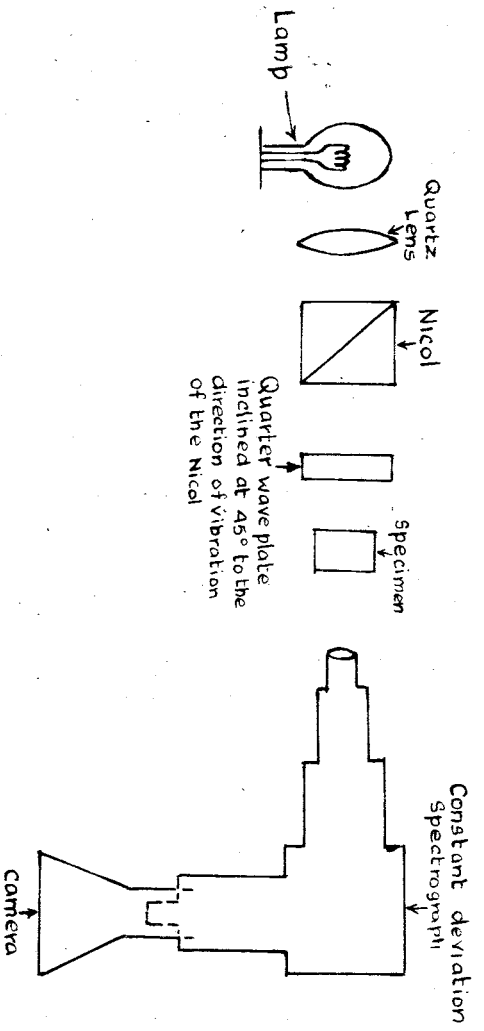
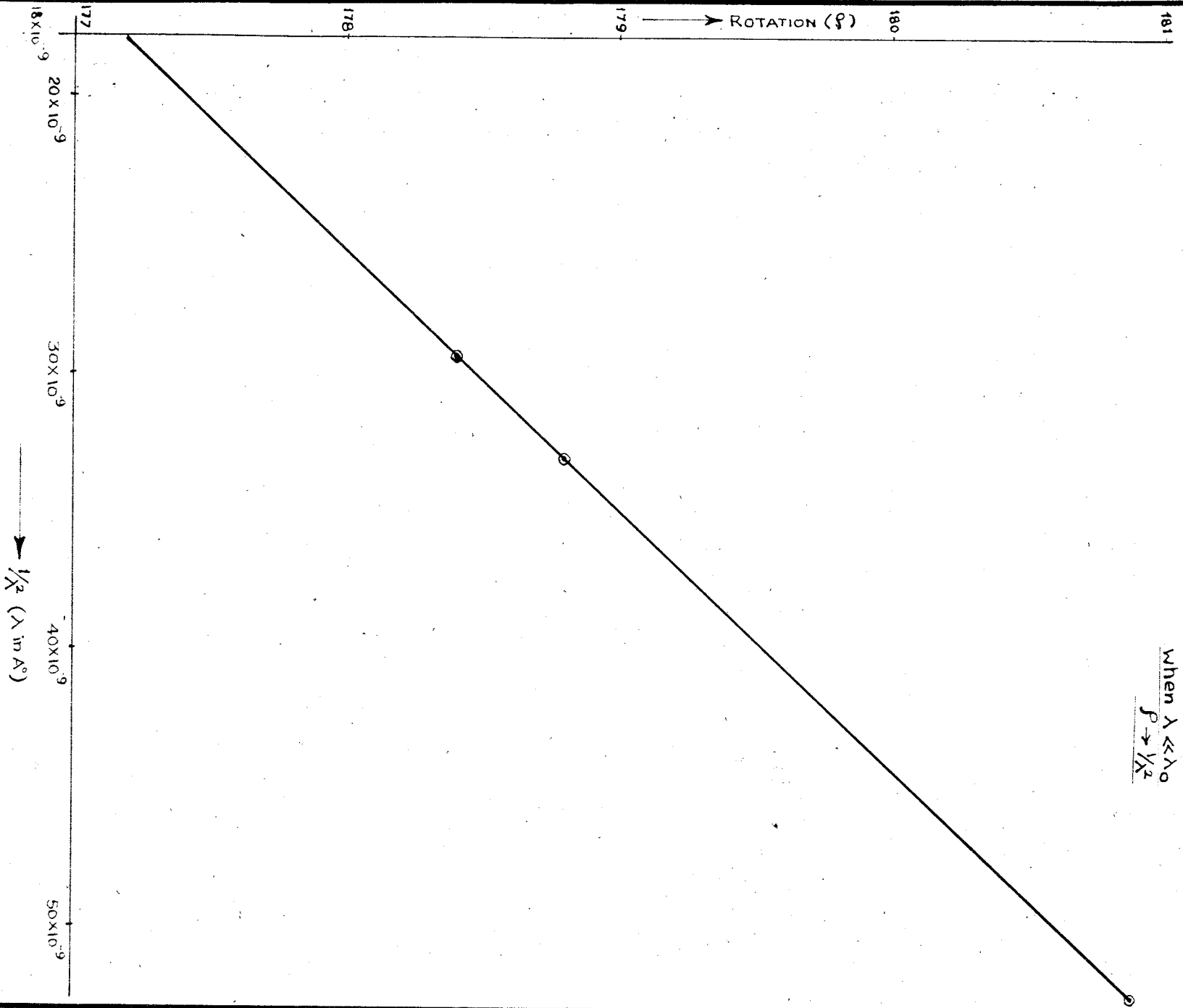


Fig. 4. Setup for reflection band.

TABLE - I
 When $\lambda \ll \lambda_0$
 $f \rightarrow 1/\lambda^2$



Wavelength	Without Specimen	With Specimen	Totatation
Blue	1.68	182.6	180.92
Green	3.3	182.1	178.8
Yellow	1.9	180.3	178.4

(2) Anamolous rotation :

The same set up as per the above experiment was used. The specimen taken was cholesteryl-2-propyn-1-yl-carbonate, which gives a stable oriented cholesteric phase between cover showing brilliant colours in the super cooled state at room temperature. The compound was first heated to liquid phase between cover slides. The slides were moved against each other forward and backward in a single direction as the specimen cooled to room temperature. The specimen then becomes a single domain and shows brilliant colours in the yellow region of the spectrum. Such a specimen is referred to as a "plane texture" preparation. The measurements of rotation on one such specimen are given in table VI.

(3) Reflection of Circular Components: and Reflection of Circular Components with temperature variation :

The set up for this is shown in Fig.4. The

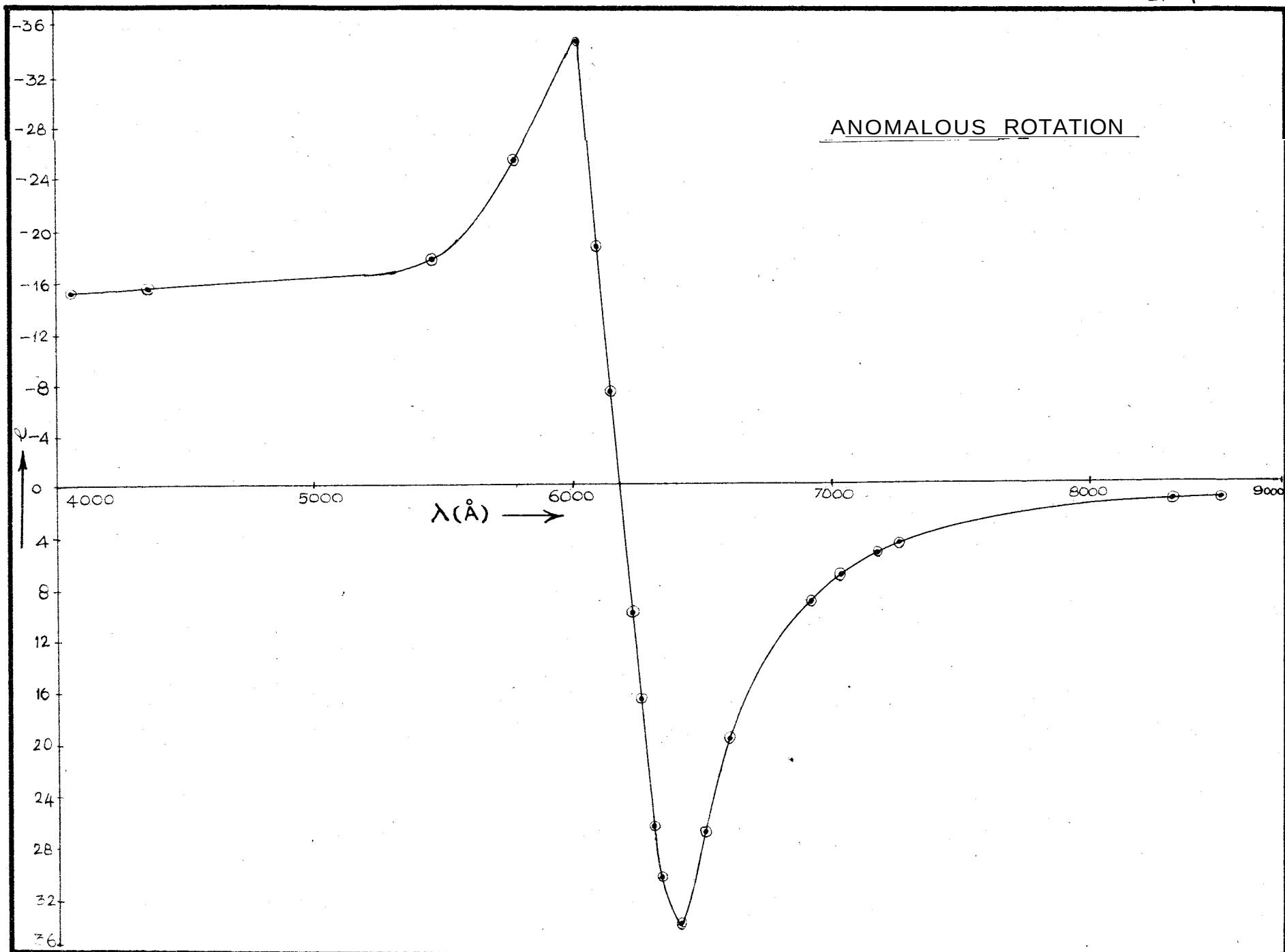
transmission photograph through a plane texture of CM mixture is shown when circularly polarized white light is incident on it. The circularly polarized light was produced in the usual manner by the use of a quarter wave plate. As can be seen from the figure when left circularly polarized light is incident hardly any light is transmitted over a spectral region of about 200 Å, because the light is almost wholly reflected.

* TABLE - II

Optical rotation measurements of cholesteryl- β -propano-1-yl-carbonate.

Wavelength in Å	Rotation in degrees	Wavelength in Å	Rotation in degrees
4046	-15.5	6382	+32.2
4077	-15.2	6402	+34.9
4359	-15.8	6506	+26.5
5461	-17.8	6598	+19.9
5770	-24.5	6629	+9.1
5790	-25.8	67032	+7.2
6029	-34.3	7173	+5.4
6074	-18.4	7245	+4.5
6143	-7.6	7468	+3.9
6163	+10.3	8300	+1.3
6217	+16.4	8377	+1.2
6266	+26.2		
6334	+30.1	8495	+1.0

* Data given by Chandrasekar and Shashidhara Prasad



T A B L E - III

Reflection of Circular Components :

Cholesteric chloride (25 percent) + cholesterol myristate (75 percent)

Film thickness 23.4 *Micron*

Film balder reading	Millivoltmeter reading	Temperature	Polarization sense	Exposure time
0	2.5 mV		47.1°	2.5 mts.
10	2.5 mV		317.1°	2.5 mts.
20	2.3 mV		47.1°	2.5 mts.
30	2.3 mV		317.1°	2.5 mts.
40	2.0 mV		47.1°	2.5 mts.
50	2.0 mV		317.1°	2.5 mts.
60		Hg		10 mts.

T A B L E - IV

(Reflection of circular components with temperature)

Cholesterol chloride (20 percent) + Cholesteric nonanoate
(50 per cent)

Film thickness - 50.8 *Micron*

Film holder reading	Millivoltmeter reading	Temperature	Polariza- tion sense	Exposur time
0	2.6 mV		49.35°	1 mt.
10	2.3 mV		49.35°	1 mt.
20	2.0 mV		49.35°	1 mt.
30	1.3 mV		49.35°	1 mt.
40	1.4 mV		49.35°	1 mt.
50	Hg			10 mt.

It was verified that with the o posite circular polariza-
tion, the transmission is practically 100.⁄ over the
same spectral range.

The photographic technique is satisfactory for
substances that are stable at room temperature for
quite a long time. The technique is however, quite
slow and is ant convenient for liquid crystals which have
to be maintained at high temperature and become impure
due to oxidation after some time. Also the photographic
technique becomes quite tedious for wavelengths in the
infrared region. So a suitable apparatus was set up
in order to overcome these disadvantages.

After making perfect alignment of the above systems
the rotatory power was measured as follows.





First of all the wavelength of interest was fixed by the wavelength drive. The analyser was rotated till a crossing is found. Knowing the crossing reading with and without the specimen, the optical rotation was determined for any wave length. The relative rotatime could be measured to an accuracy of $\pm 4'$ of arc.

The absolute value of the rotatory power was obtained by measuring the thickness of the specimen.