Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information: http://www.tandfonline.com/loi/gmcl16

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I. Rault [a] & P. E. Cladis [a]

[a] Laboratorie de Pysique des Solides Faculté des Sciences, 91, ORSAY, France

To cite this article: I. Rault & P. E. Cladis (1971): Cholesteric Texture Near T_c and in Presence of a Magnetic Field, Molecular Crystals and Liquid Crystals, 15:1, 1-13

To link to this article: http://dx.doi.org/10.1080/15421407108083219

Molecular Crystals and Liquid Crystals. 1971. Vol. 15, pp. 1–13

Cholesteric Texture Near T_c and in Presence of a Magnetic Field†

I. RAULT and P. E. CLADIS

Laboratoire de Physique des Solides‡
Faculté des Sciences – 91 ORSAY
France

Received October 19, 1970; *in revised form December* 11, 1970

Abstract—Near the mesomorphic-isotropic transition temperature T_c, only very weak clamping forces seem to occur between the liquid crystal and the glass walls which confine it. We have studied the cholesteric texture near the transition temperature, for two geometries:

(a) In the parallel plate geometry, we have prepared samples where the helical axis has a constant direction parallel to the glass plates. We describe how such a texture is obtained and how interacts with small cholesteric spherulites floating in the isotropic liquid.

(*b*) In the Cano wedge geometry, we describe a new texture which occurs near T_c.

1. Introduction

Two main types of cholesteric structure have been observed:

(a) The cholesteric planes are parallel to the glass plates (Grandjean texture). In this case, ideally, if the cholesteric sample is held between parallel glass plates, there are no disclination lines. If, on the other hand, the cholesteric preparation is confined to a wedge-shaped geometry, such as the Cano wedge, lines of disclination are observed. Knowing the distance between these lines, one can deduce the pitch of the cholesteric preparation.

(b) The cholesteric planes are perpendicular to the glass plates. In the most general case, and with a cholesteric preparation whose half-pitch is large enough, one observes a texture reminiscent of a finger-print. This finger-print texture has also been observed in concentrated solutions of polypeptides.$^{(1)}$ For a cholesteric preparation of large pitch, this texture is obtained when the temperature

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† Presented at the Third International Liquid Crystal Conference in Berlin, August 24–28, 1970.

‡ Laboratoire associé au C.N.R.S.

of the preparation is close to the cholesteric-isotropic transition temperature. In this case, the cholesteric planes are nearly normal to the glass plates, and the axis of twist has a random orientation in the plane of the plates, or slightly inclined with respect to them. If one slowly lowers the temperature of an isotropic cholesteric through the transition temperature, a periodic structure derived from the confocal structure of Friedel is observed. This latter texture has been explained by Bouligand(2) by replacing the ellipse and hyperbola of the confocal domains by a square and a straight line through the centre of the square. In this structure, the helical axis does not have constant direction.

We have studied some properties of the cholesteric phase near T_c (the mesomorphic-isotropic transition temperature) in a monocrystalline cholesteric sample, in which the helical axis has a fixed direction:

In the first case, the twist axis is parallel to the glass plates, the cholesteric planes are perpendicular to it. We have been able to prepare such samples and we describe the manner in which they grow.

In the second case, the axis is perpendicular to the plates, and we study the texture in the Cano wedge geometry near T_c.

2. Growth of a Cholesteric Monocrystal

2.1 TEXTURE AND PROPERTIES OF ONE SINGLE INTERFACE

The solution used was a mixture of M.B.B.A. (*p*-*n*-methoxybenzilidene-butylaniline) and cholesterol propionate such that the resulting half-pitch was 8μ. A small amount of solvent was added to this mixture to get an isotropic solution. Then we grow the cholesteric phase slowly from the isotropic melt between two glass plates. Under these conditions, it was possible to obtain large regions of a monocrystalline cholesteric. The confocal domains described by Friedel are conspicuously absent.

This is illustrated in Fig. 1(a), where we show the cholesteric texture gradually growing into the isotropic phase which appears black between crossed polaroids. The cholesteric phase is oriented so that its axis of twist is parallel to the isotropic-cholesteric boundary and parallel to the glass plates. The distance between stria; then, is the half-pitch.

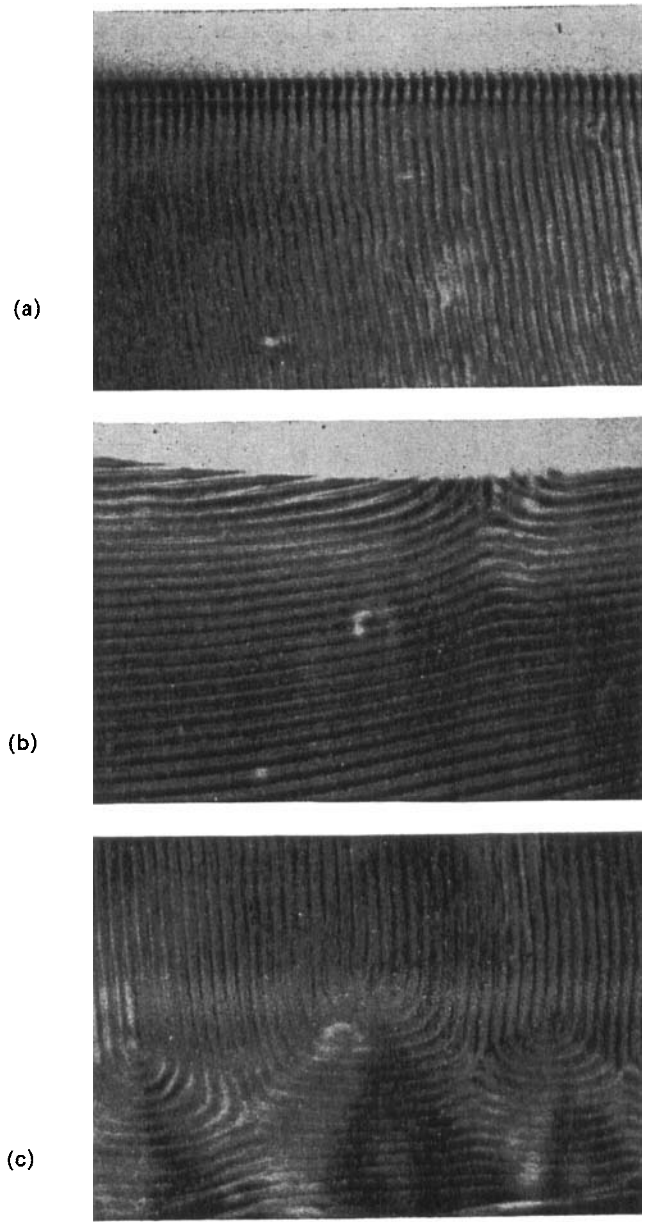


Figure 1. (a) Growth of a cholesteric monocrystal of half-pitch 8μ between crossed polaroids; (b) Formation of a disclination line when cholesteric planes are parallel to the isotropic-cholesteric boundary; (c) Domain formation by the passage of the parallel to the perpendicular texture.

At the end of each stria, there is a disclination line which is perpendicular to the axis of twist. We are probably dealing with a λ^+ configuration which has a core energy less than the τ^+ (annotation follows Ref. 3). In this case, the disclination axis is in a cholesteric plane and parallel to the molecules in this plane. If the monocrystal were to grow with the cholesteric planes parallel to the boundary, such disclination lines near the boundary will be no longer necessary. It is then remarkable that the structure adopted is the one which requires a pattern of disclination lines at the boundary.

We have then tried to observe what happens if we have a monocrystal with the helical axis perpendicular to the boundary. This can be effected, for example, by making isotropic a region of the former cholesteric monocrystal, and then, letting the new region reform. This can be seen in Fig. 1(b).

Now, the orientation of the cholesteric planes near the boundary does not stay fixed. Some undulation of these planes is observed, until finally the preferred perpendicular orientation is achieved. In Fig. 1(b), we see a λ^- disclination line, formed to allow the cholesteric planes to turn.

The transformation from the parallel to the perpendicular orientation of the cholesteric planes with respect to the boundary gives rise to an intermediate region starting in Fig. 1(b), and completely formed in Fig. 1(c). This transformation needs two kinds of disclination lines of opposite sign. Probably we are dealing with a pattern of coupled disclination lines (λ^-, λ^+) which are separated by an average distance of 6 times the half pitch.

Thus, the more stable conformation (or the conformation which grows the most rapidly) is indeed the conformation with the cholesteric planes perpendicular to the isotropic-cholesteric boundary.

2.2. Interaction Between a Spherulite and an Interface

The first observation is that small spherulites of cholesteric tend to form in the isotropic melt with their axis of twist parallel to that of the bulk mono-domain region. Figure 2(a) (Colour Plate) shows this parallel orientation. An attractive force appears to exist between the two cholesteric regions; the spherulite moves toward the monodomain region, and, at the time of contact as seen in Fig. 2(b), the cholesteric planes of the two partners are just in phase.

(2c)

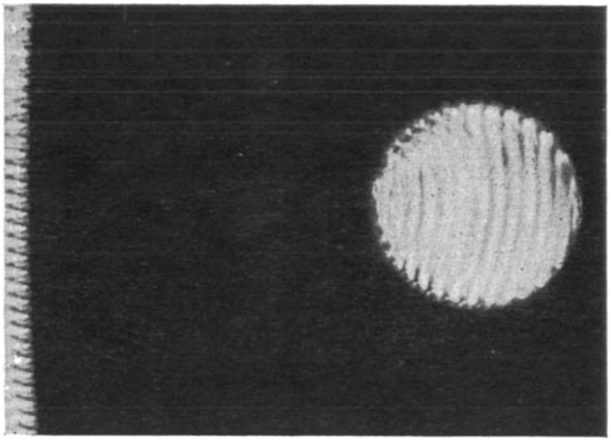


Figure 2. (a) Cholesteric spherulite in the isotropic liquid oriented by the cholesteric monocrystal; (b) Meeting between the spherulite and the main cholesteric region. Cholesteric planes are in phase; (c) Cholesteric spherulite aligned by a magnetic field of 1 Kg parallel to the cholesteric-isotropic boundary of the larger region.

Figure 6. Herring-bone texture obtained with a field of 3 Kg parallel to helix axis, near T_c.

If, on the other hand, we re-orient the spherulite by applying a magnetic field so that its twist axis is perpendicular to the monodomain region in Fig. 2(c), no attractive force is observed. If anything, there is a small repulsive force tending to widen the distance between them. In general, when the spherulite is near the boundary and with a helical axis normal to that of the large domain, cholesteric planes at the edge are distorted so as to point towards the mono-

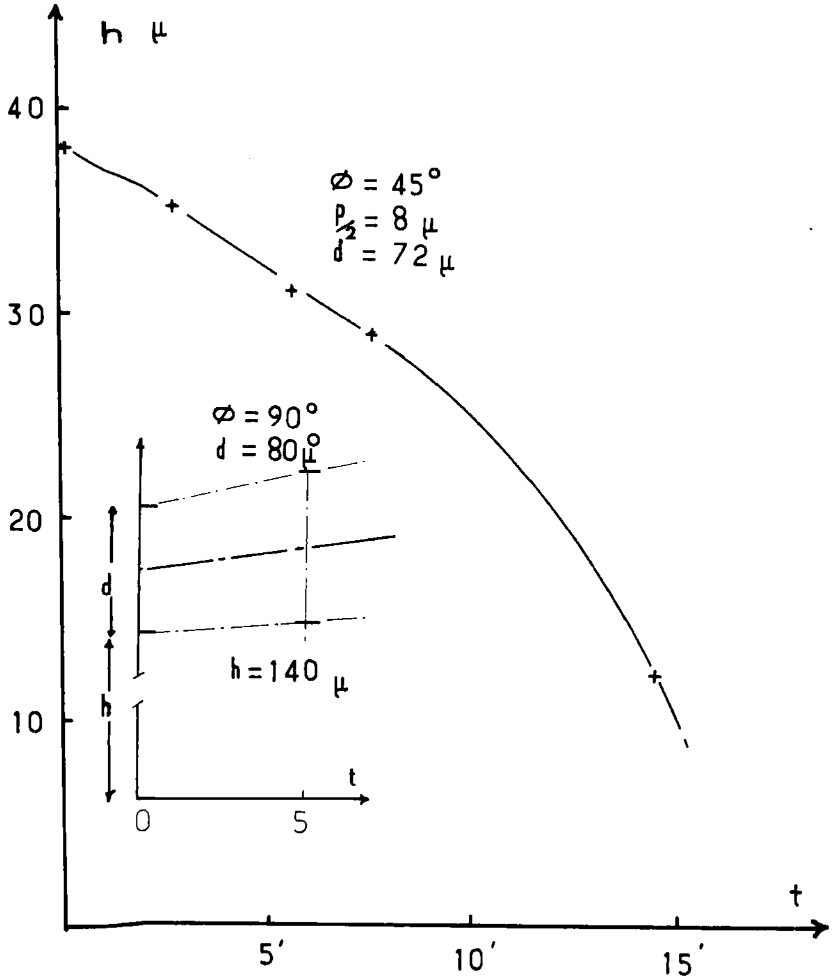


Figure 3. Distance *h* between the edge of the spherulite and the boundary versus time. ϕ is the angle between the axis of twist of the two regions. Inset—distance *h* for a spherulite oriented at 90°.

domain region: i.e., there exist an orienting effect of the mono-domain on the spherulite. Spherulites close to the boundary and aligned by a magnetic field are often disturbed in this way.

Figure 3 summarizes the foregoing results. In this figure, we show the distance h between the edge of the spherulite and the large mono-domain cholesteric as a function of time. ϕ is the angle between the twist axis of the spherulite and the large cholesteric region. When $\phi = 90°$, the distance h is increasing even though the spherulite is growing.

After turning the spherulite with a magnetic field, Fig. 4, so that its axis was oriented at 60° in 3 minutes, we then turned off the field.

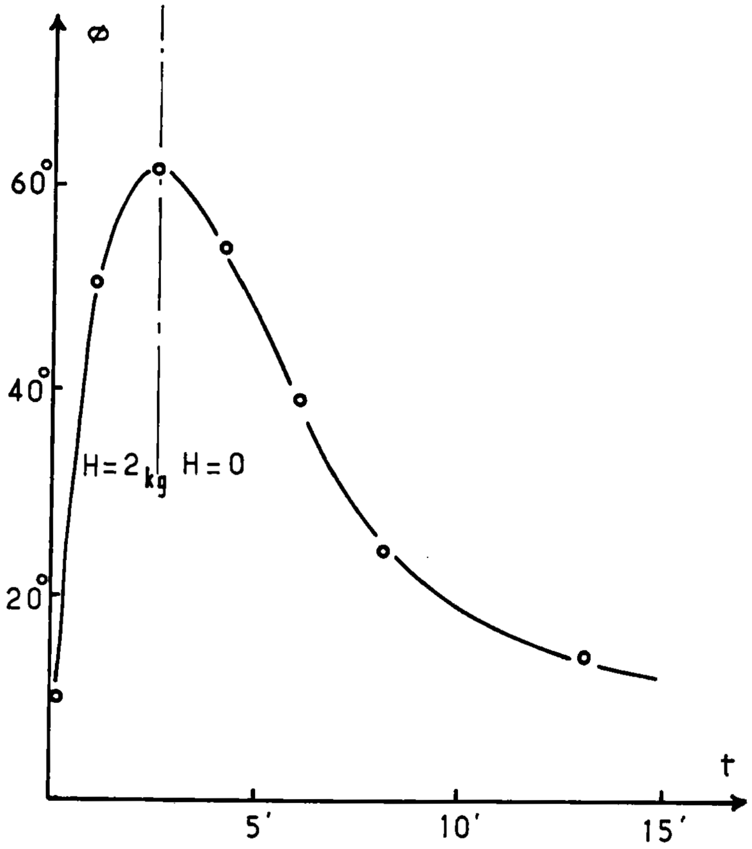


Figure 4. Orientation ϕ of a spherulite near the boundary by a magnetic field of 2 Kg, and re-orientation in zero field.

The spherulite was then observed to turn, indicating the existence of a torque acting on the spherulite by the large cholesteric monodomain. The radius of the spherulite was 40 μ, and the distance was about 100 μ. This indicates that we are dealing with rather long range interactions.

Discussing Van der Waals interactions between two anisotropic bodies separated by an isotropic liquid of the same average dielectric constant, De Gennes$^{(4)}$ has shown that the energy of interaction should depend on the angle of orientation between the two monocrystalline bodies, Fig. 5. When $\phi < 58°$, the interaction is attractive; when $\phi > 58°$, it is repulsive. This calculation applies only if h, the distance between the two regions, is less than the radius of the spherulite, but greater than the thermal coherence length. This Van der Waals effect may explain qualitatively the phenomena observed. However, from Ref. 4, the magnitude of the coupling energy between the two partners would be expected to be comparable to k_BT for a spherulite of 20 μ and at a distance of 1 μ (taking the anisotropy of the dielectric constant $\epsilon_a \simeq \epsilon_i - 1 \simeq 1$ and a Hamaker constant $A \simeq 10^{-12}$ ergs). The law of variation is in b/h. In our experiments, h is of the order of several tens of microns and b of the order of 80 μ; thus the experimentally observed interactions are larger than k_BT (in our case by a factor of ten).

The Hamaker constants$^{(9)}$ are not very well known, and have not been measured for our mixture but it would be surprising if A is of the order of 10^{-11} ergs. For optical frequencies ϵ_a has not been calculated, but a variation of ϵ_a near T_c is possible. Taking a larger value for ϵ_a near T_c could explain the very long range of the Van der Waals interaction for distances h of several tens of microns.

Quantitatively verification of the De Genne's formula is difficult for several reasons:

(1) The formation of isolated spherulites necessitates a very stable temperature. During the time of one experiment (10 to 20 minutes), if the temperature is decreasing, the spherulites disappear; if the temperature is increasing, the spherulites are too numerous, and interact with each other. Also, in such a case, they are not perfect. Many defects can be seen in them.

(2) There is always a distorted region (disclination lines) as described in Ref. 11 at the edge of the spherulite which is of the order

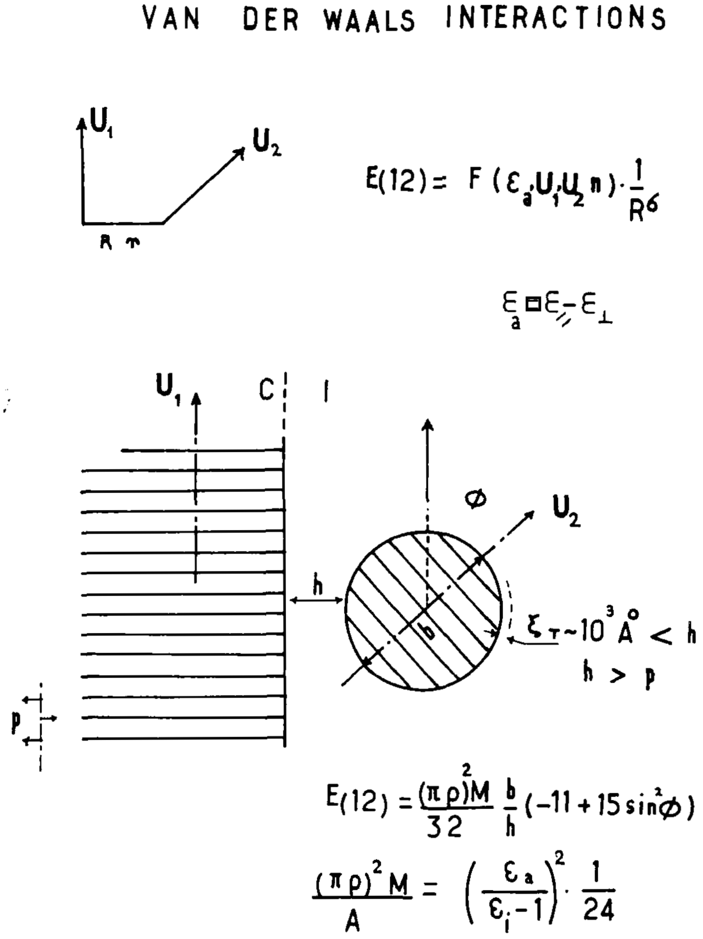


Figure 5. Interactions calculated by de Gennes[(6)] between a spherulite and a cholesteric monocrystal separated by an isotropic medium. ϕ—angle between the two helix axis; h—distance between the boundary and the edge of the spherulite; ρ—density of the cholesteric liquid crystal; ϵ_a—anisotropic dielectric constant; ϵ_i—dielectric constant of the isotropic liquid; A—Hamaker constant.

of the half-pitch. Thus, even in the best spherulites, there is a little non-homogenous region.

(3) As already pointed out, distortions are always induced by the interaction itself.

(4) Forces may be caused by the concentration gradients of the solvent in the isotropic mixture.

(5) The dielectric constant of the isotropic liquid may differ from the average dielectric constant of the spherulite. This gives a conventional attraction between spherulite and domain, and may also give rise to other types of torques (linear in ϵ_a instead of being quadratic). Effects (4) and (5) may explain why we do not observe a conspicuous repulsion between a spherulite and the cholesteric monocrystal when the spherulite is oriented perpendicular to the cholesteric monocrystal.

3.3. TEXTURE NEAR T_c IN THE PRESENCE OF A MAGNETIC FIELD

Applying a magnetic field (less than the critical field H_c at which the cholesteric-nematic transition occurs) parallel to the axis of twist has the effect of turning a small spherulite. x_a is positive so the helicoidal axis is perpendicular to the magnetic field. But there are no perceivable effects on the large mono-domain cholesteric. If we let the monocrystal grow in the presence of a magnetic field, it adopts the orientation imposed by this magnetic field.

A magnetic field perpendicular to the cholesteric planes does not orient the cholesteric monocrystal because of the clamping of the molecules at glass plates. However, near the isotropic-cholesteric transition, a small undulation appears in the cholesteric planes, which, upon further heating, gives way to the " herring bone " texture, shown in Fig. 6 (Colour Plate), with a rather regular period. There is only a slight dependance of the period of this texture on the magnetic field. The effect of the field is to increase the amplitude of the distortion rather than the period. The cholesteric planes are tilted at a constant angle from the original position. Figures 6(a) and 6(b) seem to indicate that they are tilted also with respect to the normal of the glass plates.

The junction between cholesteric planes making opposite angles with the normal gives a distorted region in the middle of the sample, while the junction between cholesteric planes tilted by the same angle does not give these distortions.

3. Cano Wedge Geometry

Another case where the helical axis of the cholesteric texture has a constant orientation is the case of the Cano wedge geometry.

Cholesteric liquid crystals that are confined in a wedge shaped space show a series of bright stripes interpreted by G. Friedel as discontinuities of the cholesteric texture. Cano(5) showed that these disclination lines correspond to discontinuities of the twist allowing discrete jumps of the pitch. Double disclination lines have also been observed and interpreted.(6) Optical studies on the Grandjean planes have shown that between two disclination lines we deal with a variable pitch and a constant helix axis, instead of a variable helix axis and a constant pitch.(7)

However, our optical investigations on the Grandjean texture show that near the cholesteric-isotropic transition temperature this is not true, anymore. The Grandjean planes do not stay parallel to the glass plates. The helix axis is no longer perpendicular to the glass plates, but turns out of the plane of symmetry of the Cano wedge.

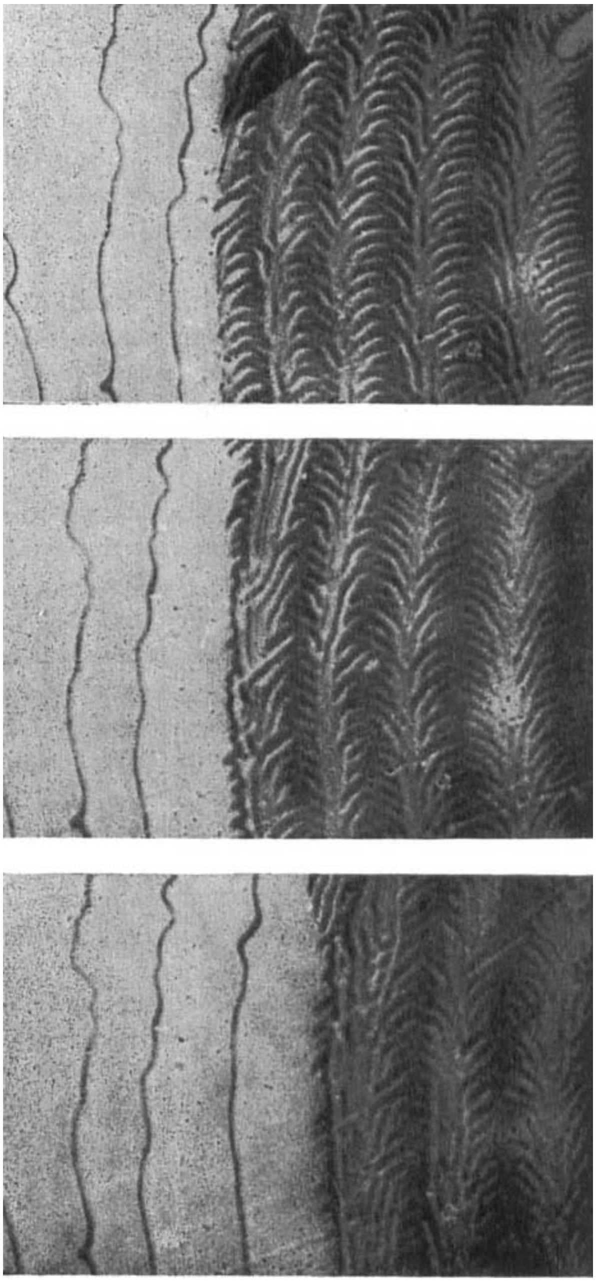
If we heat a cholesteric liquid crystal very slowly between a lens and a glass plate, near T_c we notice a change at the center. The material becomes birefringent and we see striations similar to a finger print texture. These striations grow toward the first disclination line; this line becomes thicker and takes a sinuous form (Fig. 7(a)). " Virgules " then grow from this line in the direction of the second line; each " virgule " has the same concavity (Fig. 7(b)); when this distortion reaches the 2nd line the phenomenon starts again (Fig. 7(c)).

In the thicker regions (further out from the center) where the disclinations lines are randomly distributed, we do not observe this system of " virgules ", and the standard confocal texture appears. If, instead of warming-up, we cool down from above T_c, this pattern of " virgules " is not obtained.

If the temperature is decreased, the pattern of " virgules " becomes blurred; each series of " virgules " gives rise to the corresponding disclination line. The phenomenon is reversible provided that the temperature is always maintained below T_c. This texture is reminiscent of the " virgules " observed by G. Friedel and Grandjean(8) in a free drop of cholesteric liquid crystal.

By applying a magnetic field of 2 Kg parallel to the glass plates (in the Cano wedge geometry) we destroy the texture.

We have observed that the " virgules " which are perpendicular



(a) (b) (c)

Figure 7. Texture obtained near T_c in the Cano wedge. Series of "virgules" growing as the temperature rises.

to the magnetic field disappear first the " virgules " which are parallel disappear last. This indicates that the helical axis is rotating out of the planes of symmetry of the Cano-wedge.

4. Conclusions

Near T_c only very weak clamping forces seem to occur on the glass plates.

(1) This allows one to obtain a monocrystal cholesteric with the helical axis in the plane of the plates. However, the fact that the helical axis of the cholesteric monocrystal is parallel to the isotropic-cholesteric boundary remains unexplained.

(2) In the Cano wedge geometry, the new texture observed near T_c indicates that the helical axis rotates out of the planes of symmetry of the wedge, and seems to be an intermediate texture between the Grandjean texture and the confocal texture.

Acknowledgement

We would like to thank Dr. de Gennes, Kleman and Burger for stimulating discussion.

REFERENCES

1. Robinson, C., *Trans. Faraday Soc.* **52,** 571 (1956).
   Elliot, A. and Ambrose, E. J., *Discuss. Faraday Soc.* **9,** 246 (1950).
2. Bouligand, Y., to be published.
3. Kleman, M. and Friedel, J., *Journal de Phys.* **30,** 4 (1969).
4. de Gennes, P. G., *C. R. Acad. Sci., Paris,* to be published.
   de Gennes, P. G., *Liq. Crystal-Conference,* Berlin (1970).
5. Cano, R., *Bull. Soc. Fr. Miner.* **91,** 20 (1968).
6. de Gennes, P. G., *C. R. Acad. Sci., Paris* **266,** 571 (1968).
   Orsay Liquid Crystal Group, *Phys. Letters,* **28A,** 687 (1969).
7. Kassubek, P. and Meier, G., *Mol. Cryst. and Liq. Cryst.* **8,** 305 (1969).
8. Friedel, G., *Ann. Phys.* (1922).
   Grandjean, F., *C. R. Acad. Sci., Paris* **172,** 71 (1921).
9. Lykema, Casimir Overbeck, in *Molecular Forces,* North Holland Amsterdam (1967).
   Gregory, J., *Advances in Colloid and Interface Science* **2,** 396 (1970).
10. Bouligand, Y. and Kleman, M., to be published.