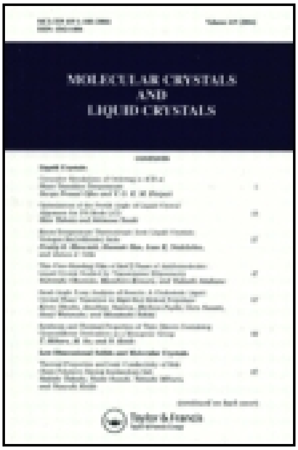

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Investigation of the Cholesteryl Oleate Mesophases by X-Ray Diffraction†

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The following phase transitions occurring in the cholesteryl oleate were investigated by X-ray diffraction: solid-isotropic liquid, isotropic liquid-cholesteric, cholesteric-smectic.

The sample purity was 98%. Strong pretransitional effects were observed at the solid-isotropic liquid phase transition and at the cholesteric-smectic phase transition.

At this last transition the longitudinal coherence length $\xi_{//}$ appears to diverge as the critical temperature is approached in the cholesteric phase, whereas the transversal coherence length $\xi_{\perp}$ increases at the critical temperature in the smectic phase in an abrupt way. It seems from the temperature dependence analysis of the angular position of the low angle peak that the smectic phase is a smectic A phase and that a progressive melting of chains occurs at the temperature increases.

1 INTRODUCTION

The cholesteryl esters present several interests in the field of liquid crystal investigations. They show interesting mesophases, like the cholesteric and smectic phases which present an intrinsic physical interest. In fact McMillan[1] carried out X-ray diffraction studies on cholesteryl nonanoate and cholesteryl myristate phase transitions in order to test a theoretical model of smectic A phase.

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Moreover cholesteryl esters may show the famous and mysterious "blue phase". In addition cholesteryl esters present a peculiar biological interest as they are contained in large fraction in alpha and beta serum lipoproteins and in the lipids of the atherosclerosis lesions: 60%–80% of such cholesteryl esters are constituted by cholesteryl oleate and cholesteryl linoleate.[2] This aspect was largely investigated by Small and coworkers.[2–3] Furthermore a knowledge of the structure of mesophases involving cholesteryl esters can be useful in the study of the conformation and of the molecular interactions involving long chain fatty acids, which are also present in biological membranes.

In this last context a systematic investigation of the crystallographic structures of several solid phases of cholesteryl esters was performed at the Pittsburg University.[4]

The present paper reports the results of an X-ray investigation of the several phases of cholesteryl oleate.

First a preliminary thermodynamic analysis was performed by differential scanning calorimetry. Then the solid-isotropic phase transition was investigated by X-ray diffraction.

Finally the isotropic liquid-cholesteric and cholesteric-smectic phase transitions were investigated.

2 THERMODYNAMIC ANALYSIS

At our knowledge the first differential scanning calorimetry (DSC) curves of the cholesteryl oleate were obtained by Small.[2]

The purity of the sample was 99%.

The solid phase was found to melt sharply to an isotropic liquid at 51°C. A monotropic cholesteric phase is formed by cooling down the sample at 47.5°C and a monotropic smectic phase at 42°C.

Davis et al. report the values 50°C, 46.4°C, 41.8°C for the three transition temperatures.[5] The most recent DSC data were obtained by Armitage,[6] by working with a sample purity of 99%. He was able to observe the transition into the "blue phase" and reported the existence of four solid phases: K_1, K_2, K_3, K_4. It seems that at room temperature only the phases K_2 and K_3 can exist. The transition temperature K_2-isotropic liquid is reported to be 46.8°C whereas the transition temperature K_3-isotropic liquid is 48.3°C. The other reported transition temperatures are 39.2°C for S_A-Ch, 44.6°C for Ch-"blue phase", 45.1°C for "blue phase"-isotropic liquid.[6]

Before doing the X-ray diffraction investigation we have also performed some DSC measurements on our sample, which has a 98% purity. We decided to present a typical thermogram in Figure 1, because this will be useful in the discussion of X-ray diffraction data. The measurements were performed with

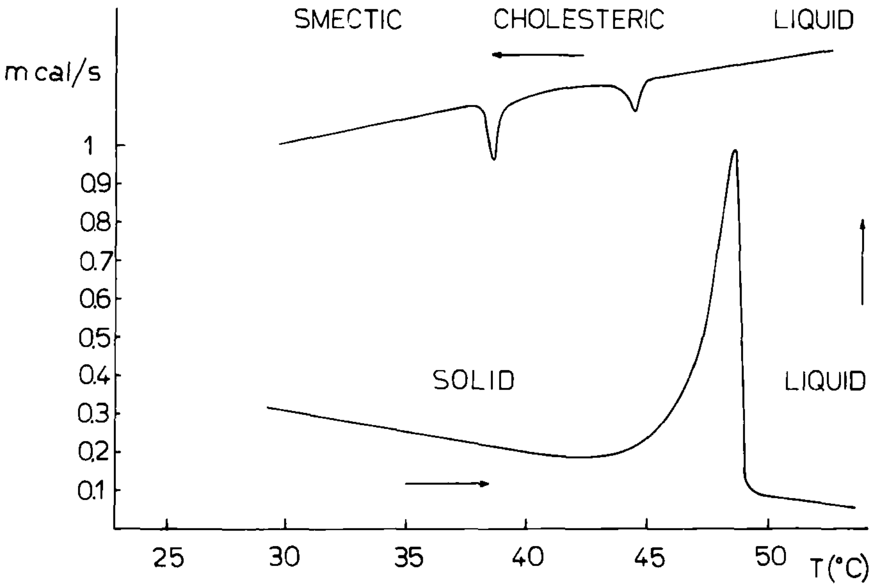

FIGURE 1 Typical DSC traces of cholesteryl oleate.

the Perkin-Elmer DSC 2. The heating rate was 1.25°K/min. The volume of the containers was 5 ml.

A pretransition effect is evident at the solid-isotropic liquid transition; whereas well defined peaks are associated to the two other transitions. This last feature, together with the good reproducibility of the transition temperatures, appearing from Figure 2, which will be discussed below, seems to confirm that no deterioration, like oxidation, occurred in the sample. In fact the sample, which was supplied from the Supelco and is normally used as a standard for chromatography, was handled with care in order to avoid degeneration: the container was opened and the sample holder was filled under a nitrogen atmosphere and the sample was stored at a temperature of about −2°C.

Figure 2 reports the histograms, concerning the different phase transitions, obtained by repeating measurements on different samples and different loops as it was performed in Ref. 7.

Table I reports the average DSC data.

Concerning the solid phase results, we believe that they should be referred to the K_3 solid mentioned in Ref. 6, because our samples were either "virgin" in the sense reported in Ref. 7 or annealed at room temperature for several days.

No "blue phase" transition was clearly visible.

The obtained transition temperatures are slightly lower as compared to

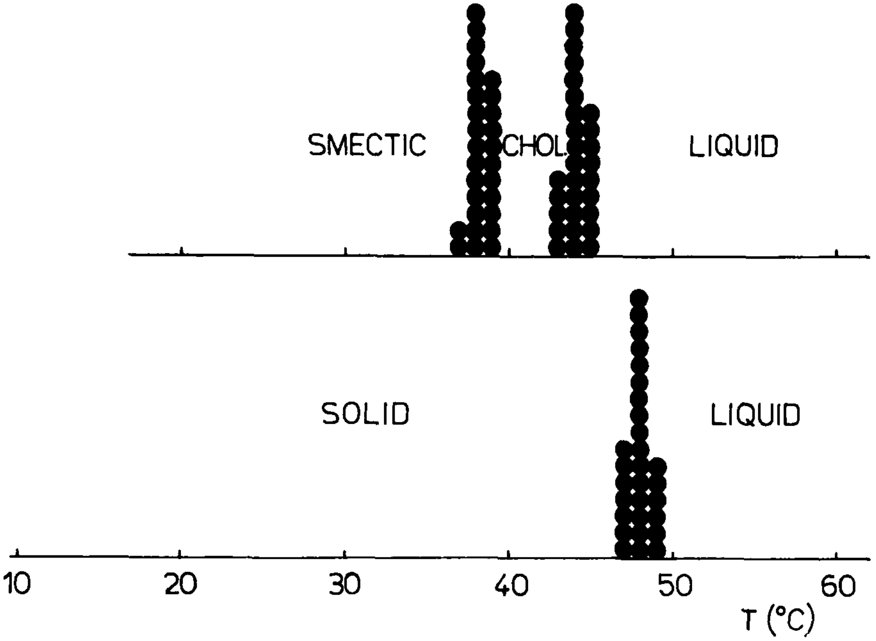

FIGURE 2 Histogram concerning the different phase transitions, obtained by repeating DSC measurements.

those of Ref. 6, as a consequence of a probable influence of the sample lower purity.

A satisfactory agreement exists concerning the transition enthalpies with the data reported in Ref. 6.

DSC data are not reported for the transition S_A-solid phase, as this transition does not occur by cooling the sample to room temperature, but only after an annealing of several minutes, as already reported by Small.[2]

TABLE I

Measured enthalpies and entropies for the different phase transitions of Cholesteryl oleate.

	ΔH		ΔS
Phase Transition	(cal/g)	(Kcal/mole)	[cal/mole T° (K)]
Crystal-Isotropic Liquid	10.2 ± 0.5	6.64 ± 0.33	20.9 ± 1.7
Isotropic Liquid-Cholesteric	0.20 ± 0.03	0.13 ± 0.02	0.421 ± 0.04
Cholesteric-Smectic	0.36 ± 0.03	0.23 ± 0.02	0.754 ± 0.07

3 X-RAY DIFFRACTION RESULTS

The experiments by X-ray diffraction were carried out by using the same apparatus and with the same experimental details described in Ref. 8.

3.1 The solid-isotropic liquid transition

The crystal structure of cholesteryl oleate ($C_{45}H_{78}O_2$) was recently determined by Craven and Guerina.[9] The unit cell is monoclinic and contains two molecules, space group $P2_1$, with $a = 12.65(3)$Å, $b = 9.13(3)$ Å, $c = 18.79(5)$ Å, $\beta = 93.3(3)°$.

The chains of the oleate molecule are almost straight apart a kink at the cis-double bond.

Figure 3a reports a typical diffraction pattern from a polycrystalline sample in the solid phase.

Figure 4b reports the normalized intensities associted to the Bragg peaks (001) $(11\bar{3})$ (020) as a function of temperature. An apparent pretransitional effect, resulting in a continuous decrease of the diffracted intensities starting about 4°C before the transition temperature, is observed for the three reflections. This fact should be related to the DSC data of Figure 1, where a similar pretransitional effect is observed for the same temperature interval.

A similar pretransitional effect was observed by Riste and Pynn at the solid-nematic phase transition of PAA.[10]

Figure 4a reports the observed full widths at half maximum for the three reflections as a function of temperature. It appears that the peak widths do not change appreciably as a function of temperature also in the pretransitional region, as it was the case for the PAA.

Another similarity with PAA is the absence of a detectable shift of the Bragg angle as a function of temperature.

Figure 4c reports the scattered intensities at $Q = 0.21$ Å^{-1} and $Q = 1.23$ Å^{-1}, which correspond to the maxima of the two peaks of the diffuse radiation observed in the isotropic liquid phase.

The quantity Q is defined as $Q = (4\pi/\lambda) \sin\theta$.

A pretransitional continuous increase of the diffuse radiation is observed in the same temperature interval corresponding to the previously observed pretransitional effects associated to DSC and Bragg peaks. A similar effect was also observed for the PAA. In this last case the authors suggest that no phase coexistence occurs in the pretransitional condition, but the melting of PAA occurs in correspondence to certain reorientational motions of the molecules becoming more and more larger till a critical amplitude is reached. In the present case, without being so precise in defining the kind of molecular motion, it is likely to believe that the continuous decrease of Bragg peak

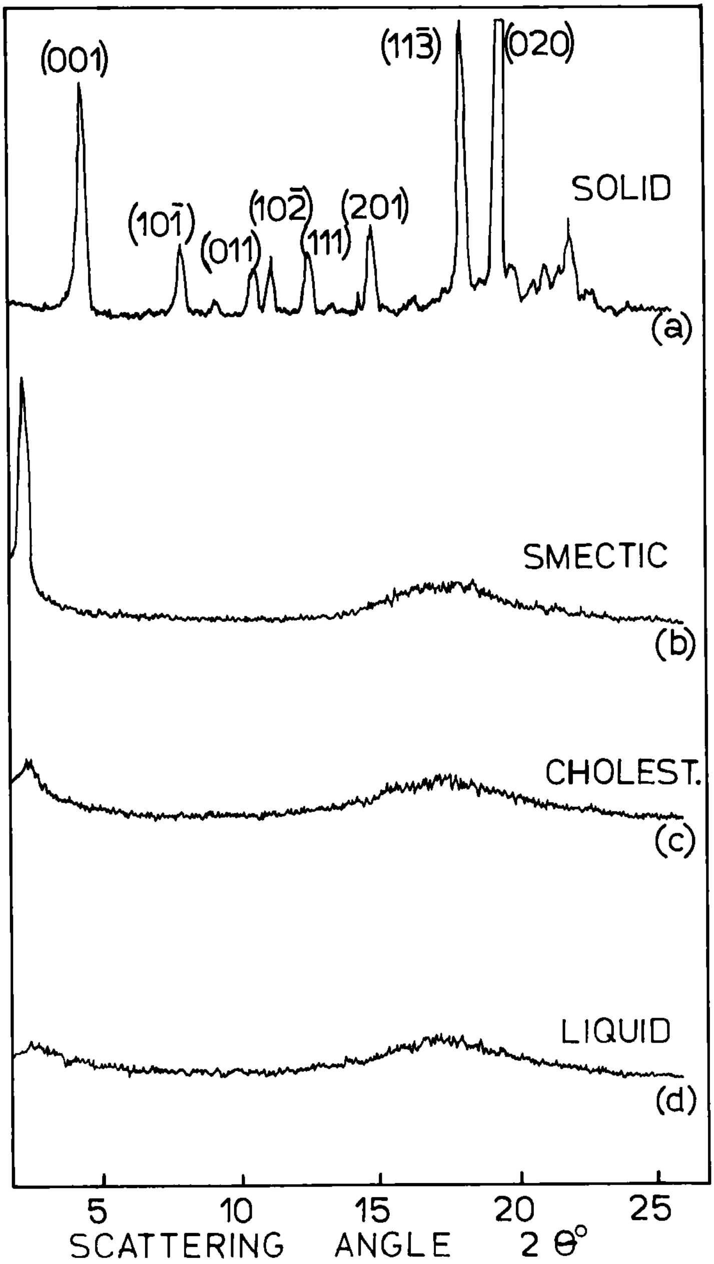

FIGURE 3 X-ray diffraction patterns obtained by cholesteryl oleate in the solid phase (*a*), in the smectic phase (*b*), in the cholesteric phase, (*c*), in the liquid phase (*d*).

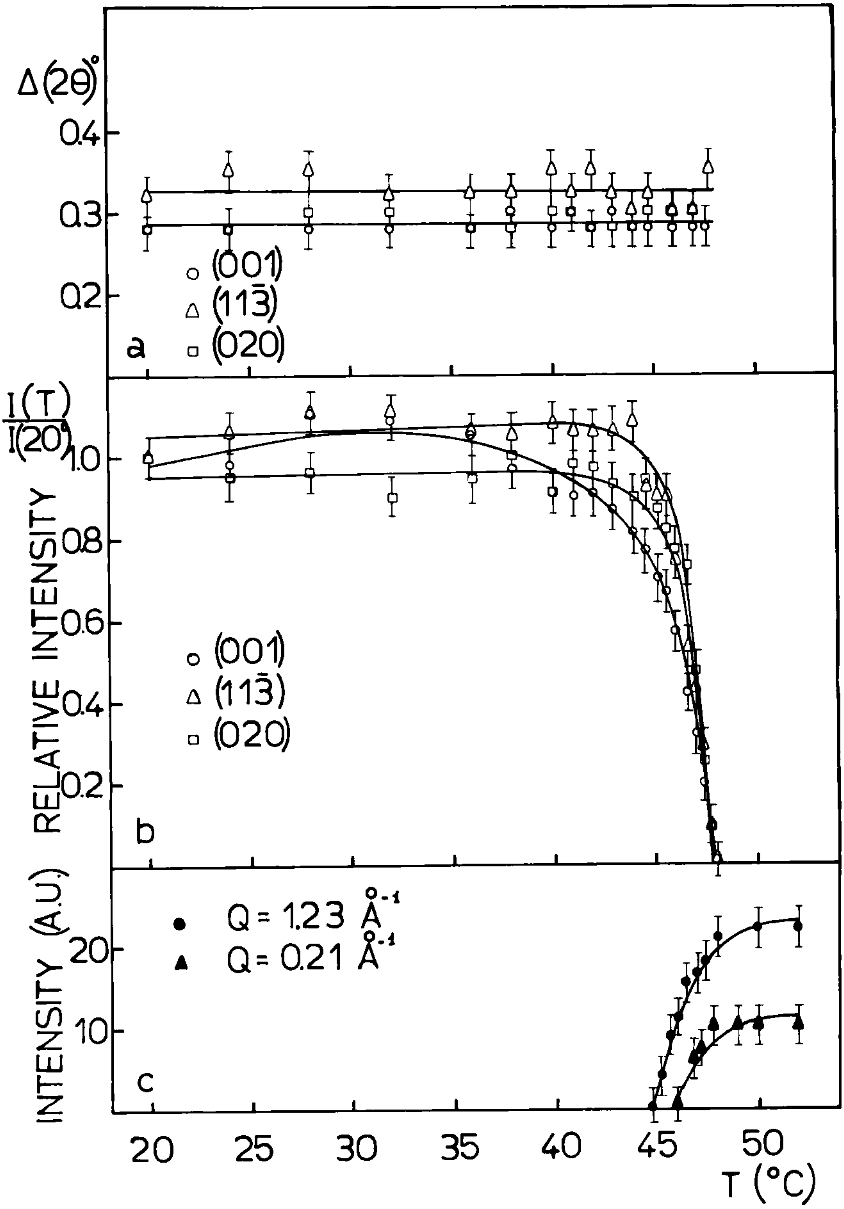

FIGURE 4 Solid-isotropic liquid transition: (a) Full widths at half maximum of the (001) (11$\bar{3}$) and (020) peaks vs. temperature. (b) Intensities of the (001) (11$\bar{3}$) and (020) peaks normalized to the intensities at 20°C as a function of temperature. (c) Intensities of diffuse peaks at $Q = 1.23$ Å^{-1} and $Q = 0.21$ Å^{-1} vs. temperature.

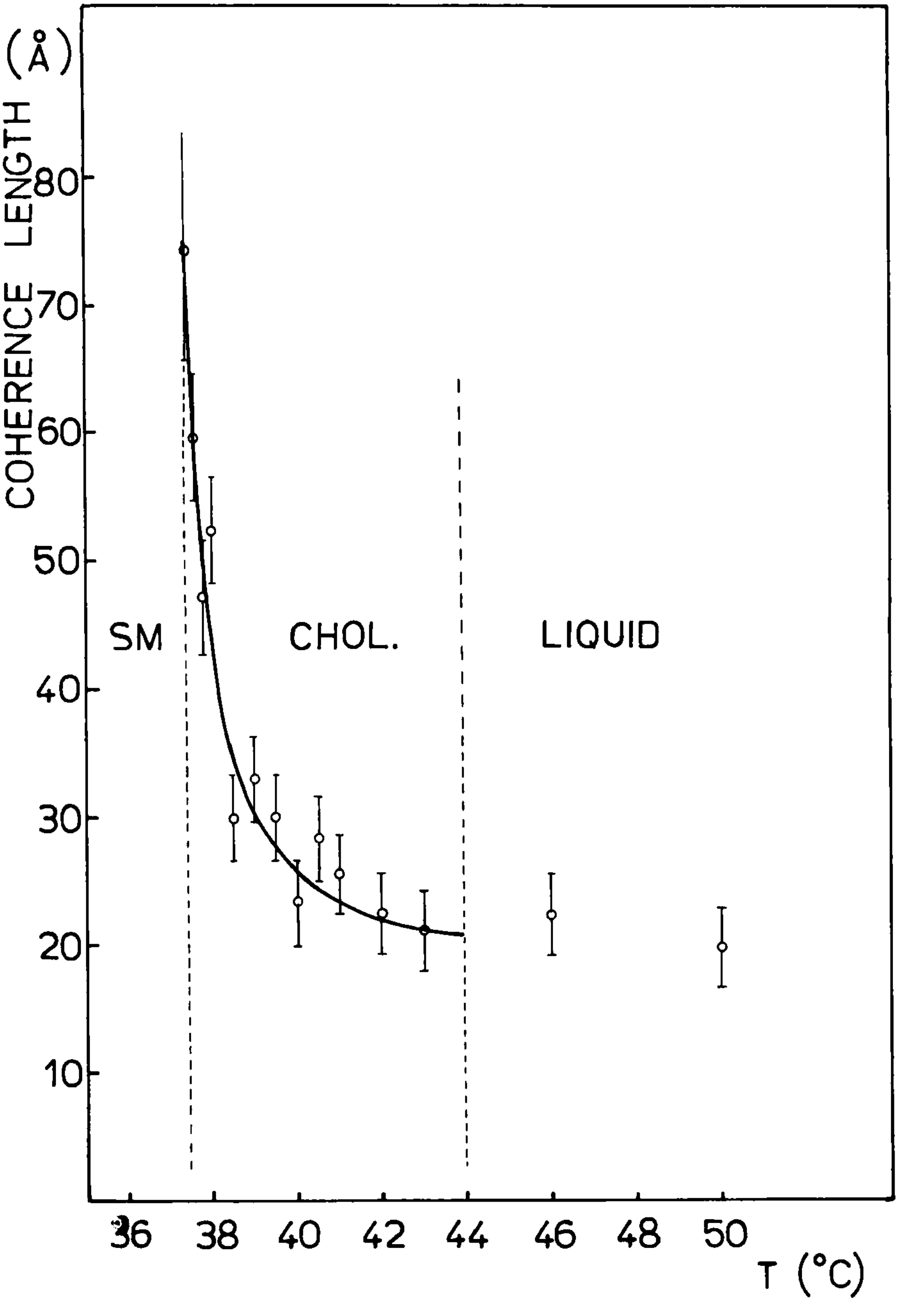

FIGURE 5 Longitudinal coherence length $\xi_{//}$ vs. temperature.

intensities and the progressive increase of diffuse scattering at low and high Q values should be related to progressively larger and larger molecular motions.

If this would be the case, the nature of the molecular motions could be put in evidence by typical spettroscopic techniques.

However an alternative explanation in terms of a phase coexistence can not be completely ruled out at this stage.

We plan to repeat the measurements on samples of higher and lower purities.

3.2 The isotropic liquid-cholesteric and cholesteric-smectic phase transitions.

By cooling the sample from the isotropic liquid phase, the transitions to the cholesteric and to the smectic phase occur as it appears from Figure 1. Figure 3b, c, d report the diffraction patterns observed in these three phases.

The maximum intensity of the diffuse peak, which in the smectic phase becomes a Bragg peak centered at $Q = 0.17$ Å^{-1}, is presented in Figure 6 as a function of temperature.

The reported intensities are corrected for the instrumental resolution by the method which was used in Ref. 11.

A small increase of the intensity is observed at the isotropic liquid-cholesteric transition as already observed by McMillan.[1]

That means a slight increase of the positional order along the direction of the molecules.

At the cholesteric-smectic transition a continuous increase of the intensity is observed as the critical temperature is approached, in a similar way to the cholesteryl myristate and cholesteryl nonanoate,[1] and to the case of the nematic-smectic A phase transition in TBBA.[11]

The partial superposition of the diffuse peak to the primary beam makes difficult the evaluation of the intensity of the diffuse peak.

As a consequence it is impossible to obtain a reasonably accurate value of the critical exponent associated to the increase of this intensity. On the other hand this is out of the aim of the present work.

It should be emphasized that this apparent pretransitional effect concerning the intensity of the low angle diffuse peak is related to larger and larger cholesteric regions fluctuating to and from a smectic configuration (order parameter fluctuations which are called cybotactic clusters).

From the small angle peak widths, after correction for the experimental resolution,[11] it was possible to calculate the longitudinal coherence length $\xi_{//}$ through the equation:[11]

$$\xi_{//} = 2/\Delta Q_{//}$$

where $\Delta Q_{//}$ is the full width at half maximum of the peak.

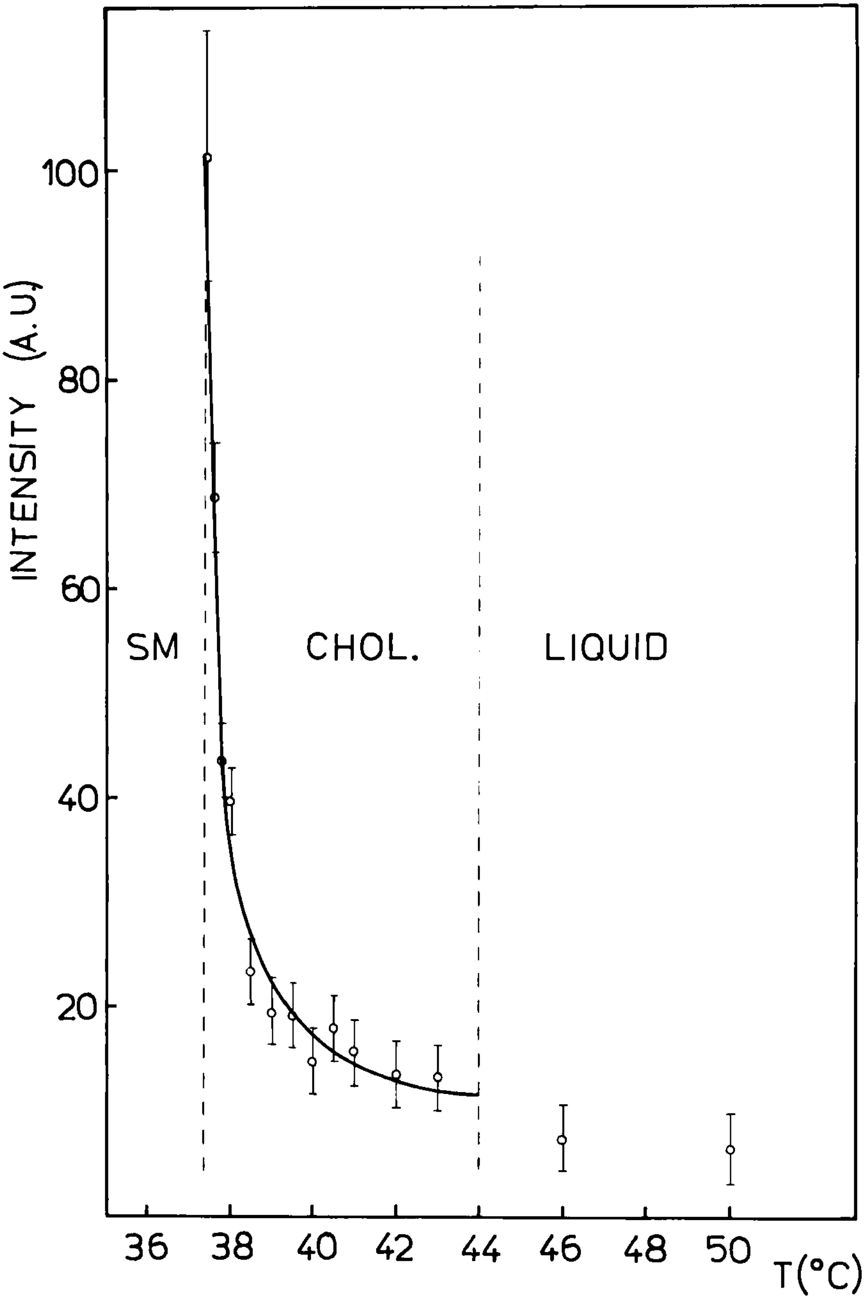

FIGURE 6 Maximum intensity of the small angle peak vs. temperature.

The temperature dependence of $\xi_{\parallel}$ is reported in Figure 5.

Pretransitional effects are visible, as it was the case considered in Ref. 11, where a similar qualitative behaviour was observed. Also for this quantity behaviour was observed. Also for this quantity the experimental accuracy is not sufficient in order to derive a critical exponent.

It appears that the longitudinal coherence length (which in a very rough way could be considered as a linear dimension of the cybotactic cluster) increases progressively as the critical temperature is approached in the cholesteric phase.

Figure 7 shows the position Q_p in Q units of the low angle Bragg peak in the smectic phase and the corresponding diffuse peak in the cholesteric and isotropic liquid phases. In the smectic phase it is possible to apply the Bragg law and an interplanar distance d = 36.7 Å is obtained. In the cholesteric and isotropic liquid phases the Bragg law is not anymore applicable. The strong increase of the Q_p values appears much higher than in the case of cholesteryl nonanoate and cholesteryl myristate, where the variations were respectively 1% and 2%. These variations were attributed by McMillan to a shortening of the average molecular length, due to increased flexibility of the end chains with increasing temperature.

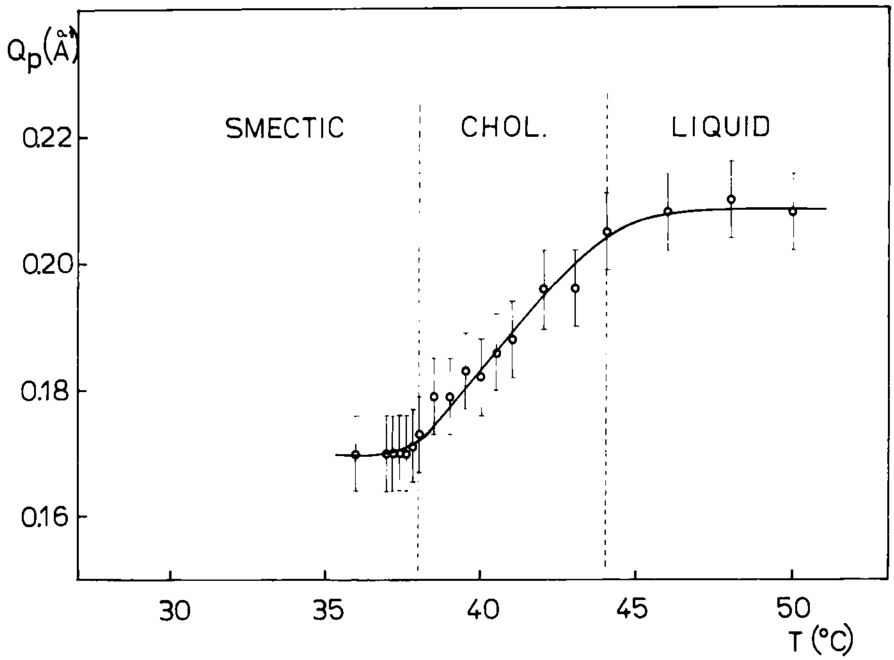

FIGURE 7 Position Q_P of the low angle Bragg peak in the smectic phase and of the corresponding diffuse peak in the cholesteric and isotropic liquid phases as a function of temperature.

Implicitely he supposed that the Bragg law is applicable in the case of cholesteric phase too. Actually it is not at all evident that it can be applied in this case.

However, we believe that in our experiment an eventual correction factor applied to the Bragg law in the cholesteric phase should not completely cancel out the effect of the apparent decrease of the interplanar distance (or intermolecular distance along the longitudinal axis in cholesteric and isotropic liquid phases), when the temperature is increased. If this would be the case, one could deduce that the smectic phase is a smectic *A* and not a smectic *C*.

In fact, a priori, both these two phases are compatible with the interplanar distance $d = 36.7$ Å observed in the smectic phase.

This value is lower than the 42 Å end-to-end repeat distance of the molecules which are parallel to [301]-axis in the solid phase as reported in Ref. 9. However if the phase would be a smectic *C* with tilted molecules, one should expect that the repeat distance would increase in the cholesteric and isotropic liquid phase where the tilt is removed. But this would be in disagreement with the results reported in Figure 7, so that we believe that the smectic phase is smectic A with molecules perpendicular to the smectic layers and eventually in antiparallel position.

It is probable, on the basis of the previous discussion of Figure 7, that a progressive melting of the chains occurs as the temperature increases.

Figure 8a reports the maximum intensity of the large angle ($Q = 1.23$ Å^{-1} at $T = 50$°C) diffuse peak. An increase is observed at the cholesteric-smectic *A* phase transition which can be interpreted as a decrease of the liquid-like disorder associated to the lateral packing of the molecules.

Figure 8b presents the coherence length $\xi_\perp$ derived from the widths of the large angle diffuse peak, as it was done for the small angle peak. A slight increase of $\xi_\perp$ appears at the isotropic liquid - cholesteric phase transition and a marked increase of the same quantity appears at the cholesteric-smectic *A* phase transition. This is a further evidence that, when entering the smectic *A* phase, a decrease of the disorder occurs concerning the lateral packing of the molecules.

Figure 8c reports the intermolecular lateral distance as a function of temperature, as deduced from the angular position of the large angle diffuse peak by using the corrected Bragg law according to the suggestion of De Vries:[12]

$$1.117\ \lambda = 2\ x_m \sin\theta_m.$$

A continuous increase of lateral distance as a function of temperature appears, without any apparent discontinuity, through the three disordered phases.

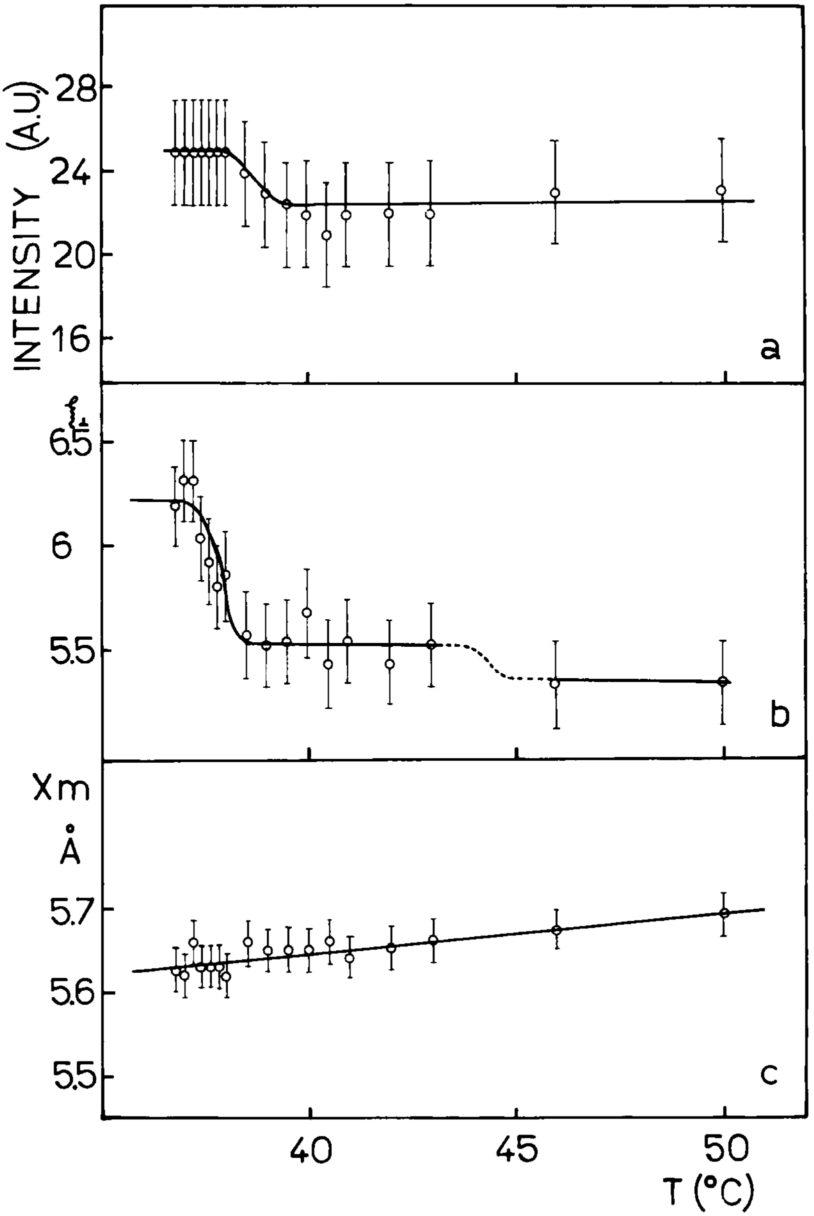

FIGURE 8 Isotropic liquid-cholesteric and cholesteric-smectic transitions: (a) Maximum intensity of the large angle diffuse peak vs. temperature. (b) Transversal coherence length $\xi_\perp$ vs. temperature. (c) Intermolecular lateral distance as a function of temperature.

CONCLUSIONS

The different phase transitions of the cholesteryl oleate were investigated by X-ray diffraction. The results are coherent with a preliminary DSC investigation. In particular at the solid-isotropic liquid phase transition a well established pretransitional effect was observed corresponding to a continuous decrease of the Bragg peak intensities which can be attributed to larger and larger molecular motions. In fact, inside the resolution, no reduction of the infinite correlation length is observed.

A conclusion on the possible nature of the smectic phase as a smectic A was derived from the data.

A divergence of the longitudinal coherence length $\xi_{/\!/}$ and of the low angle peak maximum intensity was observed at the cholesteric-smectic A phase transition.

Also the temperature dependence of the transversal coherence length $\xi_{\perp}$, which is related to the lateral molecular packing, was obtained. An abrupt increase of this quantity was observed at the cholesteric-smectic A phase transition. This should be interpreted as a reduction of the two-dimensional liquid-like disorder in directions perpendicular to the molecular axes.

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