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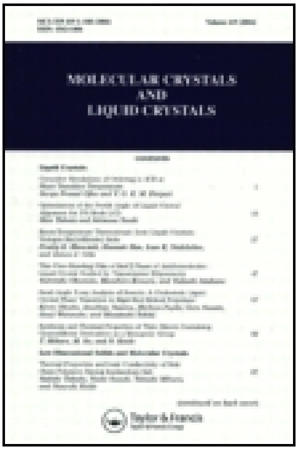

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The Depolarization of Light Scattered from Liquid Crystals

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The Depolarization of Light Scattered from Liquid Crystals

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Abstract—A helium-neon gas laser was used to determine the depolarization factors as a function of temperature and scattering angle for bulk mesomorphic materials. These studies were conducted with the incoming polarization both parallel and perpendicular to the plane formed by the incident and scattered waves. In general there exist fairly constant values of the depolarization factors except in a temperature region near a meso-mesophase or clearing point transition. The data also exhibit pretransitional and post-transitional fluctuation regions, i.e., regions where the scattered intensities vary rapidly with time. The measurement of the depolarization factors is an ideal way to test thermal equilibrium processes. After temperature equilibrium is maintained the smectic and cholesteric phases require at least an hour to reach thermal equilibrium. This result is of prime importance for studies of bulk mesomorphic materials.

The depolarization of light scattered by bulk homogeneous media arises from the scattering centers being not too small compared with the incoming wavelength, and the scattering elements being anisotropic in structure.[1] For mesomorphic materials these scattering elements are probably some type of density or orientation fluctuations within an ordered region. By investigating this depolarization as a function of angle and temperature in the region of meso-mesophase or clearing point transition, information can be obtained about the changes in the size and shape of the scattering elements.

A theory proposed by Krishnan[1–5] and extended by Perrin[6] establishes a relationship between the intensities of certain components of the scattered light for a particular condition of polarization of the incident beam.

The parallel depolarization factor, Eq. (1),

$$\rho_{\parallel} = \frac{I_{\perp}}{I_{\parallel}} \tag{1}$$

for incident light polarized parallel to the plane containing the incident and scattered waves is defined as the ratio of the intensities of the perpendicular and parallel components of the scattered light, henceforth called the perpendicular and parallel intensities (Fig. 1). Similarly the perpendicular depolarization factor, Eq. (2),

$$\rho_{\perp} = \frac{I_{\parallel}}{I_{\perp}} \tag{2}$$

for incident light polarized perpendicular to the plane containing

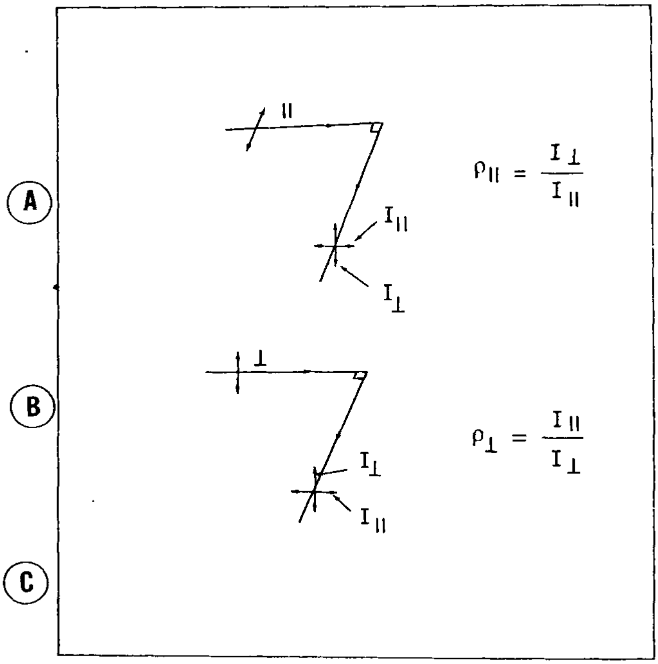

Figure 1. Schematic drawing of the depolarization factor.

the incident and scattered waves is defined as the ratio of the parallel and perpendicular intensities of the scattered light. The perpendicular depolarization factor depends mainly on the lack of spherical symmetry, while the parallel depolarization factor depends on the size of the scattering element.

An eight milliwatt helium-neon gas laser beam chopped at four hundred cycles per second was used for the incident beam. By rotating the laser tube 90° the incident light was polarized either perpendicular or parallel to the plane formed by the incident and scattered waves. The parallel and perpendicular intensities of the scattered beam were measured with a special built radiometer used in conjunction with a Glan-Thompson prism.

Figure 2 is a schematic diagram of the scattering chamber.

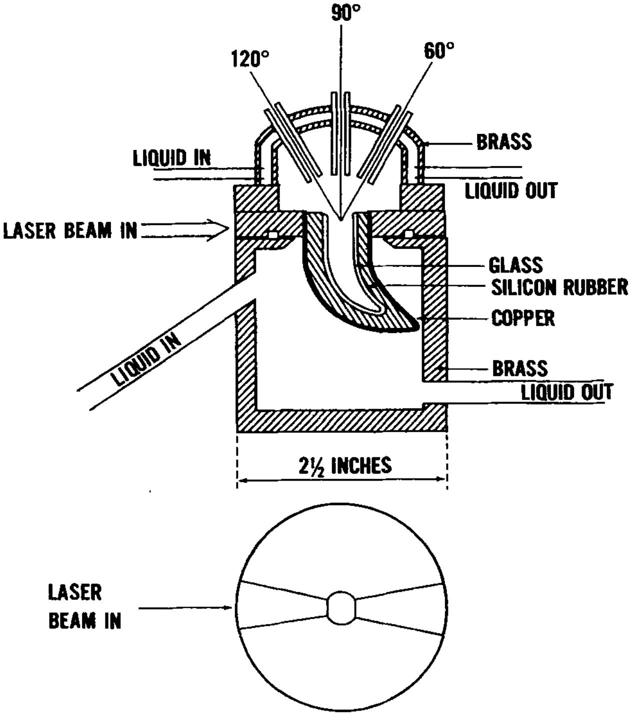

Figure 2. Schematic drawing of the light scattering chamber.

This particular design eliminates multiple scattered beams from reaching the detector. The temperature of the chamber was maintained by two temperature controlled circulators which were accurate to ± 0.02 °C and recorded by a precision quartz thermometer (DYMEC-MODEL 2800) placed against the copper sleeve. A heated helium atmosphere was maintained over the sample to avoid oxidation. As illustrated in Fig. 2 angular measurements were made at 60°, 90°, and 120°. By a similar arrangement 45°, 90°, and 135° were measured, thus allowing comparisons at 45°, 60°, 90°, 120°, and 135°. To eliminate the possibility of surface or wall effects, the laser beam entered the cell one-quarter of an inch below the surface, and the detector saw only the center of the three-eighths inch wide cell.

All data were taken under conditions of thermal equilibrium (to be discussed later). Since the depolarization factor is dependent on density or orientation fluctuations, thermal equilibrium was indicated by measuring a constant depolarization factor as a function of time for a highly temperature stabilized system. By applying this criterion on the data, the results were reproducible over a period of months.

Cholesteric-Isotropic Transition

Figure 3 shows the perpendicular depolarization factor for cholesteryl nonanoate from 88 °C to 91.5 °C. For this material the cholesteric-isotropic transition occurs at 90.7 °C. Below 89.8 °C the depolarization factor is a constant except at 135° where a slight decrease occurs. In the region from 89.8 °C to 89.95 °C (cross-hatched region) rapid fluctuations in the scattered intensities excluded any accurate determination of the depolarization factor (henceforth, this region will be designed as the fluctuation region). However, it was determined that the depolarization factor lies somewhere between the upper and lower curves. Above 90 °C the perpendicular depolarization factor continues to decrease exhibiting a minimum at approximately 90.8 °C for 60° and 120°.

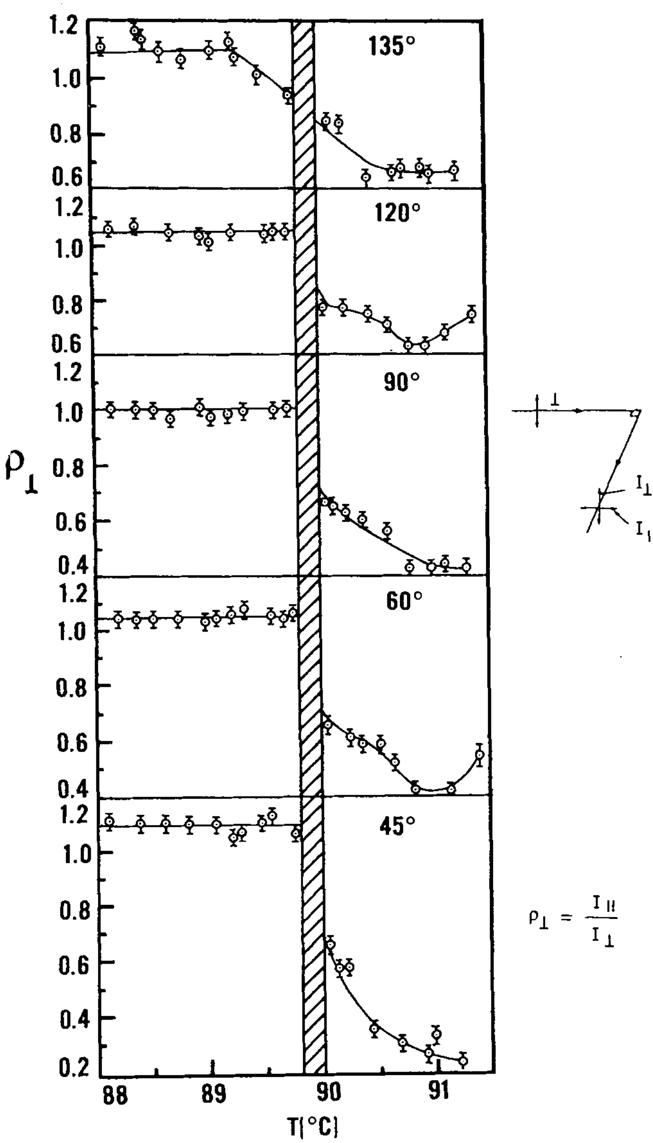

Figure 3. A plot of perpendicular depolarization factors for cholesteryl nonanoate from 88 °C to 91.5 °C.

By very accurately calibrating the temperature measurement among the scattering chamber, a differential scanning calorimeter, and a microscope stage with zone refined materials a comparison of this fluctuation region with the cholesteric-isotropic transition was made. Figure 4 indicates the cholesteric-isotropic region of latent heat absorption for cholesteryl nonanoate as measured by a differential scanning calorimeter. Heat is absorbed in the region from 89.2 °C to 90.7 °C. The fluctuation region lies within this temperature range.

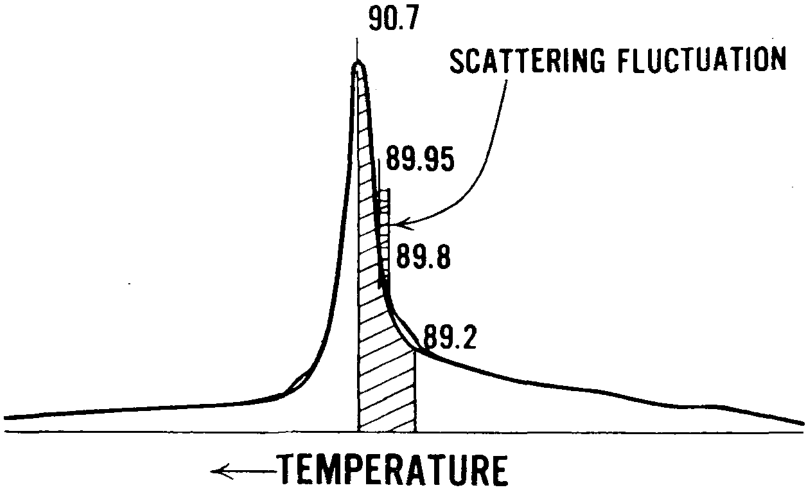

Figure 4. Region of latent heat absorption for the cholesteric-isotropic transition for cholesteryl nonanoate.

It should be pointed out that, because of temperature gradients within the sample during a transition, differential scanning calorimetry provides only precise temperature measurements at the beginning and end of the region of latent heat absorption. The end temperature, i.e., the corrected peak temperature, or the temperature at which the entire sample is in the new state is called the transition point. The corrected clearing point temperature as determined by a differential scanning calorimeter and a static optical observation (microscope) differs by less than

0.1 °C. Therefore, the precise location of the fluctuation region within the transition region as shown in Fig. 4 is only approximate. However, it can be accurately determined whether the fluctuation region is above or below the transition temperature.

Figure 5 is a plot of the perpendicular depolarization factor for cholesteryl nonanoate in the temperature region 86 °C to 93 °C.

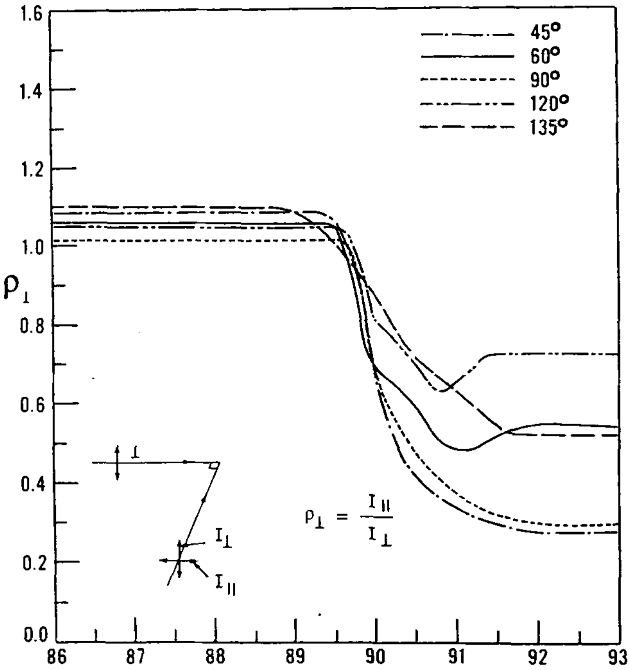

Figure 5. A plot of the perpendicular depolarization factors for cholesteryl nonanoate from 86 °C to 93 °C.

Below the fluctuation region (89.8 °C to 89.95 °C) there is a constant depolarization factor that is symmetrical about 90°. For 60° and 90° a minimum in $\rho_\perp$ occurs at the clearing point. Temperatures above 91.5 °C have constant depolarization factors which are very asymmetrical about 90°.

The parallel depolarization factor for cholesteryl nonanoate in the temperature region from 86 °C to 93 °C is shown in Fig. 6.

From 86 °C to 89.2 °C there is a constant depolarization factor that is slightly asymmetrical about 90°. A rapid increase in $\rho_\parallel$ occurs below and above the fluctuation region (89.8 to 89.95 °C) with a maximum occurring at 90.2 °C for 90°. Above 90.2 °C there is a decrease in $\rho_\parallel$ with a minimum at 90.7 °C and then a constant factor which is very asymmetrical about 90°.

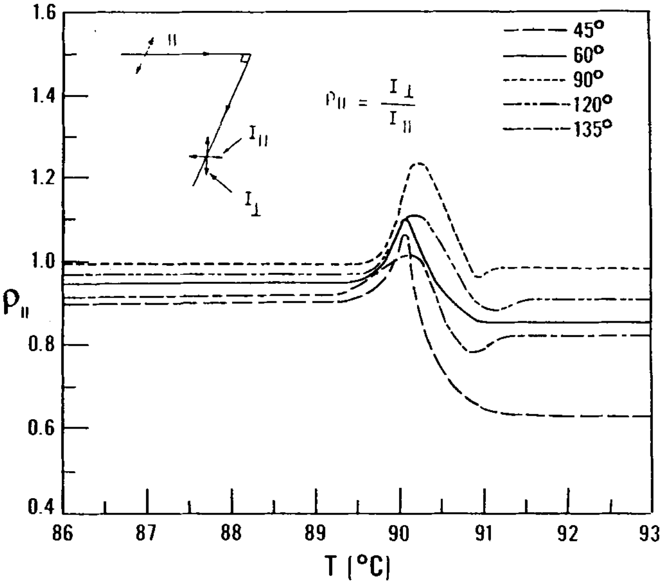

Figure 6. A plot of the parallel depolarization factors for cholesteryl nonanoate from 86 °C to 93 °C.

The constant values for both $\rho_\perp$ and $\rho_\parallel$ below 89.8 °C indicate that no change occurs in the size and anisotropy of the scattering centers while in the cholesteric mesophase. The change in $\rho_\parallel$ from 89.5 °C to 90.7 °C suggests first an increase or expansion in the size of the scattering elements and then a sharp decrease with a minimum size occurring at the thermodynamically obtained clearing point. In this temperature interval the constant decrease in $\rho_\perp$ suggests that the scattering elements are becoming more spherical as they change in size.

Nematic-Isotropic Transition

Figure 7 is a plot of the perpendicular depolarization factor for *p*-[N-(*p*-methoxybenzylidene)amino]phenyl acetate from 101 °C to 108° C. This material exhibits a nematic-isotropic transition at 104.9 °C. Below 103.6 °C there is a constant $\rho_\perp$ which is very asymmetrical about 90°. From 103.6 °C to 104 °C a region of rapid fluctuations occurs in the scattered intensities, fluctuation region. A constant $\rho_\perp$ exists above 104 °C which is slightly asymmetrical about 90°.

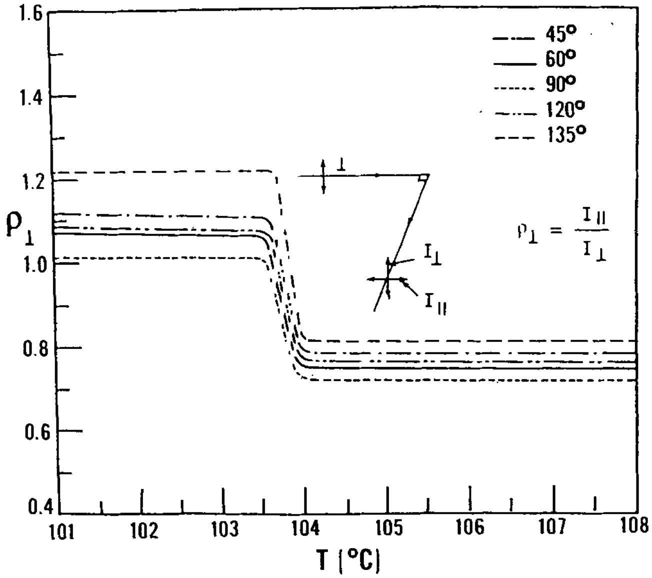

Figure 7. A plot of the perpendicular depolarization factors for *p*-[N-(*p*-methoxybenzylidene)amino]phenyl acetate from 101 °C to 108 °C.

The parallel depolarization factor for this nematic material in the region of 101 °C to 108 °C is shown in Fig. 8. Below 103.6 °C there is a constant parallel depolarization factor except at 45° and 60° where both exhibit slight increases with maximum occurring at 103.6 °C. The fluctuation region occurs from

103.6 °C to 104 °C. A constant $\rho_{\parallel}$, which is very asymmetrical about 90°, exists above 104 °C.

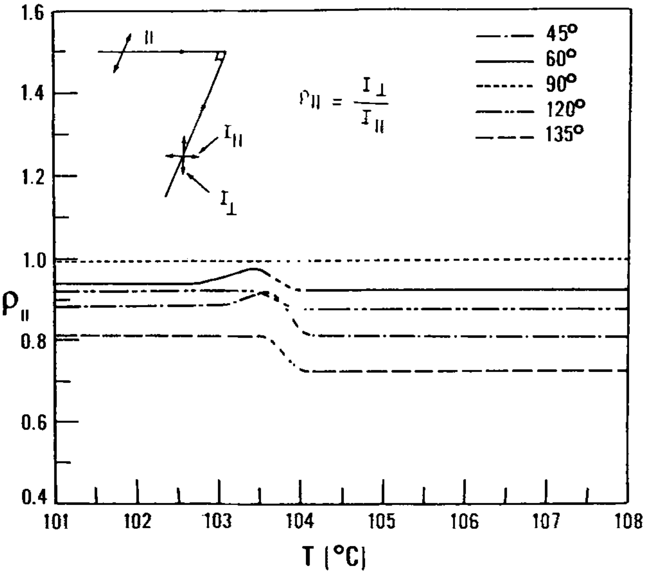

Figure 8. A plot of the parallel depolarization factors for *p*-[N-(*p*-methoxybenzylidene)amino]phenyl acetate from 101 °C to 108 °C.

Figure 9 indicates the region of latent heat absorption for p-[N-(p-methoxybenzylidene)amino]phenyl acetate as measured by a differential scanning calorimeter. Heat is absorbed in the region from 102.5 °C to 104.9 °C. The fluctuation region lies within this temperature range.

The constant values of $\rho_{\perp}$ and $\rho_{\parallel}$ below 102.8 °C indicate that no change occurs in the size and anisotropy of the scattering elements while in the nematic mesophase. The increase in $\rho_{\parallel}$ just below the fluctuation region suggests a slight increase in the size of the scattering elements. This nematic material is different with respect to cholesteryl nonanoate in that the maximum value of $\rho_{\parallel}$ occurs at the beginning of the fluctuation region instead of the middle.

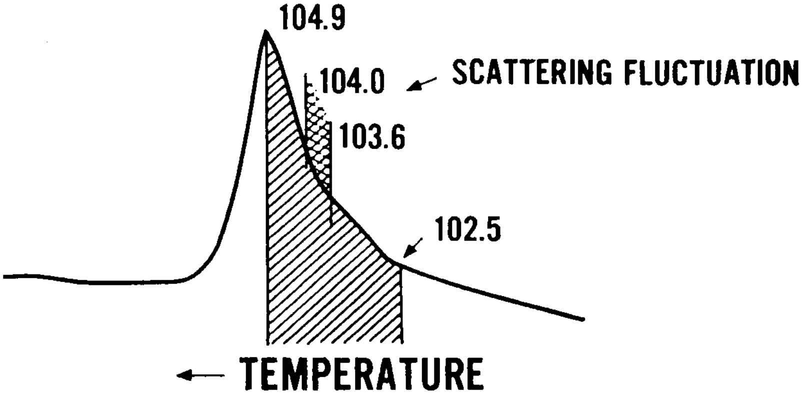

Figure 9. Region of latent heat absorption for the nematic-isotropic transition for *p*-[N-(*p*-methoxybenzylidene)amino]phenyl acetate.

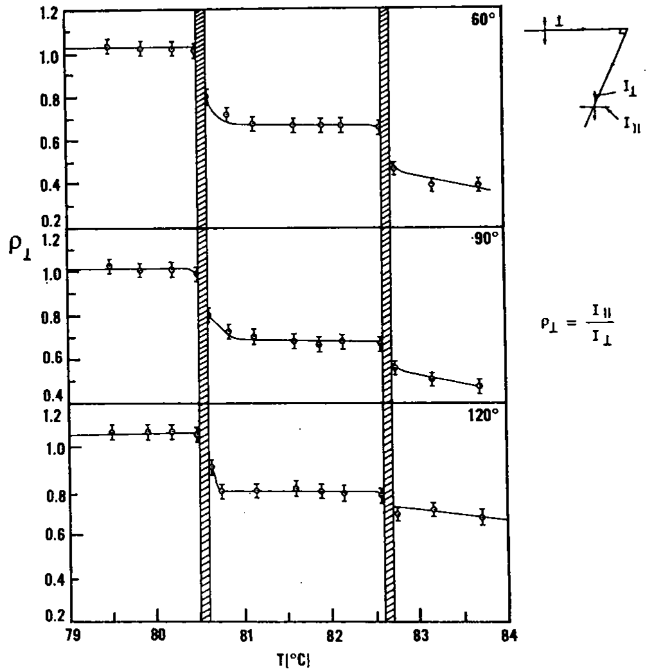

Figure 10. A plot of the perpendicular depolarization factors for cholesteryl tetradecanoate from 79 °C to 84 °C.

Smectic-Cholesteric and Cholesteric-Isotropic Transition

Figure 10 is a plot of the perpendicular depolarization factors for cholesteryl tetradecanoate in the temperature range, 79 °C to 84 °C. This material exhibits a smectic-cholesteric transition at 78.4 °C and a cholesteric-isotropic transition at 83.9 °C. Below 80.5 °C there is a constant $\rho_\perp$ which is slightly asymmetrical about 90°. Two fluctuation regions from 80.5 °C to 80.6 °C and from 82.6 °C to 82.7 °C occur for this material. A decrease in $\rho_\perp$ occurs after each of these scattered fluctuation regions.

Figure 11 indicates the region of latent heat absorption for cholesteryl tetradecanoate as measured by a differential scanning

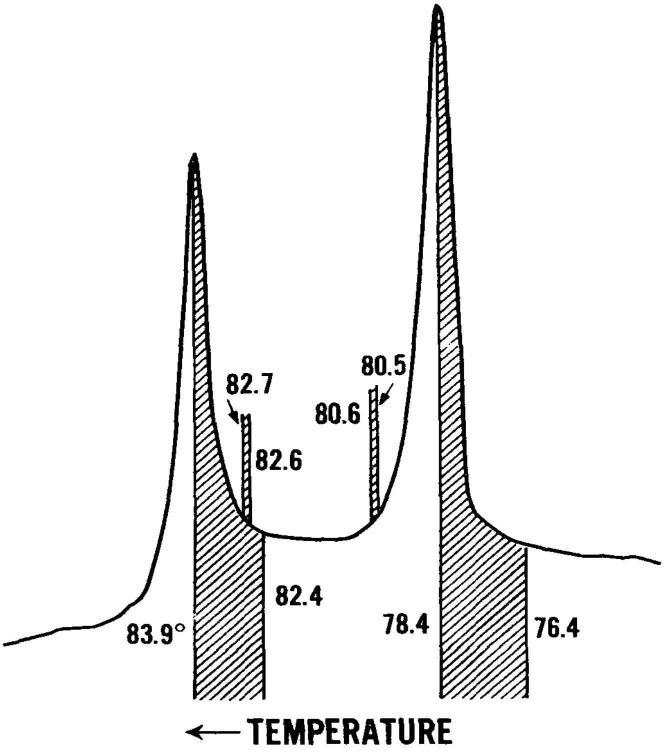

Figure 11. Region of latent heat absorption for the smectic-cholesteric and cholesteric-isotropic transitions for cholesteryl tetradecanoate.

calorimeter. Heat is absorbed for the smectic-cholesteric transition from 76.4 °C to 78.4 °C and for the cholesteric-isotropic transition from 82.4 °C to 83.9 °C. The higher temperature fluctuation region lies within the temperature range for the cholesteric-isotropic transition but the lower temperature fluctuation region is 2.1 °C higher in temperature than the smectic-cholesteric transition temperature.

The perpendicular depolarization factor for cholesteryl tetradecanoate from 75 °C to 86 °C is shown in Fig. 12. In the smectic mesophase a constant $\rho_\perp$ occurs which is slightly asymmetrical about 90°. The cholesteric mesophase has two sudden decreases in $\rho_\perp$, one at 80.5 °C and the other at 82.6 °C. Between these two temperatures the perpendicular depolarization factor is a constant. In the isotropic liquid state there is a slow decrease in $\rho_\perp$ with temperature.

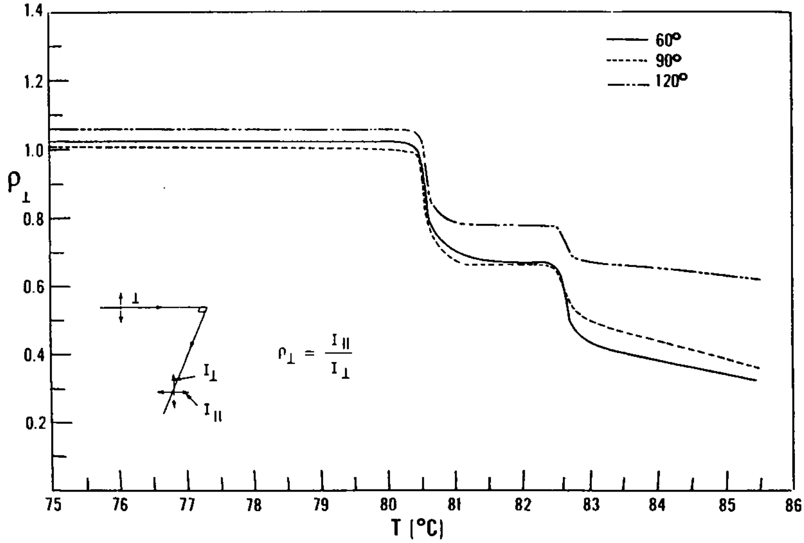

Figure 12. A plot of the perpendicular depolarization factors for cholesteryl tetradecanoate from 75 °C to 86 °C.

Figure 13 shows the parallel depolarization factor for cholesteryl tetradecanoate in the range from 75 °C to 86 °C. The smectic mesophase exhibits a constant $\rho_{\perp}$. In the cholesteric mesophase there is a sudden increase at 80.6 °C and a sudden decrease at 82.7 °C. For $\rho_{\parallel}$ two fluctuation regions occur from 80.5 °C to 80.6 °C and from 82.6 °C to 82.7 °C. There is a constant parallel depolarization factor in the isotropic liquid.

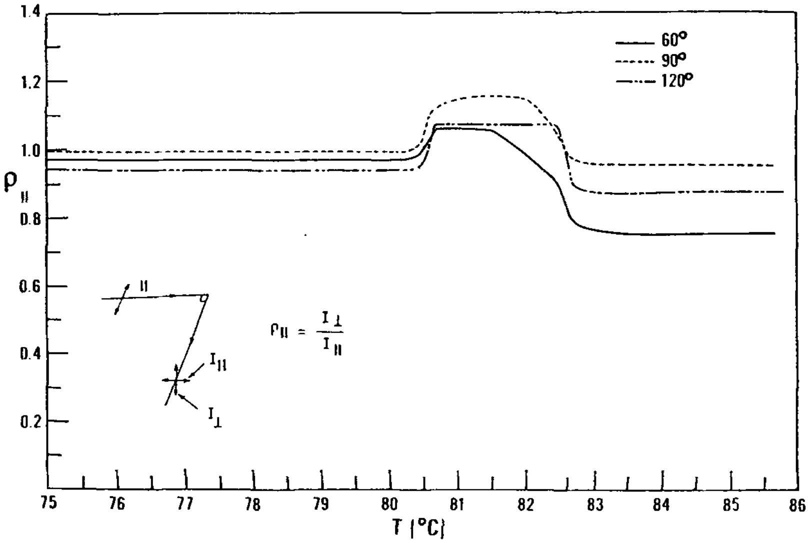

Figure 13. A plot of the parallel depolarization factors for cholesteryl tetradecanoate from 75 °C to 86 °C.

Constant values of $\rho_{\perp}$ and $\rho_{\parallel}$ below 78.4 °C indicate that there is no change in the size and anisotropy of the scattering element while in the smectic mesophase. The occurrence of a scattered fluctuation region with a sharp change in both depolarization factors 2.1 °C above the smectic-cholesteric transition is difficult to understand. The increase in $\rho_{\parallel}$ above 80.6 °C indicates an increase in the size of the scattering elements for the cholesteric mesophase. The second scattered fluctuation region which corresponds to the cholesteric-isotropic transition is similar to that for cholesteryl nonanoate.

Temperature and Thermal Equilibrium

In any experiment involving bulk mesomorphic materials the question of thermal equilibrium must be considered. A differential thermocouple with one side placed against the quartz thermometer and the other in the center of the mesomorphic material was used. Figure 14 is a plot of the differential temperature between the two legs of the thermocouple as a function of time for a rapid temperature change of five degrees. The point at which the quartz thermometer maintained a stable reading is indicated for both heating and cooling. From these data a period of ten minutes must elapse after the quartz thermometer is stable before temperature equilibrium in the material is obtained.

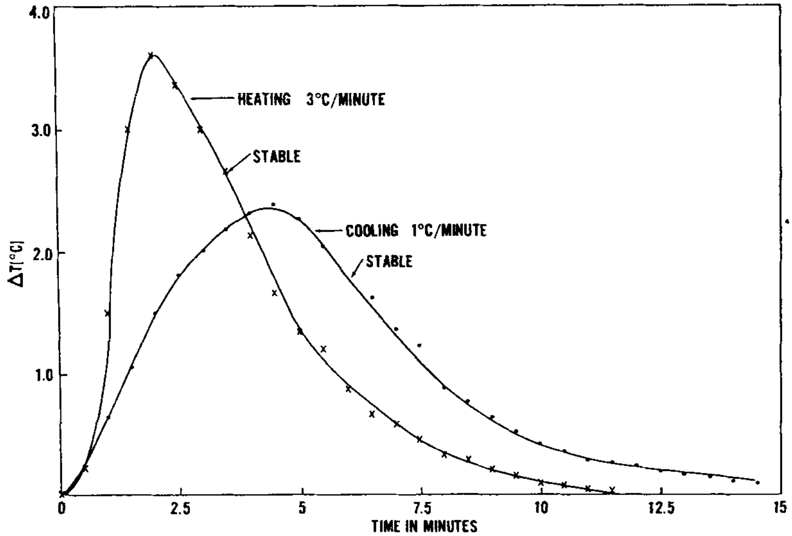

Figure 14. A plot of the differential temperature between the quartz thermometer and the center of the cell as a function of time.

In order to determine thermal equilibrium a five degree change was made across the transition region. After a period of fifteen minutes the perpendicular depolarization factor at 90° was recorded as a function of time. As expected, since we are going from an ordered to a less ordered state, no change in the depolarization factor is observed on heating. Figure 15 is a plot of $\rho_\perp$ as a function of time for cooling. For the nematic material no change was observed. However, for cholesteryl nonanoate and cholesteryl tetradecanoate over an hour elapsed before thermal equilibrium was maintained. Clearly temperature and thermal equilibrium are quite different for rapid cooling of large samples of mesomorphic materials.

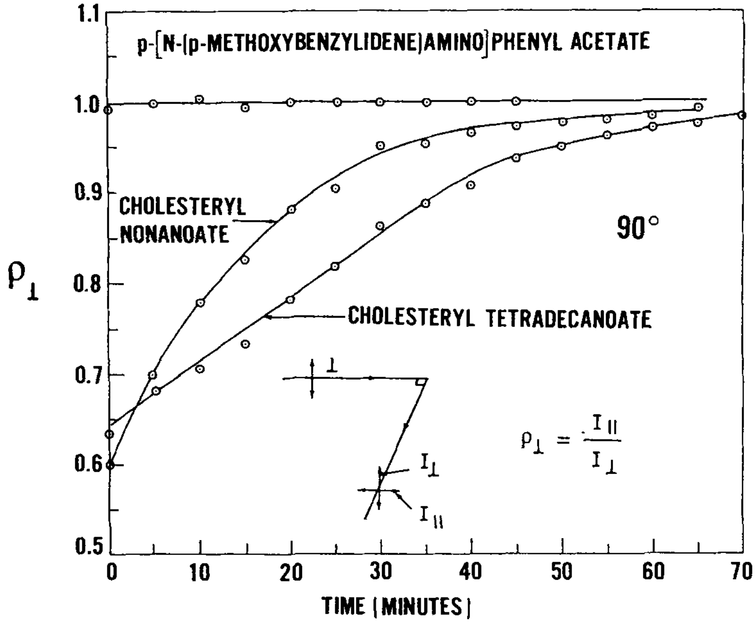

Figure 15. A plot of the perpendicular depolarization factors at 90° as a function of time on rapid cooling.

General Consideration

In general we find fairly constant values of the depolarization factors except in a temperature region near a meso-mesophase or clearing point transition. In this region very rapid changes in the depolarization factors occur. These changes indicate an alteration in size and anisotropy of scattering elements.

The data exhibit three pretransitional and one post-transitional fluctuation region. The width of these fluctuation regions indicates a temperature range in which variations of the molecular arrangement take place. That is, rapid changes occur either in the type of the scattering elements, or in the order within the scattering elements, or a combination of both.

According to the theory of Frenkel[7] pretransitional effects for a thermodynamically stable system are to be expected in cases where the heat of transition is small, which is the case for a meso-mesophase or clearing point transition. As the temperature of the transition is approached, Frenkel postulates large fluctuations, heterophase fluctuations, which are caused by the occurrence, change, and disappearance of small elements associated with the higher temperature phase, i.e., a change in the type of region. This phenonemon has the effect of producing pretransitional variations in all physical properties which differ in the two phases. Hoyer and Nolle[8] have reported pretransitional effects, which seem to be consistent with the theory of heterophase fluctuations, for ultrasonic-wave absorption and density measurements for anisotropic-isotropic transitions. Barrall, Porter, and Johnson[9] have observed similar effects in specific heat data for nematic-isotropic transitions. However, the existence of these heterophase fluctuations in a thermodynamically stable system has not been experimentally determined. Therefore, additional data similar to that reported in this paper and more direct data permitting a quantative test of heterophase fluctuation theory are required before this theory can be adequately applied to these experimental data.

Since a post-transitional phenonemon about 2 °C above the transition temperature can only be treated as a change within an ordered element, Frenkel's theory cannot be applied to the fluctuation region associated with the smectic-cholesteric transition of cholesteryl-tetradecanoate. Possibly a theoretical treatment which considers density or orientation fluctuations within an ordered element can be used to describe this phenonemon. However, additional experimental evidence on post-transitional effects is required before this can be realized.

Thin layer chromatograms of cholesteryl nonanoate and cholesteryl tetradecanoate exhibit only one spot, thus indicating a high purity. The nematic material used is estimated to be 96% pure. Even though Pohlmann and Elser[10] have pointed out the possibility of impurities of close homologues for one spot thin layer chromatograms, it is extremely unlikely that the width of the fluctuation region is an impurity effect. However, this is presently being investigated by repeating the data for extremely pure *p*-[N-(*p*-methoxybenzylidene)amino]phenyl acetate.

It is difficult to estimate if the relatively large values of the depolarization factors above the clearing point are due to molecular scattering or some type of long range cooperative effect.

From these data it is obvious that the measurement of the depolarization factor is a very sensitive measure of internal changes in mesomorphic materials. However, more experimental data must be obtained before any adequate explanation of these phenomenon can be realized. This work is presently in progress and will be reported at a later date.

Acknowledgments

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