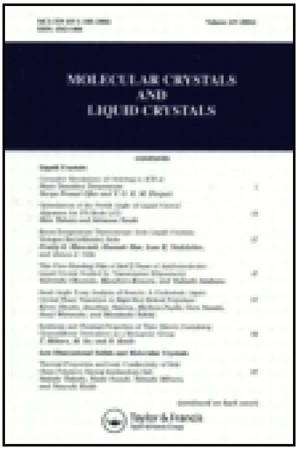

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The Temperature Sensitivity of the Selective Reflection by Cholesteric Mesophases and Its Possible Limitations

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The Temperature Sensitivity of the Selective Reflection by Cholesteric Mesophases and Its Possible Limitations

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The selective reflectance of S-cholesteryl 14-phenyltetradecanethioate was determined as a function of the wavelength and temperature at several constant values of temperature and wavelength respectively. The dependence of wavelength λ_p measured at maximum selective reflectance on temperature T could be curve fitted within the measurement uncertanty of ± 0.2 m°C to Keating's formula and to the empirical expression $\lambda_p = \lambda_0 + A(T - T_0)^{-2}$. Since T_0 is the temperature at which the cholesteric helix assumes an infinite pitch, we conclude that the region of extremely high temperature dependence of the selective reflectance of a cholesteric liquid crystal may be linked with a pretransitional effect at the cholesteric-smectic phase transition. We measured a maximum temperature coefficient of selective reflectance of about 50,000% per °C and found that the spontaneous temperature fluctuations of the sample must be smaller than 2×10^{-5} °C. A theoretical estimate, using the generalized Nyquist theorem, indicates that for a bandwidth of 1 Hz (centered at about 1 Hz) the spontaneous temperature fluctuations caused by the statistical nature of the heat transfer between sample and environment cannot be smaller than 10^{-8} °C.

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In a previous paper[1] we reported on the temperature sensitivity of the selective reflection exhibited in cholesteryl oleyl carbonate, cholesteryl nonanoate, a 1:1 mixture of cholesteryl oleyl and erucyl carbonate, and cholesteryl erucyl carbonate (containing 5% of cholesteryl chloride to stabilize the plane texture). In this paper we extend this investigation to one of the most temperature-sensitive materials which we have found among the 14 homologous series prepared by our group. The material, S-cholesteryl 14-phenyltetradecanethioate, is the first even member of its homologous series which selectively reflects the full visible spectrum. We attempt to determine the functional relationship between wavelength at peak intensity of the selectively reflected light and temperature. The results should yield useful information pertaining to the pretransitional unwinding of the helical plane texture (described by Alben's theory[2]) as the material passes from the cholesteric phase and its selective reflection region to the smectic phase. In addition we estimate possible limitations of the temperature sensitivity of the selective reflectance prescribed by the statistical temperature fluctuations due to heat transport and by the proximity of the cholesteric-smectic phase transition.

EXPERIMENTAL APPROACH

We used essentially the same experimental set-up described earlier,[1] that is, a metallurgical microscope equipped with a grating monochromator to provide monochromatic illumination and a photomultiplier radiometer to measure the relative intensity of the selectively reflected light. A movable deflector in the microscope provided the option to either view the sample or to measure the light intensity. This feature enabled us to ascertain that the sample texture was properly aligned and uniform and that the texture did not change during the measurements.

Since we knew that small temperature fluctations in this sensitive liquid crystal would produce large intensity variations or wavelength shifts, we did not

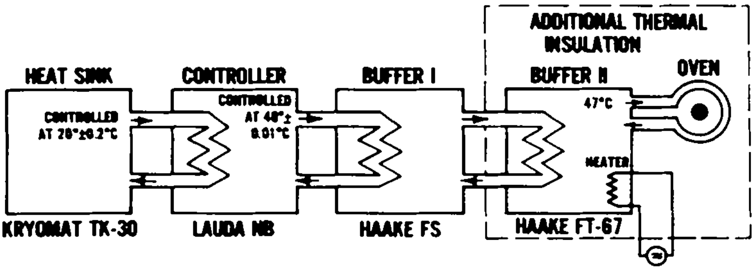

FIGURE 1 Schematics of temperature drift device.

attempt to control the sample temperature directly by a feedback mechanism. Instead we conducted our mesurements on samples undergoing slow, unidirectional temperature drifts. The experimental set-up consisted of a series connection of four circulators and a special oven. The flow diagram in Figure 1 shows that each circulator pumps its water through the heat exchanger of the next one and that the last one feeds its water through the hollow brass walls of the cylinderical sample oven. The first circulator serves as a heat sink for the second one, which is controlled to 40°C within less than ± 10 m°C. A constant electrical power applied to the heater of the last circulator (i.e. buffer II) establishes the operating temperature of 47°C. Since the heat flow from this insulated buffer to the heat sink is large as compared to the heat loss of the entire set-up, the small variations of the environmental temperature did not noticeably affect the sample temperature. Furthermore, the complicated thermal RC network comprised of the resistances and capacities, associated with the two buffer circulators and the oven (see Figure 2), operated as an efficient filter. It attenuated the control oscillations inserted by the second circulator (i.e. the controller) to a level not detectable in the sample. Once the system was in stationary thermal equilibrium, a defined drift of the sample temperature could be introduced by lowering the temperature of the controller by about 0.2°C. This change caused unidirectional drifts of 2 to 5 m°C per minute for up to 15 min. All measurements were conducted during this drift period.

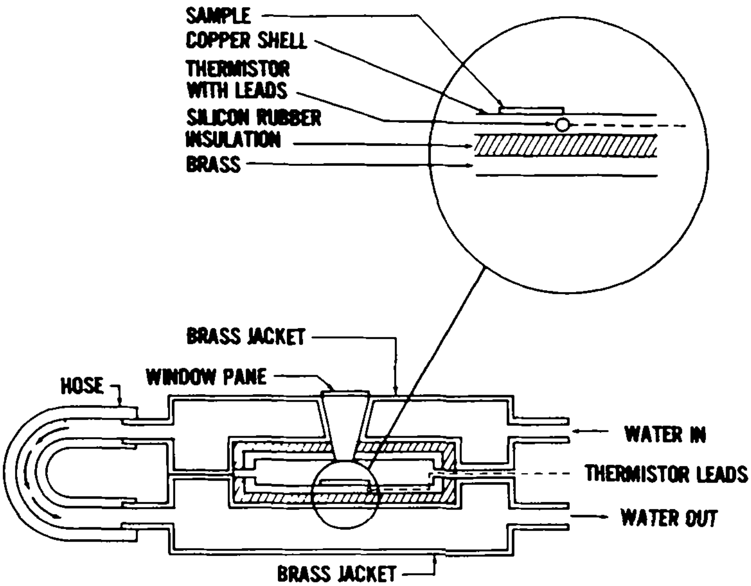

FIGURE 2 Cross section of sample oven.

The sample was isothermally enclosed by two copper shells thermally coupled to the interior of the oven wall by a thin layer of silicon rubber, as indicated in Figure 2. The upper shell contained a small hole for the admission of light. A window pane mounted in the brass jacket reduced the exchange of heat along the light path to a negligible amount.

The sample temperature was measured by a thermistor attached to the inner side of the copper shell. To avoid voltage drifts typical for dc operation, the thermistor was connected to an ac bridge. As shown in Figure 3, the amplified and rectified output voltage of this bridge drove the *x*-channel of the intensity versus temperature plotter. This voltage depended linearily on the temperature difference causing the bridge unbalance, because the associated change of the thermistor resistance was smaller than 1%. The electronics limited the uncertainty of the relative temperature measurement to ± 0.2 m°C. However, the bridge could only be balanced within ± 0.1 Ω or ± 3 m°C and the absolute temperature uncertainty due to the instability of the thermistor (caused by thermal history, aging, etc.) amounted to roughly ± 0.5°C.

In order to obtain reproducible samples of high uniformity and selective reflectance, material of better than 99% purity[3] was melted and carefully sandwiched between clean, degreased glass slides. Both the uniformity of the plane texture and the intensity of the selective reflectance were optimized by shearing and squeezing the liquid crystalline film between the slides. We observed the typical mosaic of uniform plane texture domains varying in lateral dimensions between 10 to 50 μm and differing in their hue. We infer from the angular dependence of the selective reflection[4] that these domains are plane

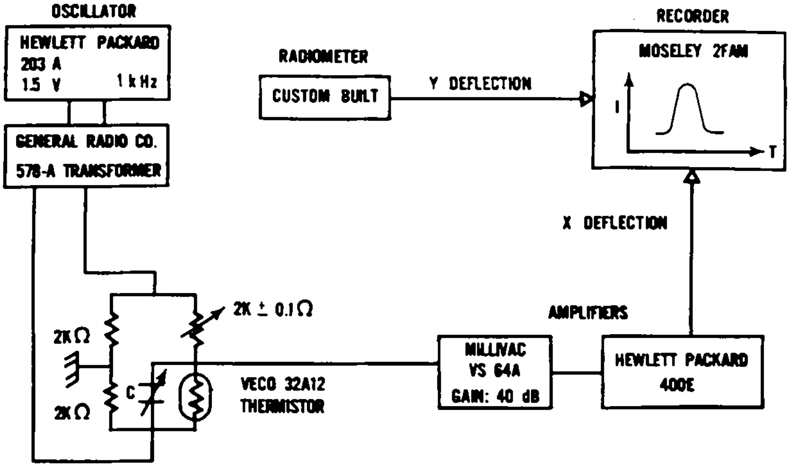

FIGURE 3 Schematics of experimental set-up.

texture regions varying slightly in the angular orientation of their helical axes. A comparison of data measured on different samples (e.g. see Figure 9) indicates that these differences in sample appearance are negligible in the context of our investigation. The best results were achieved with sample thicknesses between 10 and 20 μm. For reasons discussed elsewhere[1] we did not attempt to determine the selective reflectivity and thus did not need to measure the thicknesses.† We painted a black dot on the outside of the glass-liquid crystal sandwich and placed it with its painted side on the lower copper shell of the oven. The black spot absorbed the transmitted light to such a degree that only a negligible part returned to the microscope. A thin layer of excess liquid crystal provided a good thermal contact between the sample and the lower copper shell of the oven. Possible effects of thermal history were annealed out by heating the sample beyond the clearing point and subsequently cooling it slowly through the region of selective reflection. To save time the cooling rate was initially kept at approximately 1°C per min and from about 2°C above the selective reflection region was gradually reduced to a value between 2 and 5 m°C per min. The latter drift rate was slow enough to permit accurate recording of temperature and light intensity.

EXPERIMENTAL RESULTS

The measurements were taken under the following conditions:

1.) Crossed polarizers (to reduce the effect of specular reflection);

2.) Circular spot of 0.5 mm^2 on the sample illuminated by a 2 degree cone of light at normal incidence;

3.) Relative intensity of reflected light measured within a 17 degree cone normal to the sample surface;

4.) Spectral halfwidth of illumination adjusted to 16Å;

5.) Intensity data corrected for spectral response of experimental set-up;

6.) Cooling of sample from above the clearing point and measurements conducted at cooling rates between 2 and 5 m°C per minute.

Intensity vs. wavelength at constant temperature

The results shown in Figure 4 were obtained by increasing the wavelength in steps of 50 Å and by recording both the associated intensity change and the

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†Theoretical work[5] indicates that the selective reflectivity approaches unity with increasing thickness.

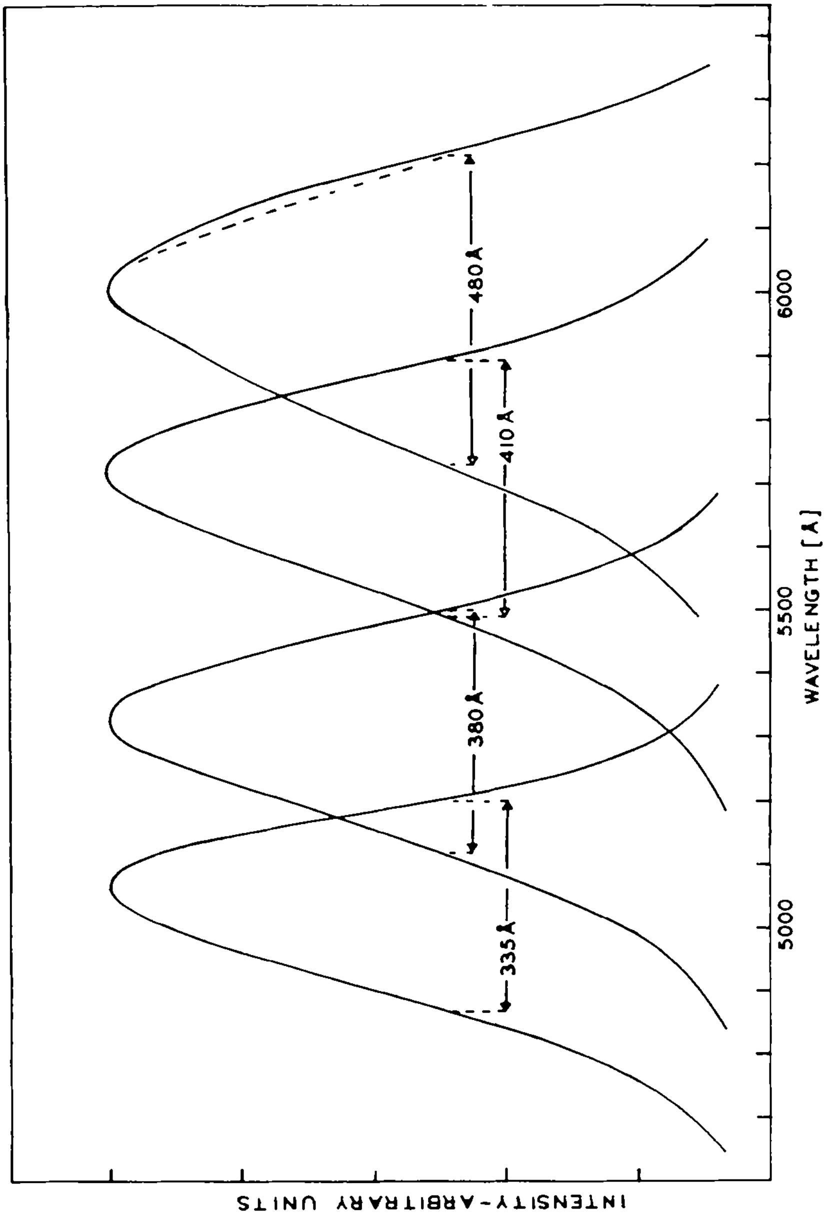

FIGURE 4 Normalized intensity of selectively reflected light at constant temperatures as a function of wavelength.

temperature decrease due to the drift. For each measurement we determined the temperature difference in respect to a conveniently chosen data point. Using the wavelength shift per °C of the peak reflectance derived from a separate experiment (see Figure 10), we corrected each wavelength for the respective temperature variation. This procedure resulted in a spectral response curve for a temperature varying by less than 0.5 m°C. The spectral response curve peaking at 6000Å bulges outwards on the high wavelength side. The maximum of the difference between the extrapolated curve (dashed line) and the actual one has a maximum value of about 25 Å. This discrepancy may be caused by a temperature variation of about 0.4 m°C, since according to Figure 10 this response curve shifts at the rate of 68000 Å per °C.

The relation between halfwidth $\Delta\lambda_H$ and peak wavelength λ_p of the response curve is of theoretical significance. Based on de Vries' theory Leder and co-workers[6] obtained

$$\frac{\Delta\lambda_H}{\lambda_p} = 2\,\frac{n_2 - n_1}{n_2 + n_1}\,k = \alpha k$$

where n_1 and n_2 are the principal indices of refraction and k is a parameter having an average value of 1.33 for α-values between 0.01 to 0.1†. According to this reference the latter condition should be generally fulfilled by cholesteric liquid crystals (see also Ref. 7). Assuming negligible dispersion, we expect $\frac{\Delta\lambda_H}{\lambda_p}$ to be independent of the peak wavelength λ_p. However, the results of our previous and present work, summarized in Table I, show that only S-cholesteryl 14-phenyltetradecanethioate exhibits the expected relationship within the uncertainty of the measurement (i.e. ± 10% due to the temperature uncertainty of ± 0.5 m°C). The substantial increase of $\frac{\Delta\lambda_H}{\lambda_p}$ with wavelength λ_p observed with the other materials may be caused by the angular dependence of the selective reflection,[4] because these measurements were conducted with an illumination having a seven times larger angle of convergence.[1] Nevertheless, for cholesteryl oleyl carbonate the measured data agree reasonably well with the result derived from Eq. (1) and the published α-value.[7]

Intensity vs. temperature at constant wavelength

In order to prevent the modulation of the recorded light intensity by temperature fronts running across the sample, changes of alignment and textures and

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†Theoretical results shown in Figure 1 of Ref. 5 indicate the $\Delta\lambda_H$ does not vary much with sample thickness for thicknesses between 10 and 20 μm.

TABLE I

	$\frac{\Delta\lambda_H}{\lambda_p}$	λ_p [Å]	Ref.
cholesteryl nonanoate	0.069	4654	(1)
	0.071	5055	(1)
	0.077	5385	(1)
	0.111	5940	(1)
	0.095	3300	(6)
cholesteryl oleyl carbonate	0.020	4236	(1)
	0.023	4736	(1)
	0.027	5078	(1)
	0.045	5542	(1)
	0.014	3300	(6)
calculated, using $\frac{2\Delta n}{n} = 0.03$	0.02		(7)
cholesteryl erucyl carbonate + 5% cholesteryl chloride	0.034	4038	(1)
	0.030	4596	(1)
	0.033	5000	(1)
	0.048	5250	(1)
S-cholesteryl 14-phenyl-tetradecanethioate	0.066	5060	
	0.071	5350	
	0.072	5725	
	0.080	6000	

similar effects which could mask the basic properties of the selective reflection, these experiments had to be performed with great care. The sample was visually inspected during a separate test run and before and after the actual measurements. In addition the shape of the recorded intensity versus temperature curve was critically assessed. Figure 5 shows a typical trace of an acceptable test run. The smoothness and the high degree of symmetry of the curve indicate that the sample was uniformly heated and that it did not change texture and alignment during the test.† Notice that the half-width amounts to only 7.6 m°C. This is about one third of the smallest value reported so far.[1] Figure 6 depicts the relative intensity change per °C derived from the curve of Figure 5, and Figures 7 and 8 show the results for the wavelengths 4200 Å and 6000 Å respectively. The maximum value of about 50000% per °C may be the largest temperature coefficient

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†Once the experimental procedure was established, most of the test runs were acceptable.

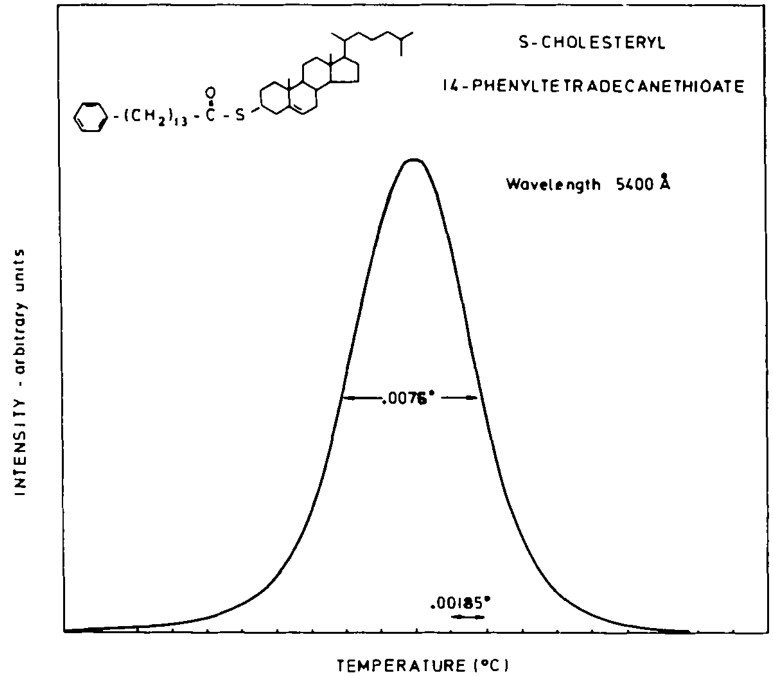

FIGURE 5 Intensity of selectively reflected light at 5400Å as a function of temperature as plotted by X Y recorder.

reported for an optical quantity. Since a value of 40000% per °C occurs at about one third of full scale of the intensity curve for λ_p = 5400 Å (e.g. see dotted line of Figure 6) and since the uncertainty of the intensity recording is ± 0.25% of full scale, we obtain a minimum detectable intensity variation of 0.75%; which corresponds to a temperature variation than 2×10^{-5} °C. In the appendix we estimate the temperature fluctuation of the sample caused by the statistical nature of the heat exchange between sample and its surroundings. Considering frequency (about 1 Hz) and bandwidth (about 1 Hz) of the recording channel, we obtain a minimum rms temperature fluctuation of about 10^{-8} °C. This value is 3 orders of magnitude below the limit of our measurements. Unless other fluctations are active, 10^{-8} °C per square root Hz constitutes the ultimate temperature resolution of a cholesteric liquid crystal.

Peak wavelength λ_p versus temperature

We used essentially the same measurement procedures described in the last sections. During the slow temperature decrease we always "advanced" the wave-

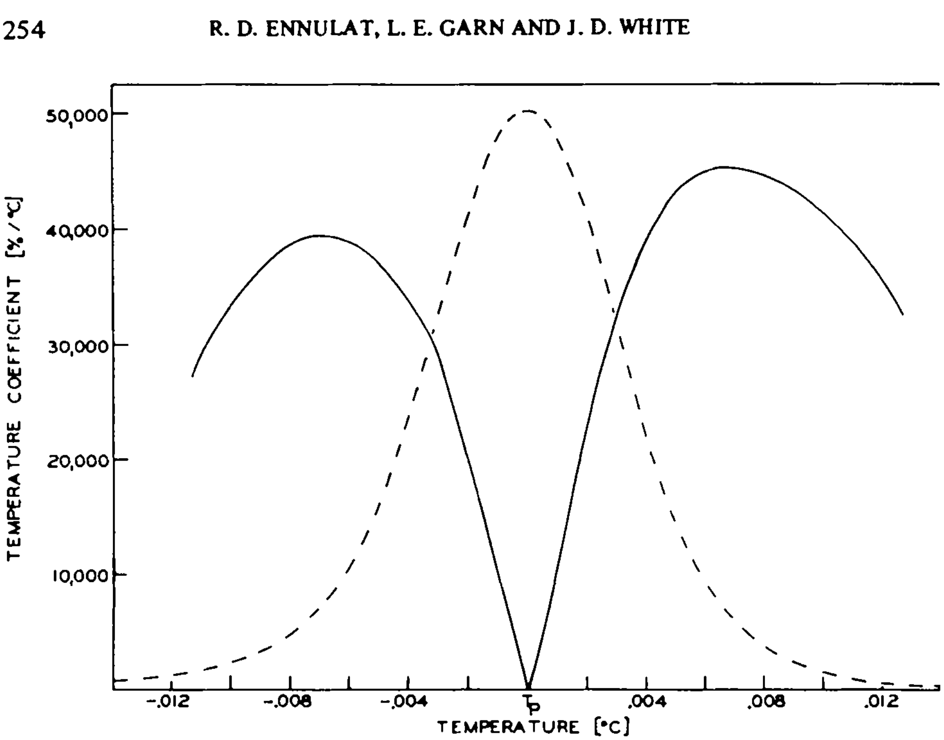

FIGURE 6 Intensity of selectively reflected light versus temperature (dashed line) and temperature coefficient of selective reflection versus temperature (solid line) for 5400Å illumination.

length in steps of about 200 Å, recorded the intensity peak of the respective wavelength and its nearest vicinity, and then increased the wavelength again. Thus we were able to determine the temperature of up to 14 intensity peaks during one cooling run. In order to use the full benefit of the relative uncertainty of ± 0.2 m°C, we balanced the bridge only at the beginning of the test run, then deliberately unbalanced it by 2 Ω which correspond to a minus 64 m°C unbalance for our thermistor. Thus the unbalance decreased as the temperature drifted through the selective reflection region. The temperatures at the intensity peaks were obtained by linear extrapolation. The results of test runs measured on the same sample during different days deviated by constant amounts. This was possibly caused by effects of thermal history on the thermistor and by variations of the contact resistance of the switches in the ac bridge. This is not surprising since a resistance change of only 0.01 Ω corresponds to a temperature change of 0.25 m°C. Figure 9 shows the results of four test runs. Two of these were taken with the same sample on the same day, while the other ones represent different samples measured several days apart. Notice that for any given peak wavelength the associated temperatures do not differ by more than 3 m°C. This agrees well with the uncertainty estimated for the balanced bridge. Figure 10 depicts the shift $\Delta\lambda$ of the peak wavelength per °C. The maximum value of 100,000 Å was obtained for the longest wavelength of 7,000 Å.

Determination of the relation $\lambda_p(T)$

In order to exploit the low relative uncertainty of individual test runs, a curve fit was made for each one of the associated data sets. We selected the reference functions used in the regression analysis (least square fit) for the following reasons:

$$\lambda_p = \frac{A}{T-T_o}$$

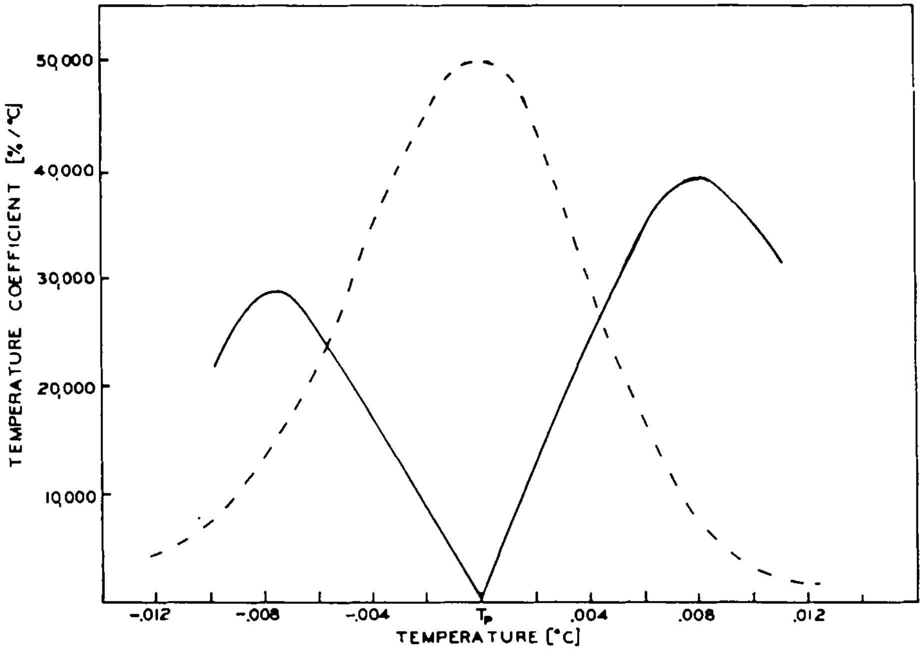

FIGURE 7 Intensity of selectively reflected light versus temperature (dashed line) and temperature coefficient of selective reflection versus temperature (solid line) for 4200Å illumination.

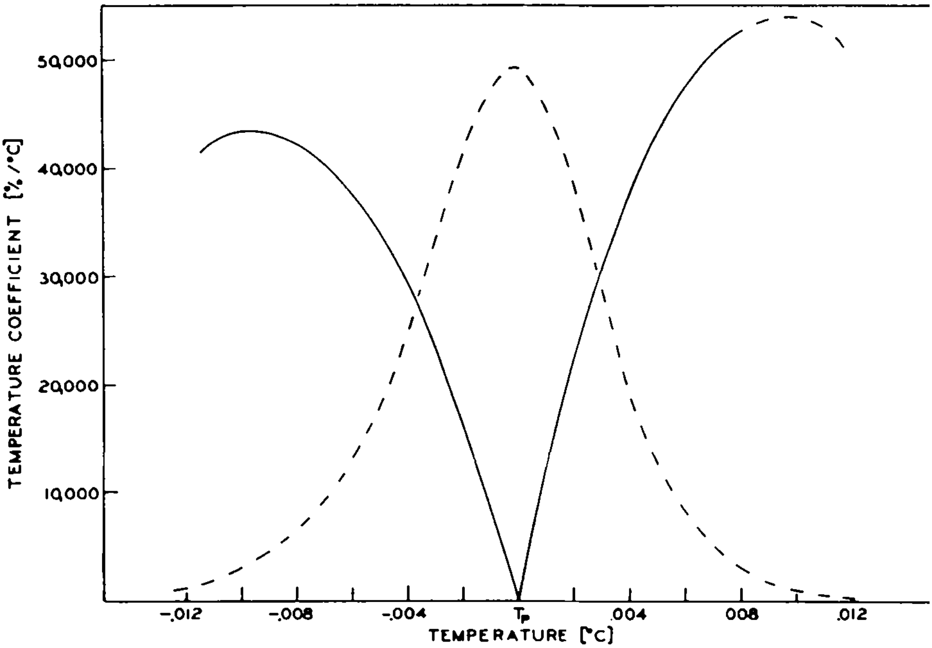

FIGURE 8 Intensity of selectively reflected light versus temperature (dashed line) and temperature coefficient of selective reflection versus temperature (solid Line) for 6000Å illumination.

In the past[1] we favored this function because of the appearance of the experimental curve and because of the analogy to the Curie-Weiss law describing the pretransitional behavior of ferroelectric and ferromagnetic materials.

$$\lambda_p = \frac{A}{T - T_0} + \frac{A}{T - T_1}$$

Since one hyperbola would fit well only the steep or the flat part of the experimental curve, we used two hyperbolas shifted against each other by an amount $T_0 - T_1$. We argued[1] that this modification would allow for the slight angular deviation of the domain orientations from the sample normal and for the convergence of the incident light. This reasoning is supported by the angular de pendance of the peak wavelength.[4]

$$\lambda_p = \frac{A}{T}\left(1 + \frac{B}{T - T_0}\right)^2$$

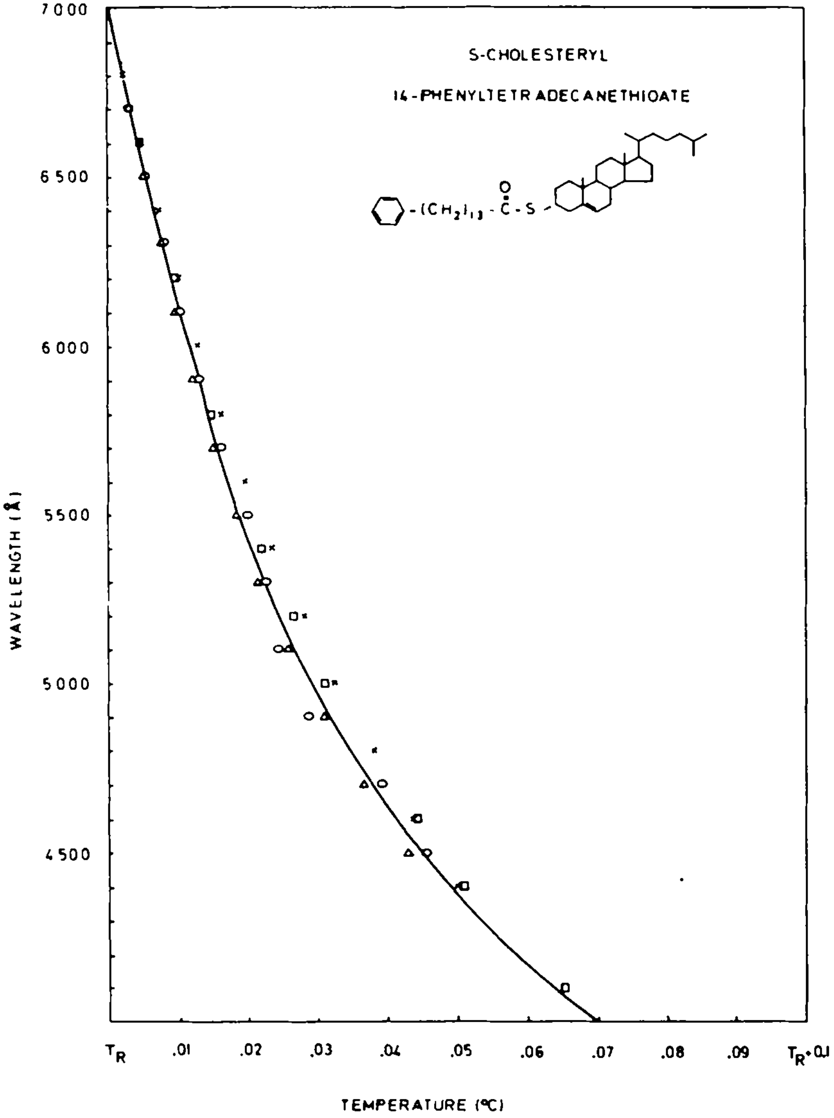

FIGURE 9 Wavelength λ_p of maximum selective reflection as a function of temperature.
X = Data set I
□ = Data set II–measured same day on same sample as data set I.
△ = Data set III–second sample cooled at 2m°C/min–measured 8 days after data set I.
○ / Data set IV–third sample cooled at 5m°C/min–measuered 9 days after data set I.

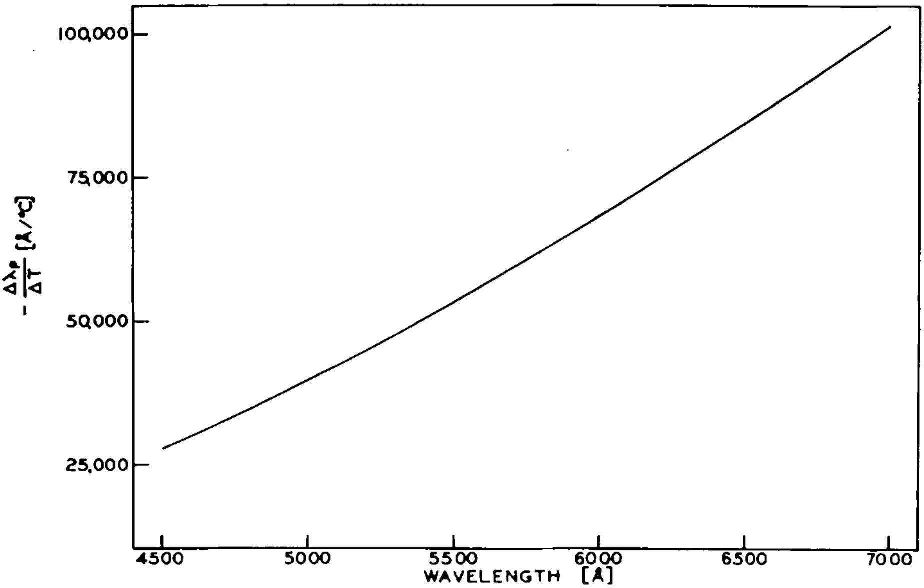

FIGURE 10 Wavelength dependence of slope $\frac{\Delta\lambda_p}{\Delta T}$ of function shown in Figure 9.

This function is the result of Keating's theory[8] relating the spontaneous twist of cholesteric mesophases with the anharmonicity of thermally generated molecular rotations.

$$\lambda_p = \lambda_0 + \frac{A}{(T - T_0)^2}$$

Since this relation yields larger λ_p values for small differences of $T-T_0$ than the hyperbolic functions, we should expect a better fit for both the steep and the flat part of the experimental curve. Kahn[7] reports satisfactory agreement of his results with a similar function (see also Ref. 2).

Table 2 lists the standard errors of estimate between each reference funtion and the data sets obtained from the four test runs (see Figure 9). These results indicate that the hyperbolic reference functions are not acceptable and that the other functions represent the experimental results within the measurement uncertainty of ± 0.2 m°C. The latter should not be surprising, since an expansion of Keating's formula contains the term $\frac{B^2}{(T-T_0)^2}$, which is predominantly determining the temperature dependence of the peak wavelength. This argument is supported by the fact that the parameters T_0 of both reference functions in

TABLE 2

Best Fit of $\lambda_p\ (T)$

S-Cholesteryl 14-phenyltetradecanethioate

Data set	^{a} Standard error of estimate [Millidegrees] (m°) I	 II	 III	 IV
Equation:				
$\lambda_p = \frac{A}{T - T_0}$	0.6	2.3	1.1	0.8
$\lambda_p = \frac{A}{T - T_0} + \frac{A}{T - T_1}$	0.4	1.9	0.9	0.6
$\lambda_p = \frac{A}{T}\ 1 + \frac{B}{T - T_0})^2$	0.2	0.3	0.2	0.1
$\lambda_p = \lambda_0 + \frac{A}{(T - T_0)^2}$	0.2	0.4	0.2	0.2

^{a} SEE $= \sqrt{\frac{\Sigma (T_{\text{exp}} - T_{\text{calc}})^2}{N}}$

Table 3 agree within 0.01% regardless of test run. Thus we have to conclude that both functions are equivalent in respect to closeness of fit and with respect to the characteristic temperature T_0.

TABLE 3

Parameters of successful curve fits $\lambda_p\ (T)$

		Data set I	 II	 III	 IV
$\lambda_p = \frac{A}{T}\left(1 + \frac{B}{(T - T_0)}\right)^2$	T_0 [°K]	320.070	320.093	320.097	320.085
	A [Å °K]	479319	699985	693706	607294
	B [°K]	0.0930	0.0455	0.0422	0.0601
$\lambda_p = \lambda_0 + \frac{A}{(T - T_0)^2}$	T_0 [°K]	320.048	320.071	320.080	320.065
	λ_0 [Å]	2287.5	2863.4	2933.5	2695.5
	A [Å °K^2]	48.903	26.112	19.970	30.889

DISCUSSION

The Limitation of the temperature coefficient of the selective reflectance

Previous work[1, 7, 9, 10, 11, 12] and our experimental results indicate that the selectively reflected light intensity is a well behaved function of temperature and wavelength, and that both the temperature coefficient of the selective reflectance and the peak wavelength increase steadily with decreasing temperature. Therefore, we can derive an empirical relationship between the maximum temperature coefficient of the selective reflectance and the proximity of the operating point to the cholesteric-smectic phase transition.

If we vary the wavelength λ_1 by $\Delta\lambda$ and the temperature T_1 by ΔT so that the intensity change due to the first variation is equal and opposite to that due to the second variation, we obtain

$$\left.\frac{\Delta I}{\Delta T}\right|_{\lambda_1} = -\left.\frac{\Delta I}{\Delta\lambda}\right|_{T_1} \left.\frac{\Delta\lambda_p}{\Delta T}\right|_{I} \tag{2}$$

Since the maximum slope $\frac{\Delta I}{\Delta\lambda}$ occurs at about half the peak intensity I_p (see Figure 4 and Ref. 1), we approximate it according to Figure 11

$$\frac{\Delta I}{\Delta\lambda} \approx 2\frac{\Delta I_1}{\Delta\lambda_H} \approx \frac{I_p}{\Delta\lambda_H} \tag{3}$$

Applying Eq. (1) and considering that the temperature coefficient $C(I)$ at intensity I is the relative intensity change $\frac{\Delta I}{I}$ per °C, we can write

$$C\left(\frac{I_p}{2}\right) = \left.\frac{1}{I}\frac{\Delta I}{\Delta T}\right|_{\frac{I_p}{2}} = \frac{2}{I_p}\frac{\Delta I}{\Delta T} = \frac{2}{\alpha k\lambda_p}\frac{\Delta\lambda}{\Delta T} \tag{4}$$

Since the wavelength λ at $I_p/2$ is approximately

$$\lambda \approx \lambda_p \pm \frac{\Delta\lambda_H}{2}$$

we obtain by using Eq. (1) and the curve fit $\lambda_p = \lambda_0 + \dfrac{A}{(T_p - T_0)^2}$

$$\lambda = \left(1 \pm \frac{\alpha k}{2}\right)\left(\lambda_0 + \frac{A}{(T_p - T_0)^2}\right)$$

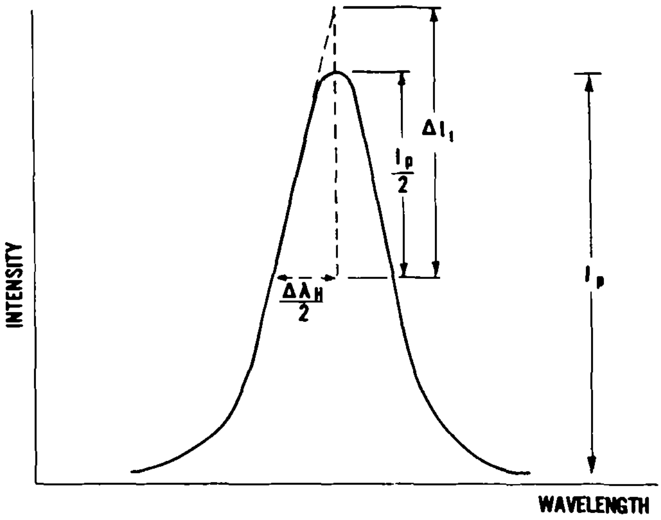

FIGURE 11 Approximation of slope $\frac{\Delta I}{\Delta\lambda}$.

and thus

$$\frac{\Delta\lambda}{\Delta T} = -2\left(1 \pm \frac{\alpha k}{2}\right)\frac{\lambda_p - \lambda_0}{T_p - T_0}$$

and because $\alpha k \ll 2$ (see Refs. 6, 7 and Table 1)

$$\left|\frac{\Delta\lambda}{\Delta T}\right| \approx 2\,\frac{\lambda_p - \lambda_0}{T_p - T_0}$$

This results in the temperature coefficient

$$C\left(\frac{I_p}{2}\right) \approx \frac{4}{\alpha k\lambda_p}\,\frac{\lambda_p - \lambda_0}{T_p - T_0} \tag{5}$$

Table 4 shows that because of approximation (3) the data calculated by Eq. (5) are somewhat smaller than the measured ones except for $\lambda_p = 6000$ Å at which the $\frac{\Delta\lambda}{\lambda_p}$ value deviates from the average of 0.072. Since the slope $\left.\frac{\Delta I}{\Delta T}\right|_{\lambda}$ decreases slower than the intensity on both sides of the peak temperature T_p (see Figures 5 through 8 and Ref. 1), the maximum temperature coefficient C_m occurs usually at an intensity smaller than $I_p/2$ and amounts to about twice the value obtained at $I_p/2$:

$$C_m \approx \frac{8}{\alpha k \lambda_p} \frac{\lambda_p - \lambda_0}{T_p - T_0} \quad . \tag{6}$$

TABLE 4

Wavelength	Temperature Coefficient $C(I_p/2)$ [%°C^{-1}]			
	Measured			$\frac{\Delta\lambda_H}{\lambda_p}$
	$T < T_p$	$T > T_p$	Calculated by Formula (3)	
4200	2.3×10^4	2.8×10^4	1.3×10^4	0.072
5400	3.3×10^4	3.6×10^4	2.6×10^4	0.072
6000	2.9×10^4	3.3×10^4	3.2×10^4	0.072
6000			2.8×10^4	0.080

This relation indicates that for a given wavelength the maximum temperature coefficient is proportional to the slope of the function $\lambda_p(T)$ and thus depends on the asymptotes λ_0 and T_0.

Both Eq. (6) and the curve fits for $\lambda_p(T)$ indicate that the maximum temperature coefficient and the peak wavelength increase to infinity as the temperature approaches T_0, i.e. the temperature at which the pitch,[10] $p = \frac{2\lambda_p}{n_1 + n_2}$ is infinitely large. Since by definition the cholesteric mesophase ceases to exist at T_0, and since experimental experience implies a cholesteric-smectic phase transition within 0.1°C of T_0,† we conclude that the high temperature sensitivity of the selective reflection is associated with a pretransitional effect.‡ Apparently in response to an external agency the pliable cholesteric structure tends to unwind its helix before changing into a different molecular arrangement. This view is supported by the unwinding of the helix observed in the vicinity of the "nematic temperature" of a compensated mixture of laevo and dextro cholesterics[13, 14] and in cholesteric films exposed to electric[15] and magnetic fields[16] (field induced cholesteric-nematic transitions).

The maximum value of the temperature coefficient C_m and the upper limit of the peak wavelength depend on the lowest temperature T at which the cholesteric phase is stable, or on the lowest temperature at which the plane texture can be maintained in the proper alignment. Nevertheless, for a sufficiently large pitch, fluctuations typical for pretransitional phenomena will terminate the selective reflection. Such fluctuations may be indicated, for example, by the

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† Determined optically with a Mettler FP-2 hot stage.

‡ No such pretransitional effects have been reported in the vicinity of clearing points.

fluctuation regions of light scattered by cholesteryl myristate at a temperature of 2.1°C above the cholesteric-smectic phase transition.[17] Recently Lubensky published a theoretical study on fluctuations of cholesterics with infinite pitch.[18]

The Theoretical significance of $\lambda_p(T)$

Although the phenomenological theories of cholesteric mesophases are not able to determine directly the dependence of peak wavelength on temperature, they connect this function with other macroscopic physical parameters and thus predict types of relationships. The test of their validity requires the mathematical representation of experimental results within the limits of measurement uncertainty.

Alben's theoretical work[2] addresses the pretransitional effect of the cholesteric-smectic phase transition. Using the general theory of curvature-elasticity and deriving a simplified mean field theory for the molecular interaction he predicts that both the twist elastic constant k_{22} and the pitch p of the helix should increase rapidly as the temperature approaches the cholesteric-smectic transition, while the variation of the ratio $\frac{k_{22}}{p}$ should be relatively small. Since the average index of refraction is not very temperature sensitive,[19-21], k_{22} should exhibit roughly the same temperature dependence as λ_p. If this is correct, this theory would explain the pretransitional effects as a consequence of the coupling of the director of the cholesteric structure with that of the incipient smectic structure.†

The phenomenological theory by Keating[8] explains the peak wavelength vs. temperature relationship in terms of anharmonic molecular oscillations generated by thermal agitation. However, this theory requires some rather unrealistic and complicated assumptions about the model and the temperature dependence of the restoring forces. Based on the results of light scattering experiments on nematic phases Alben[2] questions the existence of the types of oscillations required for Keating's model. Nevertheless, Keating's formula for $\lambda_p(T)$ fits our data within the measurement uncertainty of ± 0.2 m°C. Recently Böttcher[22] modified Keating's model and introduced viscous forces into the theory. He obtained

$$\lambda_p \approx \frac{C_1}{T}\left(1 + C_2\,\eta\right) \tag{7}$$

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† Alben[2] suggests to determine $k_{22}(T)$ by field effect experiments.

where η is the viscosity, measured at low shear rate,

$$\eta = \eta_0 \exp\left(\frac{C}{T - T_0}\right)$$

and C_1, C_2, η_0, C, and T_0 are constants. He reports that this formula fits well the measured data used by Keating[8] and the ones determined by Magne and Pinard.[11] Unfortunately we did not have the opportunity to test this formula in our regression analysis.

CONCLUSION

We have shown that S-cholesteryl 14-phenyltetradecanethioate exhibits an extraordinarily high temperature coefficient of selective reflectance in the visible and that in spite of this the peak wavelength versus temperature curve can be fitted within the measurement uncertainty of ± 0.2 m°C by both expressions

$$\lambda_p = \frac{A}{T}\left(1 + \frac{B}{T - T_0}\right)^2$$

and

$$\lambda_p = \lambda_0 + \frac{A}{(T - T_0)^2}$$

Considering that the cholesteric-smectic transition temperature occurs in the vicinity of T_0 (i.e. the temperature of infinite helical pitch), we conclude that the high temperature dependence of the selective reflection is linked with a pretransitional effect. Consequently the temperature coefficient of the selective reflection increases as the operating temperature approaches the cholesteric-smectic phase transition. In particular one can determine the maximum coefficient from the slope of the $\lambda_p(T)$ curve, which in turn depends on the operating temperature and the two asymptotes λ_0 and T_0. The hypothesis linking the high temperature sensitivity of selective reflection with pretransitional effects agrees well with our experimental experience with about twenty steryl derivatives. Therefore, we submit that this hypothesis of a pretransitional effect has significant implications to both the theory of cholesteric-smectic phase transition (Alben's theory[2]) and to the application of cholesteric mesophases having high temperature coefficients of selective reflectance in the visible.

APPENDIX

Temperature noise in the liquid crystal sample

Since the liquid crystal sample is in contact with its environment by thermal conduction and radiation, it exhibits random temperature fluctuations due to the statistical nature of this heat exchange. We will drastically simplify the theory of this thermal interaction in order to estimate roughly the magnitude of these spontaneous flucatuations without being burdened by excessive mathematical complications.

Applying the generalized Nyquist theorem[23] R. C. Jones[24] obtains for the mean square temperature fluctuation of a body coupled to its surroundings by the thermal conductance K

$$\overline{\Delta T_f^2} = \frac{4kT^2}{K} \quad \frac{1}{1+(2\pi f\tau)^2} \cdot \Delta f \; \dagger \tag{8}$$

k Boltzman constant
T absolute sample temperature ($T \approx 320^\circ K$)
f, Δf frequency and bandwidth
τ thermal time constant of sample

Since our recording radiometer responded from dc to about one cycle per second, f and Δf are equal to 1 Hz. The remaining problem is to estimate the thermal time constant τ and the conducance K.

As described in a previous section, the liquid crystal sandwiched between 0.1 mm thick glass slides rests on an isothermal metal platform and is enclosed by an isothermal surface. The heat exchange between the liquid crystal and its surroundings is dominated by thermal conduction through the 0.1 mm glass slide to an ideal heat sink. This is based on the fact that the thermal flux through the slide is orders of magnitude larger than the radiation flux and that the heat capacity and thermal conductance of the supporting platform are much larger than those of the sample. To estimate the time constant we consider the worst case, i.e. we replace the glass-liquid crystal-glass sandwich by a homogeneous layer of equal thickness, having the lower thermal conductivity of liquid crystals and the higher specific heat of the glass. For thin films attached to an ideal heat sink one can approximate the infinite series describing the transient temperature response[25] by its first term. This results in a time constant

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† This holds for frequency independent heat capacity of the body and thermal conductance K.

$$\tau = \frac{4}{\pi^2}\ \frac{\ell^2 c}{H} \qquad \dagger$$

If the thickness of the film is $\ell = 2\times10^{-2}$ cm, its specific heat $c = 2$ J cm^{-3} °C^{-1} and the thermal conductivity $H = 10^{-3}$ W cm^{-1} °C^{-1} (we measured 1.2×10^{-3} W cm^{-1} °C^{-1} for cholesteryl oleyl carbonate), we obtain a thermal time constant τ of about 0.4 sec and thus

$$\frac{\Delta f}{1 + (2\,\pi f \tau)^2} \approx \frac{1}{\tau}$$

Considering that the main heat flux from the sample to the surroundings flows through the glass slide to the heat sink,* the thermal conductance K can be approximated by

$$K = H_g \frac{A}{d} \tag{9}$$

Since $H_g \approx 10^{-2}$ W cm^{-1} °C^{-1} is the thermal conductivity of glass, $d = 10^{-2}$ cm the thickness of the slide, and A the area of liquid crystal coupled to the heat sink, Eq. (8) and (9) yield

$$\sqrt{\overline{\Delta T_f^2}} \approx \frac{10^{-9}}{\sqrt{A}} \tag{10}$$

The rms temperature fluctuation associated with the entire liquid crystal film of about 1 cm^2 area amounts to about 10^{-9} °C. However, if such fluctuations modulate the selective reflection, a radiometer can only measure the associated intensity fluctuations averaged over the illuminated area. Since the thickness of the liquid crystal film is thin as compared to the lateral dimensions of the illuminated region, the illuminated volume element is coupled primarily to the heat sink rather than to the rest of the sample. ‡ Hence we can consider the illuminated volume element of liquid crystal as the body coupled to the environment by the conductance K where A is now the illuminated area of 5×10^{-3} cm^2. Therefore, we estimate that for our experimental set-up the rms

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† Since $h << \alpha$, Eq. (6) of Ref. 25 can be approximated by $\cot(\alpha_n \ell) = \frac{-h}{\alpha_n} \approx 0$ This results in the roots $\alpha_n = (2n-1)\frac{\pi}{2}$ and thus in our expression far τ.

‡ The effect of the lateral heat conduction due to the top over slide is not significant at a distance of 100 μm (i.e. one slide thickness) beyond the illuminated region of 800 μm diameter.

temperature noise amounts to about 10^{-8} °C. Of course, other noise mechanisms such as fluctuations in orientation, density and pitch of the liquid crystal can produce substantial excess noise.

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