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Scattering of circularly polarized light from the isotropic to the cholesteric phase of cholesteryl oleyl carbonate

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The Rayleigh intensity and linewidth of circularly polarized incident light have been measured in the isotropic phases and blue phases of cholesteryl oleyl carbonate. In the isotropic phase the intensity data show mean field behaviour. In the blue phase region the scattering of right handed or left handed circularly polarized light shows a different q dependence for the intensity as well as for the linewidth. The correlation function of the intensity fluctuations can be fitted to two exponentials. The experimental results are compared with the predictions of the theory proposed by Hornreich and Shtrikman.

1. Introduction

Light scattering studies of collective orientational fluctuations in cholesteryl oleyl carbonate (COC) have been reported by several authors [1, 2, 3]. They have all used linearly polarized incident light. Only the nematic pretransitional behaviour could be observed in these measurements. Chiral nematics show in a planar texture, the following properties [4]. For a light beam parallel to the helix axis the reflected light is found to be circularly polarized. A right handed circularly polarized beam (RHCPL) which matches exactly a right-handed helix is completely reflected, while a left handed beam (LHCPL) is completely transmitted. If circularly polarized incident light is used, then circularly intensity differential scattering (CIDS) is a measure of the ability of chiral substances to scatter preferentially right or left circular polarized light [5]. CIDS is defined as

$$\Delta(\theta) = \frac{I_{\mathrm{L}}(\theta) - I_{\mathrm{R}}(\theta)}{I_{\mathrm{L}}(\theta) + I_{\mathrm{R}}(\theta)}, \tag{1}$$

where

$$I_{\mathrm{L,R}}(\theta) = F(\theta) S_{\mathrm{OL,R}}(\theta) \tag{2}$$

and $F(\theta)$ is an angle dependent scattering factor, caused by orientational fluctuations of the molecules. $S_{\mathrm{OL,R}}(\theta)$ is the scattering intensity caused by a chiral unit cell which has the length of the pitch P. Bustamante [5] has developed a simple theory for CIDS of a cholesteric where this is treated as a twisted field of anisotropic point scatterers, described by the polarizability density

$$\boldsymbol{\alpha}(\mathbf{r}) = \alpha_1 \hat{t}(z)\hat{t}(z) + \alpha_2 [\mathbf{1} - \hat{t}(z)\hat{t}(z)]$$

$$\hat{t}(z) = \cos\left(\frac{2\pi z}{P}\right)\hat{x} + \sin\left(\frac{2\pi z}{P}\right)\hat{y},$$

where ^ denotes a unit vector and $\alpha_{1,2}$ is the polarizability density magnitude.

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The CIDS pattern depends on three parameters r, γ, a where r is P/λ, $\gamma = (\alpha_1 + \alpha_2)/(\alpha_1 - \alpha_2)$ and controls the anisotropy of the scattering groups while $a = (\pi/2)(\alpha_1 - \alpha_2)$ and controls the degree to which groups are coupled to each other by multiple scattering and interaction between induced dipole moments. From this

$$\Delta(\theta) = \frac{I_{\mathrm{L}} - I_{\mathrm{R}}}{I_{\mathrm{L}} + I_{\mathrm{R}}} = \frac{\Delta_0(\theta) + \Delta(0)}{1 + \Delta_0(\theta)\Delta(0)}, \tag{3}$$

where

$$\Delta_0(\theta) = \frac{x^3}{\dfrac{1 + |\gamma|^2}{2} x^4 + \dfrac{1 - 2|\gamma|^2}{2} x^2 + \dfrac{|\gamma|^2}{2}}, \tag{4}$$

$$\Delta(0) = \frac{-2ar^2[1 + (a-1)r^2]}{(r^2 - 1)^2 - ar^2[ar^2(1 + r^2) - 2(r^2 - 1)]}, \tag{5}$$

with

$$x = \frac{r(\cos\theta - 1)}{2}.$$

2. Pretransitional effects

To describe the phase transition in a cholesteric liquid crystal five modes of the order parameter fluctuations have to be taken into account. The free energy density in the disordered phase up to order ε^2 can be written as [7]

$$F - F_0 = \frac{1}{2}\sum_{qm}\left\{a - mdq\left[c_1 + \frac{c_2}{b}(4 - m^2)\right]q^2\right\} \times \varepsilon_m^2(q), \tag{6}$$

where m is the mode label. $\varepsilon_m(q)$ is the amplitude for the mode m and q the wavevector. The parameter a has a temperature dependence given by

$$a = a_0(T - T_m^*),$$

$c_{1,2}$ are elastic constants in the isotropic phase and they are assumed to be temperature independent. From the equipartition theorem

$$\langle\varepsilon_m(q)\varepsilon_{m'}(-q')\rangle = \delta_{mm'}\delta_{\mathrm{qq}}\frac{kT}{V\left(a - mdq + \left[c_1 + \frac{c_2}{b}(4 - m^2)\right]q^2\right)}. \tag{7}$$

The angular brackets denote a thermodynamic average.

Hornreich and Shtrikman [7] use the Mueller matrix formalism to describe the scattering of arbitrary polarized radiation by a linear medium. The properties of the input and output beams are described by the Stokes vectors S_α and S_β which are 4 × 1 column matrices. For circularly polarized incident light

$$S_2 = S_3 = 0 \quad \text{and} \quad S_4 = \pm S_1,$$

(+) for right handed circularly polarized light and (−) for left handed with the assumption that the modes are uncoupled, the scattered intensity comes from the dominant $m = \pm 2$ contributions. The reduced Mueller matrix for $m = \pm 2$

has the form

$$\tilde{\boldsymbol{\mu}} = \varepsilon^2_{\pm 2} \begin{bmatrix} (s^2+1)^2 & (1-s^4) & 0 & \pm 2s(s^2+1) \\ (1-s^4) & c^4 & 0 & \pm 2sc^2 \\ 0 & 0 & 0 & 0 \\ \pm s(s^2+1) & \pm 2sc^2 & 0 & 4s^2 \end{bmatrix}, \tag{8}$$

$s = \sin(\theta/2)$ $c = \cos(\theta/2)$ $S_\beta \sim \tilde{\boldsymbol{\mu}} S_\alpha$ and θ is the scattering angle. The differential scattered intensity for right handed circularly polarized light, which is proportional to S_β and S_α can be written as

$$I_{\pm 2}(q) \approx \frac{kT\,[(s^2+1)^2 \pm 2s(s^2+1)]}{a_0(T - T^2_{\pm 2})(1 \mp 2q_0\xi_{\pm 2}q + \xi^2_{\pm 2}q^2)} \tag{9}$$

where the chirality of the system is $q_0 = 4\pi/P = d/c_1$, and $\xi^2_{\pm 2} = c_1/\alpha = c_1/a_0(T - T^*_{\pm 2})$. The linewidth Γ is proportional to the inverse of the static structure factor.

$$\Gamma_{\pm 2} \approx \frac{a_0(T - T^*_{\pm 2})}{v}(1 \mp 2q_0\xi_{\pm 2}q + \xi^2_{\pm 2}q^2), \tag{10}$$

v is an effective viscosity and

$$T^*_{\pm 2} = T^* \pm \frac{c_1 q_0^2}{a_0}. \tag{11}$$

3. Experimental

Light from a vertically polarized argon laser with $\lambda = 488$ nm was incident on a cylindrical scattering cell. The diameter of the cell was 16 mm. The beam was circularly polarized by means of a $\lambda/4$ plate. The intensity was reduced to ~ 50 mW with a neutral density filter. The beam was focused into the cell by a lens. The scattering angle could be varied between 30°–160°. The linewidth Γ was obtained from the intensity correlation function. We used a Saicor 43A correlator with 400 channels and a time resolution of 2×10^{-7} s/channel. The temperature was controlled to 2×10^{-3} K.

4. Results

4.1. *Temperature dependence*

4.1.1. *Intensity*

Figure 1 shows the temperature dependence of the scattering intensity I_R for right handed circularly polarized light and I_L left handed polarized light at a scattering angle of 130°. From heat capacity measurements by Voets [8] the transitions occur at the temperatures

I - 309·78 K - BPIII - 309·63 K - BPII - 309·36 K - BPI - 308·85 K - Ch.

At 308·65 K a jump in $I_{R,L}(T)$ occurs. The system becomes supercooled and evolves slowly to the cholesteric phase.

In figure 2 we plot $T/I_R(130°)$ as a function of temperature. The points show a $T - T^*_{\pm 2}$ behaviour as expected from the Landau–de Gennes theory [6]. Extrapolation leads to $T^*_{\pm 2}$ behaviour as expected from the Landau–de Gennes theory [6].

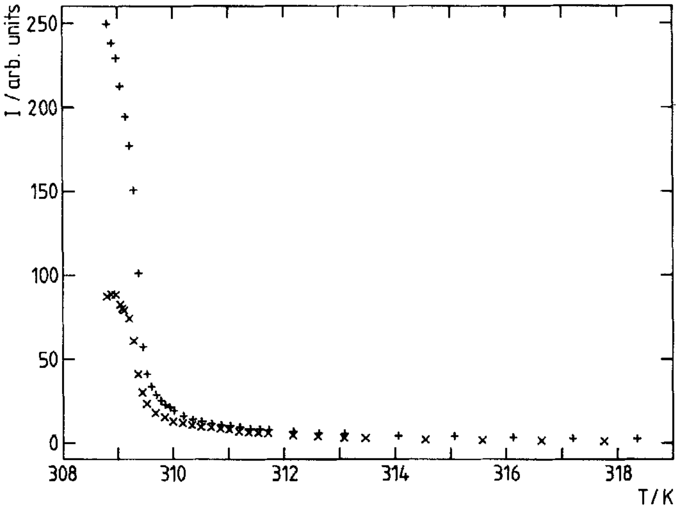

Figure 1. Intensity data (in arbitrary units) versus temperature $+I_R$; $\times I_L$.

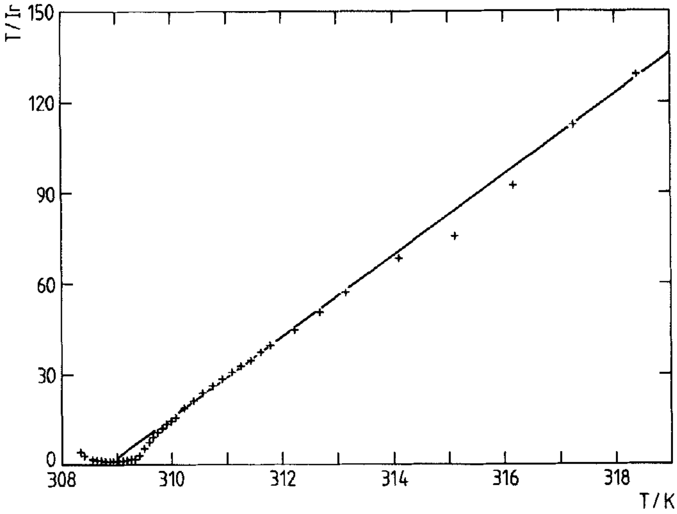

Figure 2. T/I_R data (in arbitrary units) versus temperature.

Extrapolation leads to $T^*_{\pm 2}$ = 308·79 K. This is in agreement with Mahler [1]. At the lower end of the curve, close to the I–BPIII transition, deviations from linear behaviour occur which cannot be explained by the ξq dependence in equation (9). This has also been seen in other nematogenic compounds [9].

4.1.2. *Linewidth*

In figure 3 we plot the linewidth $\Gamma_R(130°)$ as a function of temperature. We could not measure the correlation function in the isotropic phase due to limitations of our correlator in the high frequency range. For T > 309·65 K (above the BPII–BPIII transition) the correlation function $C(t)$ can be fitted to a single exponential. For

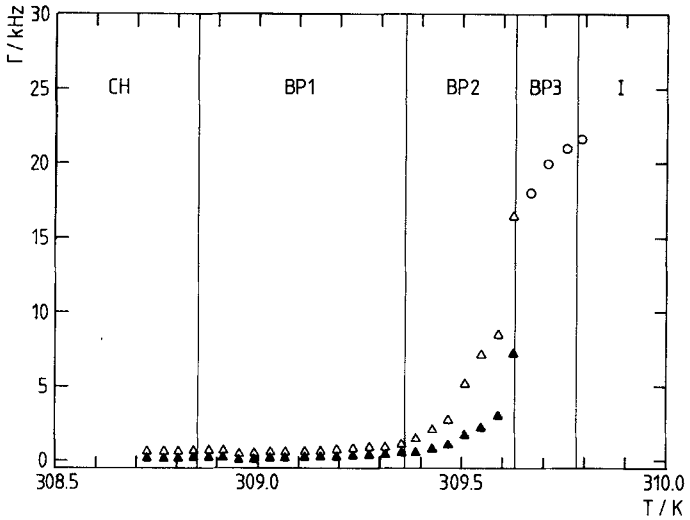

Figure 3. Linewidth Γ of the I_R spectrum versus temperature. ○ single exponential; △ double exponential.

Change of linewidth at the BPII–BPIII transition

$M = 2B_2/\Gamma^2$			$R = A_1/A_2$		
T/K	Γ_1/kHz	Γ_2/kHz	R	Γ/kHz	M
309·548	07·13	2·21	3·54	05·38	0·11
309·590	08·48	3·01	5·48	06·85	0·08
309·626	16·40	7·19	4·81	15·80	0·09
309·668	15·00	7·12	32	18·00	0·05
309·708	19·70	5·08	23	20·00	0·04
309·755	21·00	4·27	25	20·60	0·03
309·791	—	—	—	21·60	0·06

$T < 309{\cdot}65$ K $C(t)$ corresponds to two exponentials. To demonstrate this we have fitted $C(t)$ in the transition region to

$$C(t) = A_1 \exp(-\Gamma_1 t) + A_2 \exp(-\Gamma_2 t) + A_3,$$

$$C(t) = B_1 \exp(-\Gamma t + B_2 t^2) + B_3.$$

The parameters are given in the table. For $T > 309{\cdot}65$ K the ratio of the amplitudes R increases suddenly because A_2 becomes very small. A value M of about 0.04 is considered to correspond to a good single exponential decay [10].

4.2. *q dependence*

4.2.1. *Intensity*

In figure 4 we plot $I_R(q)$. Only the intensities at higher q values show a q dependence as predicted by equation (9); the curve through the points corresponds to $\xi = 23$ nm and $q_0 = 0{\cdot}036\,\mathrm{nm}^{-1}$. For $I_L(q)$ at the same temperature, $T = 309{\cdot}284$ K, see (figure 5) we obtain a reasonable fit to equation (9) for all of the points using $\xi = 23$ nm and $q_0 = 0{\cdot}036\,\mathrm{nm}^{-1}$.

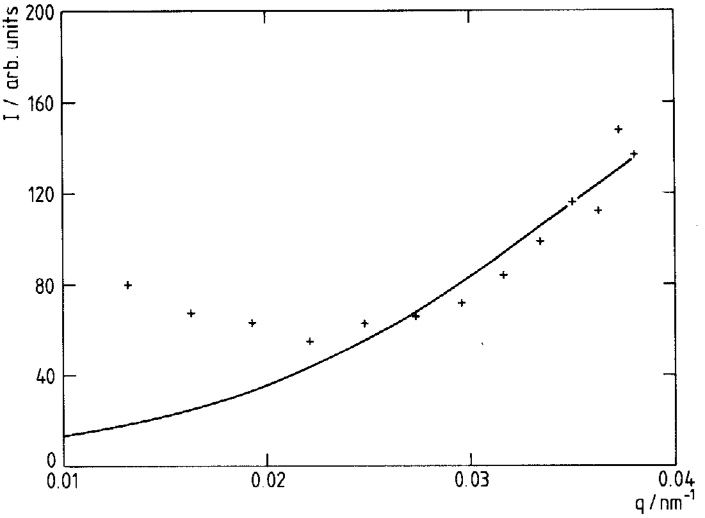

Figure 4. I_R in arbitrary units versus q. The experimental points are fitted by equation (9); T = 309·284 K; ξ = 23 nm; q_0 = 0·036 nm^{-1}.

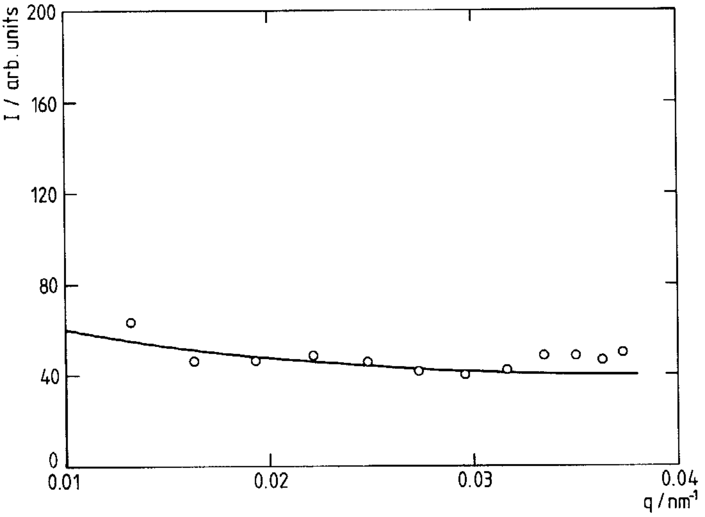

Figure 5. I_L in arbitrary units versus q. The experimental points are fitted by equation (9); T = 309·284 K; ξ = 23 nm; q_0 = 0·036 nm^{-1}.

4.2.2. *Linewidth*

In figure 6 we plot $\Gamma_R(q)$ at T = 309·321 K. Here again, only the $\Gamma_R(q)$ values at higher q show the q dependence predicted by equation (10); the curve through the points corresponds to ξ = 28 nm and q_0 = 0.035 nm^{-1}. In figure 7 we plot $\Gamma_L(q)$ at T = 309·507 K. Using the values ξ = 23 nm and q_0 = 0·036 nm^{-1}, we find the same q dependence as predicted by equation (10). Extrapolation to $q = 0$ and using T_2^* = 308·79 K we find a_0/v = 7 kHz/K. Yang [11] reported for CEEC a_0/v = 7·93 kHz/K while Harada [2] found for COC a_0/v = 35 kHz/K. The pitch P is 350 nm.

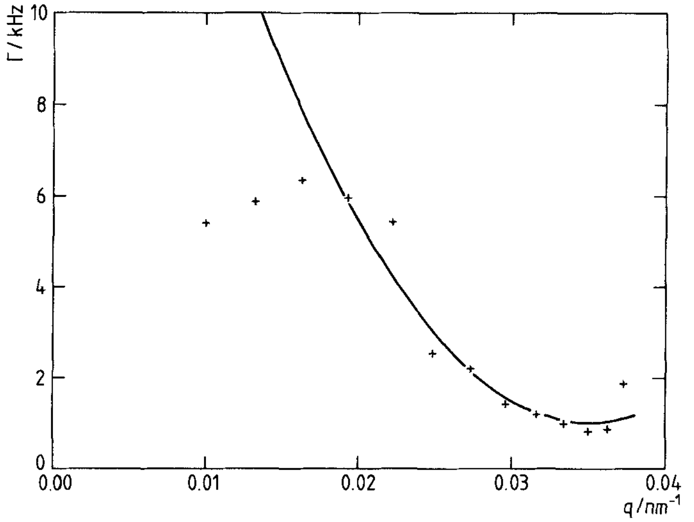

Figure 6. Γ_{Rl} versus q. The experimental points are fitted by equation (10); $T = 309{\cdot}321$ K; $\xi = 28$ nm; $q_0 = 0{\cdot}035\,\text{nm}^{-1}$.

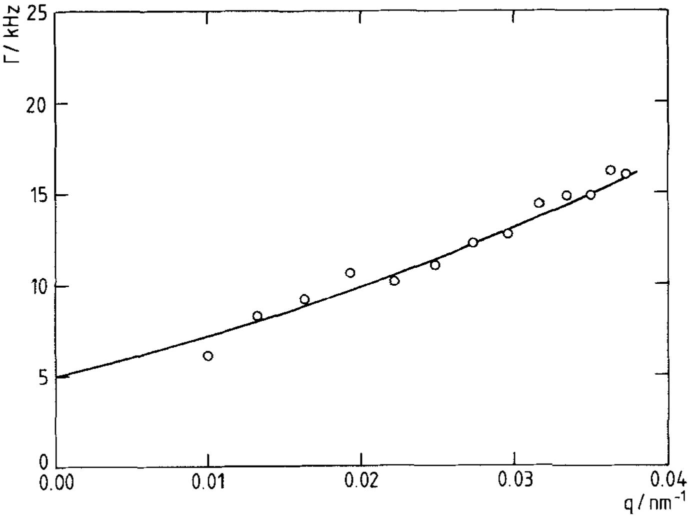

Figure 7. Γ_{Ll} versus q. The experimental points are fitted by equation (10); $T = 309{\cdot}507$ K; $\xi = 23$ nm; $q_0 = 0{\cdot}036\,\text{nm}^{-1}$.

Plotting the CIDS data as a function of the scattering angle at $T = 309{\cdot}751$ K (figure 8) and using equation (3) where $\alpha_2 = 0$ and $a \sim 0$, we find the pitch P is 536 nm. The error in the experimental data is large, however the value for the pitch is comparable with that obtained from equations (9) and (10). The discrepancy between theory and experiment indicates that possibly other modes, due to coupling between these modes, have to be taken into account. Parthasarathy and DuPré [12] found that $T_2^* < T_1^*$ for COC contrary to the theoretical expectation. If this is true then the $m = 1$ mode cannot be neglected in the theory of Hornreich and Shtrikman. Combining the $m = 2$ mode with $m = 0$ mode would make it possible to fit the $I_{R,L}(q)$ measurements. Further analysis in this direction will be made.

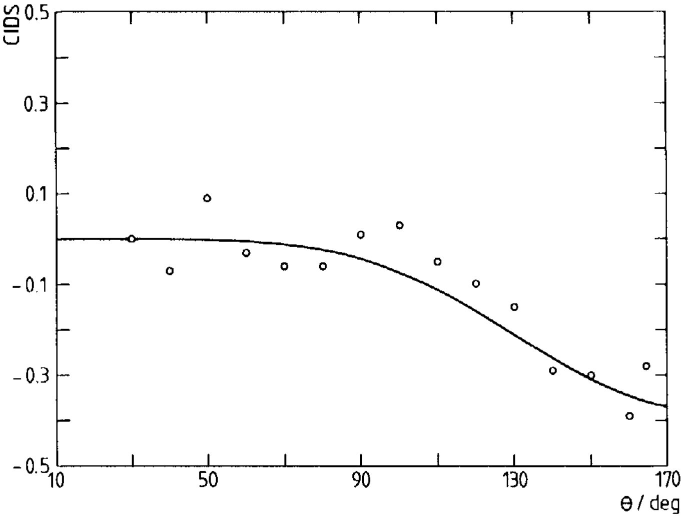

Figure 8. CIDS versus scattering angle θ for T = 309·751 K. P = 536 nm.

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