Pretransitional optical activity of short-pitched chiral nematic liquid crystals

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We have developed, using the de Gennes theory of short-range orientational order in the isotropic phase, a closed-form expression for the temperature dependence of the pretransitional optical activity of chiral nematics. Detailed calculations are included and the results are expressed in a form that can be easily tested experimentally. The theoretical predictions are supported by experimental data.

INTRODUCTION

The macroscopic order parameter associated with phase transitions of chiral nematics is normally taken to be the anisotropic part of the dielectric tensor $\mathbf{Q}_{\alpha\beta}(\mathbf{r})$. This tensor being traceless and symmetric can be represented in terms of five independent structural modes [1–3]; all of which can fluctuate about their equilibrium value at a finite temperature. These modes labeled $m = \pm 2, \pm 1$, and 0 represent the planar spiral, conical spiral, and nonchiral modes, respectively [4,5]. The Landau-de Gennes free energy for each of these modes vanishes at some temperature T_m^*. All the T_m^* are lower than the transition temperature, T_c, and $T_1^* < T_2^*$.

Highly chiral nematics are intriguing because they form the blue phase and show complex pretransitional behavior [6,7]. If the isotropic-blue phase transition is approached by cooling, thermodynamic fluctuations of the isotropic phase become more correlated and this results in a sharp increase of many properties (e.g., intensity of light scattered and the electric- or magnetic-induced birefringence). Another property, which behaves similarly, is the pretransitional optical activity. Although this effect was not anticipated [8], it has proven to be a sensitive probe into the nature of such fluctuations.

The first experimental evidence for this enhanced optical activity (ψ) was presented by Cheng and Meyer [9]. They calculated and verified the $(T - T^*)^{-0.5}$ temperature dependence of (ψ). Dolganov, Krylova, and Filev [10], using the same framework (Landau–de Gennes theory of short-range orientational order of the isotropic phase) as Cheng and Meyer, confirmed this divergent behavior in a mixture of N-(p-methoxybenzylidene)-p'-butylanine (MBBA) and 5% cholesteryl capriate. Bensimon, Domany, and Shtrikman [11] extended the theory to include the blue phase. In these earlier versions of the theory [9–11], only the contributions from the $m = \pm 1$ modes were considered.

Filev [12], in his theoretical approach, proposed a mode-coupling hypothesis whereby the $m = \pm 2$ modes could become activated, but unfortunately, did not provide all the details of the calculations. He predicted that close to T_c in highly chiral systems, the optical activity would reach a maximum and then decrease (since the $m = \pm 1$ and $m = \pm 2$ modes make opposite contributions to the optical activity). This pretransitional maximum was first detected by Demikov and Dolganov [13] in the isotropic phase of cholesteryl nonanoate.

Fluctuations of both the planar spiral and the conical spiral modes contribute directly to ψ with the conical spiral dominating and without coupling between these modes as previously suggested [12]. However, contributions from the $m = \pm 2$ modes may become comparable to those of the $m = \pm 1$ modes at temperatures close to T_c; also, contributions from the $m = \pm 2$ modes are expected to increase with increasing chirality. This contribution to ψ due to the $m = \pm 2$ modes was estimated to be approximately 10% within the temperature interval $T - T_c \cong 0.2\,\mathrm{K}$ in the highly chiral nematic 4-cyano-4-(2-methyl) butylphenyl (CB 15) [18]. The mode-coupling hypothesis has been erroneously invoked in a number of cases [5,12,14–17] in order to explain trends in optical activity data.

Demikov and Dolganov [18] claimed that contributions from the $m = \pm 2$ modes should vary as $(T - T_{\pm 2}^*)^{-1.5}$ while those of the $m = \pm 1$ modes should vary as $(T - T_{\pm 1}^*)^{-0.5}$. Collings [4] has confirmed that the fit using an exponent of -1.5 for the $m = \pm 2$ modes is significantly better than the fit obtained if an exponent of -0.5 is used. Evidence for contributions from the $m = \pm 2$ modes has been reported in a number of cases [14–17,19].

Wyse, Ennis, and Collings [20] measured both the temperature and wavelength dependence of ψ and expressed the results as a function of even powers of (k/q_0). The function contained the same exponent (-0.5) for the temperature dependence of the second- and fourth-order coefficients. However, more recent theoretical work by Dmitrienko (partially included in Ref. [18]) predicts that the $m = \pm 1$ modes contribute in the second-order term of the wavelength expansion, but both the $m = \pm 1$ and $m = \pm 2$ modes contribute directly in the fourth-order term. The exponents for the second- and fourth-order terms are -0.5 and -1.5, respectively.

THEORY

For a cholesteric liquid crystal, the Landau–de Gennes free energy to second order can be written as [21–23]

$$F_2 = F_0 + \frac{1}{2} \int d\vec{r} [a Q_{\alpha\beta}^2 + b(\partial_\gamma Q_{\alpha\beta})^2 + c\,\partial_\alpha Q_{\alpha\gamma}\partial_\beta Q_{\beta\gamma}$$
$$- 2 d e_{\alpha\beta\gamma} Q_{\alpha\delta}\partial_\gamma Q_{\beta\delta}], \tag{1}$$

where $Q_{\alpha\beta}$ is the dielectric tensor representing the local order, $e_{\alpha\beta\gamma}$ is the Levi-Civita tensor, $a = a_0(T - T^*)$, the coef-

ficients b, c, and d are temperature independent and T^* is the second-order phase-transition temperature of the racemic mixture. If the order parameter is expressed in terms of the five structural modes Eq. (1) reduces to

$$F_2 = F_0 + \frac{1}{2} \sum_m \int d^3\vec{q} \left\{ a - mdq + \left[b + \frac{c}{6}(4 - m^2) \right] q^2 \right\} |\sigma^m(\vec{q})|^2. \tag{2}$$

Here, m labels the mode, $\vec{q}$ is the wave vector of light, and $\sigma^m(\vec{q})$ is the amplitude of the mode. There is a specific value of q that minimizes the free energy of each mode.

For perturbations about the phase transition, correlation functions

$$\langle Q_{\alpha\beta}(\vec{r}) Q_{\sigma\tau}(\vec{r}') \rangle = \frac{1}{V} \sum_{\vec{q}} G_{\alpha\beta}^{\sigma\tau}(\vec{q}) e^{i\vec{q}\cdot\vec{r}} \tag{3}$$

are obtained by inverting the functional matrix of the quadratic form of F_2. In the momentum representation,

$$Q_{\alpha\beta}(\vec{r}) = V^{-1/2} \sum_{\vec{q}} Q_{\alpha\beta} e^{i\vec{q}\cdot\vec{r}}, \tag{4}$$

and F_2 can be written as

$$F_2 = \frac{1}{2} \sum_{\vec{q}} t_\alpha^\gamma(\vec{q}) \delta_\beta^\delta Q_{\alpha\beta}(\vec{q}) Q_{\gamma\delta}(-\vec{q}), \tag{5}$$

where

$$t_\alpha^\gamma(\vec{q}) = (a + bq^2)\delta_\alpha^\gamma + cq_\alpha q^\gamma - 2dq J_\alpha^\gamma(\vec{q}) \tag{6}$$

and

$$J_\alpha^\gamma(\vec{q}) = ie_{\alpha\gamma\nu} \hat{q}_\nu; \quad q = |\vec{q}|. \tag{7}$$

More symmetrically, $t_\alpha^\gamma \delta_\beta^\delta$ can be replaced by

$$4T_{\alpha\beta}^{\gamma\delta} = t_\alpha^\gamma \delta_\beta^\delta + t_\beta^\gamma \delta_\alpha^\delta + t_\alpha^\delta \delta_\beta^\gamma + t_\beta^\delta \delta_\alpha^\gamma - \frac{2}{3}(t_{\alpha\beta} + t_{\beta\alpha})\delta^{\gamma\delta}$$
$$- \frac{2}{3}(t^{\gamma\delta} + t^{\delta\gamma})\delta_{\alpha\beta} + \frac{4}{9}(t_\nu^\nu \delta_{\alpha\beta}\delta^{\gamma\delta}), \tag{8}$$

where $T_{\alpha\beta}^{\gamma\delta}(\vec{q})$ is a Hermitian operator acting on the symmetric traceless tensors $Q_{\alpha\beta}$. The inversion problem thus reduces to the solution of

$$T_{\alpha\beta}^{\mu\nu}(\bar{q}) G_{\mu\nu}^{\gamma\delta}(\vec{q}) = I_{\alpha\beta}^{\gamma\delta}, \tag{9}$$

where the unit matrix, $I_{\alpha\beta}^{\gamma\delta}$, has the form

$$I_{\alpha\beta}^{\gamma\delta} = \frac{1}{2}(\delta_\alpha^\gamma \delta_\beta^\delta + \delta_\alpha^\delta \delta_\beta^\gamma) - \frac{1}{3}\delta_{\alpha\beta}\delta^{\gamma\delta}. \tag{10}$$

The correlation function G is now constructed from polarization tensors, $\sigma_{\alpha\beta}^m(\hat{q})$, which diagonalize:

$$T_{\alpha\beta}^{\gamma\delta}(\vec{q}) \sigma_{\gamma\delta}^m(\hat{q}) = \tau^m(q) \sigma_{\alpha\beta}^m(\hat{q}). \tag{11}$$

The labels m may be chosen to measure the polarization along the momentum direction $\hat{q} \equiv \vec{q}/|\vec{q}|$, such that

$$(J\hat{q}) \sigma_{\alpha\beta}^m(\hat{q}) = m\sigma_{\alpha\beta}^m(\hat{q}). \tag{12}$$

The solution to this equation can be expressed in terms of a local orthonormal triplet of vectors oriented along $\hat{q}$: $\vartheta^1(\hat{q})$, $\vartheta^2(\hat{q})$, $\vartheta^3(\hat{q}) \equiv \hat{q}$.

The spherical unit vectors

$$\vartheta^+(\hat{q}) \equiv l(\hat{q}) \equiv (\vartheta^1 + i\vartheta^2)/\sqrt{2},$$

$$\vartheta^-(\hat{q}) \equiv l^*(\hat{q}) \equiv (\vartheta^1 - i\vartheta^2)/\sqrt{2},$$

$$\vartheta^0(\hat{q}) \equiv \vartheta^3(\hat{q}) \equiv \hat{q}, \tag{13}$$

are natural representations of helicity ± 1, 0, respectively. Thus,

$$\sigma_{\alpha\beta}^2(\hat{q}) = \vartheta_\alpha^+ \vartheta_\beta^+ = l_\alpha l_\beta \equiv \sigma_{\alpha\beta}^{-2}(\hat{q})^*,$$

$$\sigma_{\alpha\beta}^1(\hat{q}) = \frac{1}{\sqrt{2}}(\vartheta_\alpha^+ \vartheta_\beta^0 + \vartheta_\alpha^0 \vartheta_\beta^+) = \frac{1}{\sqrt{2}}(l_\alpha \hat{q}_\beta + l_\beta \hat{q}_\alpha) = \sigma_{\alpha\beta}^{-1}(\hat{q})^*,$$

$$\sigma_{\alpha\beta}^0(\hat{q}) = \vartheta_\alpha^0 \vartheta_\beta^0 = \sqrt{\tfrac{3}{2}}(\hat{q}_\alpha \hat{q}_\beta - \tfrac{1}{3}\delta_{\alpha\beta}). \tag{14}$$

The eigenvalues $\tau_m(q)$ are determined by substituting the expressions (14) into Eq. (11) to give

$$\tau^{\pm 2}(q) = a + bq^2 \pm 2dq,$$

$$\tau^{\pm 1}(q) = a + (b + c)q^2 \pm 2dq,$$

$$\tau^0(q) = a + (b + \tfrac{4}{3}c)q^2. \tag{15}$$

The correlation function $G(q)$ can now be calculated as follows:

Since the partition function Z is given by

$$Z = \sum_{\vec{q}} e^{-(F_2)/(k_B T)}, \tag{16}$$

then,

$$Z = \sum_{\sigma^m} \exp\left\{ -\frac{1}{k_B T} \sum_{\vec{q},m} \tau^m(q) \sigma_{\alpha\beta}^m(\vec{q}) \sigma_{\gamma\delta}^{m*}(-\vec{q}) \right\}, \tag{17}$$

and

$$\langle Q_{\alpha\beta}(\vec{q}) Q_{\gamma\delta}(-\vec{q}) \rangle = \delta_{\vec{q},-\vec{q}} \sum_m k_B T \frac{\sigma_{\alpha\beta}^m(\hat{q}) \sigma_{\gamma\delta}^{m*}(-\hat{q})}{\tau^m(q)}. \tag{18}$$

The correlation function is finally written as

$$G_{\alpha\beta}^{\gamma\delta}(\vec{q}) = k_B T \sum_m \frac{\sigma_{\alpha\beta}^m(\hat{q}) \sigma_{\gamma\delta}^{m*}(-\hat{q})}{\tau^m(q)}. \tag{19}$$

The rotation of the plane of polarization can be described by the antisymmetric part of the dielectric tensor, $\varepsilon_{\alpha\beta}$, which has the form

$$\Delta\varepsilon_{\alpha\beta}=i\psi e_{\alpha\beta\gamma}\vec{k}_\gamma, \tag{20}$$

where $\vec{k}$ is the wave vector; $k=\sqrt{\varepsilon_0}\omega/c$, and ψ is the optical activity. In the pretransitional isotropic region, the structural activity ψ can be obtained after the convolution of Eq. (20) with $e_{\alpha\beta\nu}\vec{k}_\nu$:

$$\Delta\varepsilon_{\alpha\beta}e_{\alpha\beta\nu}\vec{k}_\nu=i\Psi e_{\alpha\beta\gamma}\vec{k}_\gamma\otimes e_{\alpha\beta\nu}\vec{k}_\nu=2i\Psi. \tag{21}$$

Thus,

$$\psi=\frac{-i\Delta\varepsilon_{\alpha\beta}e_{\alpha\beta\nu}\vec{k}_\nu}{2}. \tag{22}$$

Now,

$$\Delta\varepsilon_{\alpha\beta}=\frac{k_0^2}{4\pi\varepsilon_0}\int\frac{d\vec{q}}{(2\pi)^3}D_{\beta\gamma}(\vec{q}+\vec{k})$$
$$\times[G_{\alpha\beta}^{\gamma\delta}(\vec{q})-G_{\alpha\beta}^{\gamma\delta}(-\vec{q})], \tag{23}$$

where

$$D_{\beta\gamma}(\vec{q})=\frac{4\pi}{q^2-k^2-i\eta}\left(\delta_{\beta\gamma}-\frac{q_\beta q_\gamma}{k^2}\right), \quad \eta\to 0 \tag{24}$$

and $|\vec{k}|=k_0$.

So,

$$\psi=-\frac{ik_0^2}{2\varepsilon_0}e_{\alpha\delta\nu}\vec{k}_\nu\int\frac{d\vec{q}}{(2\pi)^3}D_{\beta\gamma}(\vec{q}+\vec{k})$$
$$\times[G_{\alpha\beta}^{\gamma\delta}(\vec{q})-G_{\alpha\beta}^{\gamma\delta}(-\vec{q})]. \tag{25}$$

Using the symmetry properties of $G_{\alpha\beta}^{\gamma\delta}(\vec{q})$, the summation reduces to

$$G_{\alpha\beta}^{\gamma\delta}(\vec{q})-G_{\alpha\beta}^{\gamma\delta}(-\vec{q})=k_BT\left(\Omega_m\sum_m\sigma_{\alpha\beta}^m(\hat{q})\sigma_{\gamma\delta}^m(-\hat{q})-\text{c.c.}\right), \tag{26}$$

where

$$\Omega_m=\frac{2mbq_0q}{\{a+[b+\frac{c}{6}(4-m^2)]q^2\}^2-(mbq_0q)^2}. \tag{27}$$

Consequently, the $m=0$ mode makes no contribution to the optical activity. Taking into account expressions such as

$$e_{\alpha\delta\nu}\vec{k}_\nu l_\alpha l_\beta^*=-i\vec{k}(\hat{q}), \tag{28}$$

which arises in the calculations, we can perform the summation over all indices. Next, take the coordinate axis for q so that the z axis is along the vector $\vec{k}$, θ is the polar angle, and φ the azimuthal angle. The calculation thus proceeds as follows:

$$\psi=-\frac{i}{2\varepsilon_0}e_{\alpha\delta\nu}\vec{k}_\nu k_BT$$
$$\times\int\frac{d\vec{q}dxd\varphi}{(2\pi)^3}\frac{k^2\delta_{\beta\gamma}-(\vec{q}_\beta+\vec{k}_\beta)(\vec{q}_\gamma+\vec{k}_\gamma)}{k^2[q^2+2kqx-i\eta]}$$
$$\times\sum_{m=1}^{m=2}\Omega_m[\sigma_{\alpha\beta}^m(\hat{q})\sigma_{\gamma\delta}^m(-\hat{q})-\sigma_{\alpha\beta}^{m*}(\hat{q})\sigma_{\gamma\delta}^{m*}(-\hat{q})]. \tag{29}$$

Expanding the integral we arrive at $\psi=\psi_1+\psi_2$, where

$$\psi_{\pm 1}=-\frac{k_0^2k_BT}{4\varepsilon_0}\int_0^1\int_{-\infty}^\infty\frac{\Omega_1x(1+x^2)kq^2dq\,dx}{(2\pi)^2[q^2+2kqx-i\eta]}, \quad \eta\to 0, \tag{30}$$

and

$$\psi_{\pm 2}=\frac{k_0^2k_BT}{4\varepsilon_0}\int_0^1\int_{-\infty}^\infty\frac{\Omega_2(1+x^2+q\frac{x}{k})q^3dq\,dx}{(2\pi)^2[q^2+2kqx-i\eta]}, \quad \eta\to 0, \tag{31}$$

where $x=\cos\theta$.

Using the calculus of residues, we get for the q integral,

$$I_1=\frac{\pi}{B_1D_1}\left[\frac{q_3}{q_3+2kx}-\frac{q_2}{q_2+2kx}\right], \tag{32}$$

where

$$q_2=(-B_1+iD_1)/2, \quad q_3=(B_1+iD_1)/2,$$
$$D_1=\sqrt{4A_1-B_1^2}, \quad B_1=bq_0/(b+c/2), \tag{33}$$

and

$$I_2=-\frac{\pi}{B_2D_2}\left[\left(\frac{q_3^2}{q_3+2kx}-\frac{q_2^2}{q_2+2kx}\right)\right.$$
$$\left.+\left(\frac{q_3^3}{q_3+2kx}-\frac{q_2^3}{q_2+2kx}\right)\right], \tag{34}$$

where

$$A_2=a/b, \quad B_2=2q_0, \quad D_2=\sqrt{4A_2-B_2^2}. \tag{35}$$

Performing the integration over x, we get

$$\psi_{m=\pm 1}=\frac{k_0^3k_BT}{4\varepsilon_0}\frac{[f_1(a_1)-f_1(-a_1^*)]}{[4\pi(b+c/2)^2]}, \tag{36}$$

and

$$\psi_{m=\pm 2}=-\frac{k_0^3k_BT}{4\varepsilon_0}\frac{[f_2(a_2)-f_2(-a_2^*)]}{8\pi b}, \tag{37}$$

where

$$f_1(a_1) = -\tfrac{1}{2}a_1^2 + a_1^2 + a_1^2(1+a_1^2)\ln\left(1+\frac{1}{a_1}\right),$$

$$f_2(a_2) = -\tfrac{4}{3}a_2 + \tfrac{1}{2}a_2^2 - a_2^3 + a_2^2(1+a_2^2)\ln\left(1+\frac{1}{a_2}\right), \tag{38}$$

and

$$a_1 = \frac{q_1\xi_1 + i}{2k\xi_1}, \quad a_2 = \frac{q_0\xi_2 + i}{2k\xi_2}, \quad q_1 = \frac{q_0 b}{2b+c}. \tag{39}$$

Since $k\xi_{1,2} \ll 1$ and $|a_{1,2}| \gg 1$, the ln function is expanded in powers of, $1/a_{1,2}$, and ψ calculated to the lowest powers in $k\xi_{1,2}$:

$$\psi_{m=\pm1} = \frac{k_B T k_0^2 q_0 \xi_1 b}{32\pi\varepsilon_0 (b+c/2)^2}\left[\frac{2}{3} + \frac{8k_0^2\xi_1^2}{15(1+q_1^2\xi_1^2)} + \cdots\right], \tag{40}$$

$$\psi_{m=\pm2} = -\frac{k_B T k_0^2 q_0 \xi_2}{32\pi\varepsilon_0 b}\left[\frac{32k_0^2\xi_2^2}{15(1+q_0^2\xi_2^2)} + \cdots\right]. \tag{41}$$

Realizing that ξ_1 can be written as

$$\xi_1 = \frac{2}{D_1} = \frac{1}{a_0^{1/2}(b+c/2)^{-1/2}(T-T_1^*)^{1/2}}, \tag{42}$$

where

$$T_{\pm1}^* = T^* \pm \frac{b^2 q_0^2}{4a_0(b+c/2)}, \tag{43}$$

then the optical activity due to the $m=\pm1$ modes is given by

$$\psi_{m=\pm1} = \frac{k_B T b k_0^2 a_0}{48\pi\varepsilon_0 (a_0 b)^{1/2}}\left[1+\frac{c}{2b}\right]^{-3/2}\left[\frac{1}{(T-T_{\pm1}^*)^{1/2}}\right. \left. + \frac{f(q_1\tau_1)}{(T-T_{\pm1}^*)^{3/2}}\right], \tag{44}$$

where

$$f(q_1,\tau_1) = \frac{4k_0^2}{5a_0 b(b+c/2)^2(1+q_1^2\xi_1^2)} \tag{45}$$

and

$$\tau_1 = T - T_{\pm1}^*. \tag{46}$$

Similarly, the contribution of the $m=\pm2$ modes is given by

$$\psi_{m\pm2} = -\frac{k_B T k_0^2 q_0}{15\pi\varepsilon_0 b}\frac{f(q_0,\tau_2)}{(T-T_{\pm2}^*)^{3/2}}, \tag{47}$$

where

$$f(q_0,\tau_2) = \left(\frac{k_0^2}{(a_0/b)^{3/2}(1+q_0^2\xi_2^2)}\right), \tag{48}$$
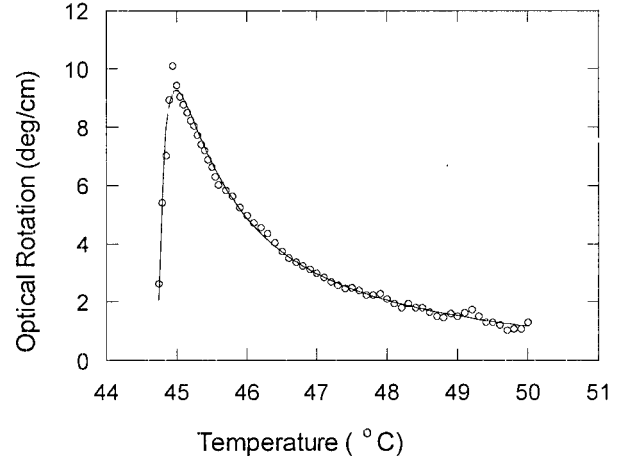

FIG. 1. Theoretical fit (solid line) to the optical activity of the isotropic phase of CE6. The circles represent the experimental data. The wavelength of light used is 633 nm.

and

$$T_{\pm2} = T^* \pm \frac{q_0^2 b}{a_0}, \tag{49}$$

with

$$\tau_2 = T - T_{\pm2}^*. \tag{50}$$

Hence, if plane-polarized light travels through an optically active medium it emerges with its plane of polarization rotated through some angle ψ,

$$\psi = \psi_0 + \psi_{m=\pm1} + \psi_{m=\pm2}. \tag{51}$$

ψ_0, the molecular optical activity that is independent of orientational order, is given by

$$\psi_0 = \frac{16\pi^3 N\beta t}{\lambda^2 c}, \tag{52}$$

where β is the optical rotatory parameter, N the number density, λ the wavelength of light, and c the velocity of light.

In addition, the optical activity due to the $m=\pm2$ mode is opposite in sense to that due to the $m=\pm1$ mode. Thus, for highly chiral systems, the optical activity should reach a maximum just before the transition to the ordered phase. Eq. (51) may be expressed as follows:

$$\psi(T) = \frac{A}{(T-T_1^*)^{0.5}} + \frac{B}{(T-T_1^*)^{1.5}} + \frac{C}{(T-T_2^*)^{1.5}} + \psi_0. \tag{53}$$

RESULTS AND DISCUSSION

We tested the validity of the theory by fitting pretransitional optical activity data of CE6. We used a rotating analyzer technique (described elsewhere [19]) to measure the optical activity. The pretransitional optical activity and the fit to Eq. (53) is shown in Fig. 1. The optical activity reaches a

maximum just above T_c and then decreases.

The data when fitted to Eq. (53) yield the following parameters:

$$A = 4.7 \pm 0.3 (°C^{0.5} \ cm^{-1}) \qquad B = 26.3 \pm 3.9 (°C^{1.5} \ cm^{-1})$$

$$\psi_0 = -1.3 \pm 0.2 (degree \ cm^{-1})$$

$$C = -19.3 \pm 3.9 (°C^{1.5} \ cm^{-1})$$

$$T_2^* = 44.43 \pm 0.4 (°C) \qquad T_1^* = 44.31 \pm 1.0 (°C)$$

The least squares fit is quite good except in the immediate vicinity of the pretransitional maximum where there is a 5% difference between theoretical and experimental predictions. Since the magnitudes of B and C are similar but of opposite sign, contributions from the second and third terms of Eq. (53) essentially cancel each other at temperatures much higher than the isotropic-BPIII transition temperature. However, owing to the large number of fitting parameters involved, the error estimates of some of the parameters can be quite high.

CONCLUSION

We have developed a closed form expression for the temperature dependence of the pretransitional optical activity of chiral nematics. The planar spiral and the conical spiral make direct but opposite contributions to the optical activity. Experimental data are quite consistent with theoretical predictions.

This paper includes the derivation for the $m = \pm 1$ fourth-order contribution to the optical activity. As far as we are aware, details of this calculation have not yet been published. Also, our calculations contain much more details than those of Ref. [18]. Hunte, Singh, and Gibbs [19] have measured the pretransitional optical of CB15 and successfully fitted the data using the three exponents predicted by Dmitrienko and our calculations.

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[1] S. A. Brazovski and S. G. Dmitriev, Zh. Eksp. Teor. Fiz. **69**, 979 (1975) [Sov. Phys. JETP **42**, 497 (1975)].

[2] R. M. Hornreich and S. Shtrikman, Phys. Rev. A **28**, 1791 (1983).

[3] S. A. Brazovski and V. M. Filev, Zh. Eksp. Teor. Fiz. **75**, 1140 (1978) [Sov. Phys. JETP **48**, 573 (1978)].

[4] P. J. Collings, Mod. Phys. Lett. B **6**, 425 (1992).

[5] J. S. Kang and D. A. Dunmur, Phys. Rev. E **51**, 2129 (1995).

[6] D. C. Wright and N. D. Mermin, Rev. Mod. Phys. **61**, 385 (1981).

[7] P. P. Crooker, Liq. Cryst. **5**, 751 (1989).

[8] P. G. deGennes, Mol. Cryst. Liq. Cryst. **12**, 193 (1971).

[9] J. Cheng and R. B. Meyer, Phys. Rev. A **9**, 2744 (1974).

[10] V. K. Dolganov, S. P. Krylova, and V. M. Filev, Zh. Eksp. Teor. Fiz. **78**, 2343 (1980) [Sov. Phys. JETP **51**, 1177 (1980)].

[11] D. Bensimon, E. Domany, and S. Shtrikman, Phys. Rev. A **28**, 427 (1983).

[12] V. M. Filev, Pis'ma Zh. Eksp. Teor. Fiz. **37**, 589 (1983) [Sov. Phys. JETP **37**, 703 (1983)].

[13] E. I. Demikov and V. K. Dolganov, Pis'ma Zh. Eksp. Teor. Fiz. **38**, 368 (1983) [JETP Lett. **38**, 445 (1984)].

[14] F. Vanweert, W. Demol, and W. Van Dael, Liq. Cryst. **5**, 853 (1989).

[15] R. Parthasarathy and D. B. Dupre, Liq. Cryst. **3**, 1231 (1988).

[16] P. R. Battle, J. D. Miller, and P. J. Collings, Phys. Rev. A **36**, 369 (1987).

[17] J. E. Wyse and P. J. Collings, Phys. Rev. A **45**, 2449 (1992).

[18] E. I. Demikov and V. K. Dolganov, Kristallografiya **34**, 1198 (1989).

[19] C. Hunte, U. Singh, and P. Gibbs, J. Phys. II **6**, 1291 (1996).

[20] J. E. Wyse, J. Ennis, and P. J. Collings, Phys. Rev. Lett. **84**, 1045 (1989).

[21] H. Grebel, R. M. Hornreich, and S. Shtrikman, Phys. Rev. A **30**, 3264 (1984).

[22] H. Grebel, R. M. Hornreich, and S. Shtrikman, Phys. Rev. A **28**, 1114 (1983).

[23] R. M. Hornreich and S. Shtrikman, Phys. Rev. A **28**, 1791 (1983).