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Optical activity measurements in the smectic blue phases

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Abstract. Optical activity measurements have been performed on the smectic blue phases ($\mathrm{BP_{Sm}}$), which are a new kind of chiral liquid crystal. $\mathrm{BP_{Sm}}$ exhibit both three-dimensional orientational order, like the classical blue phases, and smectic positional order. Thus, they can be viewed as the three-dimensional counterpart of the twist grain boundary phases. A comparison with the optical activity of the classical blue phases is carried out, and an estimation of the $\mathrm{BP_{Sm}}$ lattice parameter is reported for the first time.

PACS. 61.30.-v Liquid crystals – 78.20.Ek Optical activity

1 Introduction

Chirality leads to a marvelous variety of liquid crystalline phases, including the cholesteric (N*), the blue (BP) and the twist grain boundary (TGB) phases. The TGB phases are made of slabs of smectic material, which are regularly stacked in a helical fashion along an axis parallel to the smectic layers. Adjacent slabs are continuously connected via a grain boundary that consists of a wall of parallel equidistant screw dislocation lines producing helical twist [1]. The blue phases can be considered the three-dimensional counterpart of the cholesteric phase, exhibiting cubic lattices for BP1 and BP2 without any positional long-range order [2]. These phases are optically isotropic but are, like helicoidal structures (N* and TGB), optically active.

Recently new chiral phases, called smectic blue phases ($\mathrm{BP_{Sm}}$), have been discovered in a chiral series called *n*BTMHC, where *n* is the aliphatic chain length [3]. $\mathrm{BP_{Sm}}$ appear adjacent to twist grain boundary phases with no intermediate cholesteric state. Contrary to classical blue phases, these phases exhibit quasi–long-range smectic order that can be studied by X-ray scattering. The smectic order is correlated with the orientational three-dimensional order and therefore gives information on the symmetry of the $\mathrm{BP_{Sm}}$ unit cell. The $\mathrm{BP_{Sm}}$ lattice parameter is in the UV-range [3], preventing any optical scattering of visible light (Kossel diagram technique), which is commonly used to find the symmetry of the classical blue phases [4]. The structure of the smectic blue phases has been investigated, and $\mathrm{BP_{Sm}2}$ appears hexagonal [5] whereas $\mathrm{BP_{SmA}1}$ exhibits a cubic symmetry [6]. These studies have been carried out mainly by X-ray scattering on $\mathrm{BP_{Sm}}$ monodomains. Lately, we have shown that the $\mathrm{BP_{Sm}1}$ structure is affected by the underlying $\mathrm{TGB(_A\ or\ _C)}$ phase [7]. Indeed, a new compound, named 16FHFH-BTC1M8, has been synthesized exhibiting an unusual phase sequence: $\mathrm{TGB_C}$-$\mathrm{BP_{Sm}}$-Iso, which does not show any $\mathrm{TGB_A}$ phase [8]. In the case of a $\mathrm{TGB_C}$-$\mathrm{BP_{Sm}}$ transition, the structure of the $\mathrm{BP_{Sm}1}$ phase, called $\mathrm{BP_{SmC}1}$, seems to have a hexagonal symmetry and differs from the $\mathrm{BP_{SmA}1}$ phase nucleating at a $\mathrm{TGB_A}$-$\mathrm{BP_{Sm}}$ transition. However, the smectic peaks in $\mathrm{BP_{SmC}1}$ are weakly enhanced; this phase then appears to have a slightly anisotropic structure. Moreover, its texture as seen by optical polarizing microscopy is composed of blue "platelets" like the cubic $\mathrm{BP_{SmA}1}$ phase [8]. In both cases, the blue colour originates from the optical activity. Thus $\mathrm{BP_{SmA}1}$ and $\mathrm{BP_{SmC}1}$ are very similar from an optical point of view, and differences appear only at the scale of the smectic order. Contrary to $\mathrm{BP_{Sm}1}$ ($\mathrm{BP_{SmA}1}$ or $\mathrm{BP_{SmC}1}$), $\mathrm{BP_{Sm}2}$ shows a large structural anisotropy due to its hexagonal symmetry, and therefore exhibits birefringence [6]. The third smectic blue phase (called $\mathrm{BP_{Sm}3}$) has, like classical BP3 [9], an amorphous structure of the same macroscopic symmetry as that of the isotropic phase [10].

In this paper we report the first optical activity measurements in the smectic blue phases. A comparison with the classical blue phases is carried out, and $\mathrm{BP_{Sm}3}$ seems to be similar to BP3 from an optical point of view. The presence of smectic order, however, changes the evolution of the optical activity of $\mathrm{BP_{Sm}1}$ with respect to BP1. A study of the optical activity as a function of wavelength

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has also been performed, and the value of the BP_{Sm} lattice parameter has been estimated for the first time.

2 Theory

The main theoretical work on highly chiral liquid crystals is based on the Landau-de Gennes formulation using the anisotropic part of the dielectric tensor ε_{ij} as the orientational order parameter. Since it is a symmetric tensor with zero trace, ε_{ij} has five independent elements or basis tensors. For chiral systems, it is appropriate to represent ε_{ij} as a linear combination of five structural modes. Their amplitude is written as $\varepsilon_m(q)$, with q a wave vector of the structure and $m = 0, \pm1, \pm2$. The $m = 0$ mode is not chiral and represents a nematic-like structure. The $m = 1$ mode describes a conical spiral where two principal axes rotate around the spiral axis making an angle of 45°. The $m = 2$ mode is a planar spiral mode where two principal axes rotate around the spiral axis making an angle of 90°. The $m = -1$ and $m = -2$ modes are similar to the $m = 1$ and $m = 2$ modes, respectively, but the axes rotate in the opposite direction; they are referred to as right-handed. The plus sign describes a left-handed structure. In this formulation, a right-handed cholesteric phase can be represented by a specific combination of the $m = -2$ and $m = 0$ modes. The optical activity of such a structure for light propagating along the helical axis was first worked out by de Vries [11]:

$$\rho = \pi {\lambda_0}^3 (\Delta n)^2 / [4n\lambda^2(\lambda_0^2 - \lambda^2)] \,, \tag{1}$$

where ρ is the optical activity, $\lambda = 2\pi/k$ is the wavelength of the light (k is the wave vector of the light), n is the average refractive index, Δn is the local optical anisotropy, and $\lambda_0 = nP$, where P is the pitch. This relationship holds as long as Δn is small and λ *is not too close to* λ_0. The blue phases involve structures for which ε_{ij} has a spatial variation representative of certain cubic symmetry groups. Therefore, these structures can be represented by a set of wave vectors, q, for which the average amplitude of ε_{ij} is non-zero. With this as a starting point, Bensimon *et al.* have predicted how the optical activity, ρ, of the classical blue phases depends on their structure for $k \ll q$ ($\lambda \gg \lambda_0$) [12]:

$$\rho = A_2(k^2/q) - A_4(k^4/q^3) \,, \tag{2}$$

with $A_2 \propto (\varepsilon_1^2 - \varepsilon_{-1}^2)$ and $A_4 \propto [a(\varepsilon_2^2 - \varepsilon_{-2}^2) + b(\varepsilon_1^2 - \varepsilon_{-1}^2)]$, where a and b are constants. Thus, the first term, A_2, is proportional to the amplitude of the $m = \pm1$ modes, whereas the second term, A_4, is a function of the amplitudes of the $m = \pm1$ and $m = \pm2$ modes and contributes with an *opposite sign* to the optical activity. This formulation will be used in the following text to explain the experimental results.

3 Experiments and results

The optical activity measurement system consists of a set of two polarizers in front of and behind the sample. The first polarizer is fixed, while the analyzer is rotatable and controlled by a computer. The light is chopped and the output signal of the detector goes to a lock-in amplifier. The sample is contained between two pieces of glass in a heating stage. The temperature accuracy is better than 0.01 °C and all experiments were performed upon heating. The temperatures of the phase transitions have been determined for each compound of this experiment by optical microscopy. The thickness of the sample is maintained by a calibrated $135 \pm 2\,\mu$m mylar spacer placed between the two pieces of glass. The light source is a He-Ne laser operating at 633 nm, and for the study of the optical activity with wavelength, a 1000 W xenon lamp coupled with a monochromator is used instead of the He-Ne laser. The experimental setup is shown in Figure 1.

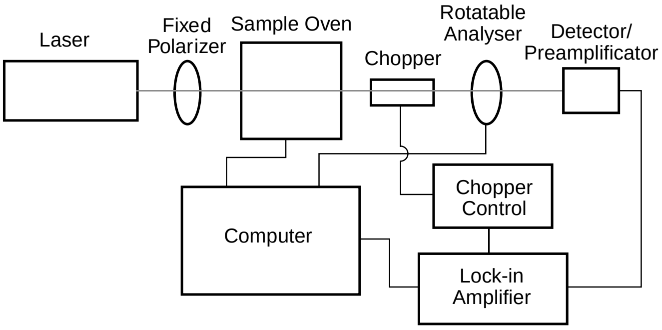

Fig. 1. Experimental apparatus for the optical activity measurements.

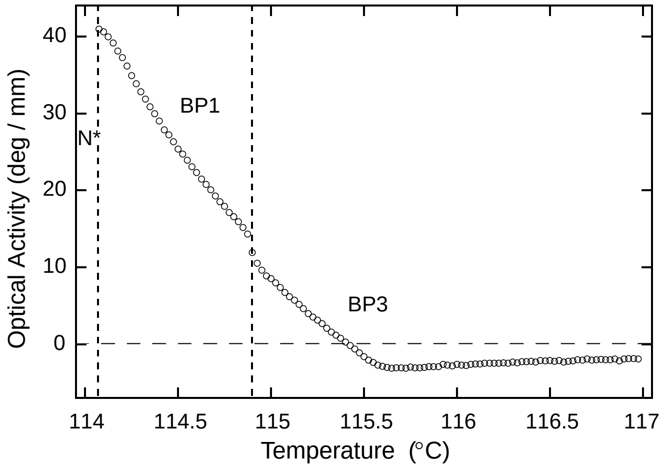

Fig. 2. Optical activity of the classical blue phases at 633 nm ($10F_2BTFO_1M_7$ compound).

We have first studied a classical blue phase ($10F_2BTFO_1M_7$ compound [13]) with a N*-BP1-BP3-Iso phase sequence, which has a lattice parameter in the near UV-range. Indeed, the pitch has been measured in the cholesteric phase at the transition to BP1 and $P = 0.22\,\mu$m [13]. This compound can then be used as a reference to be compared with the smectic blue phases. Figure 2 shows the optical activity *versus* temperature from BP1 to the isotropic phase (not in the cholesteric phase where the birefingence is too high without the planar orientation of the phase). The magnitude of the

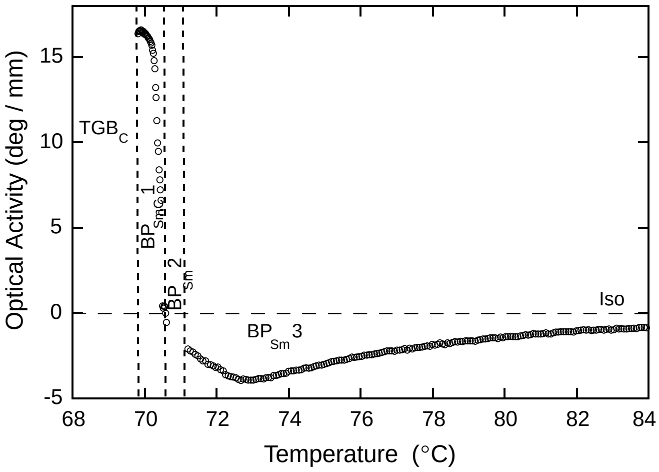

Fig. 3. Optical activity at 633 nm as a function of temperature for the smectic blue phases (16FHFH-BTC1M8 compound).

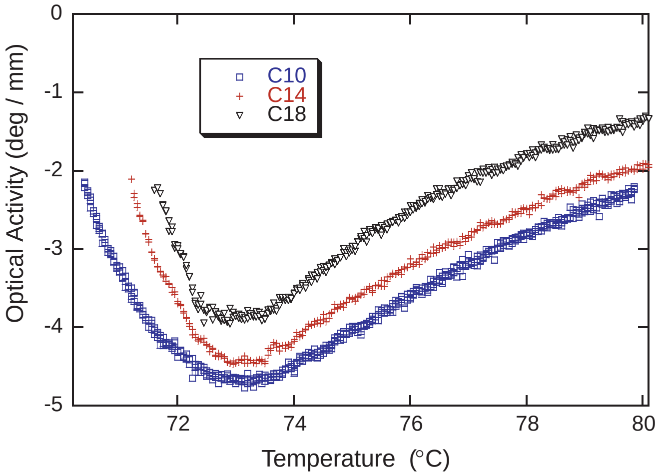

Fig. 4. Optical activity at 633 nm in the temperature range of the BP$_{\rm Sm}$3 and isotropic phases for different compounds of the nBTMHC series, where $n = 10, 14$ or 18 indicates the aliphatic chain length. A shift has been applied to the curves (−2.6 °C for C14 and −4.1 °C for C18) to allow for easy comparison.

optical activity increases as the temperature is decreased in the isotropic phase due to the $m = \pm 1$ modes, but then reaches a maximum and decreases due to the rising contribution of the $m = \pm 2$ modes (see Eq. (2)). Note the fairly linear dependence of the optical activity in the BP1 range, as previously shown for instance in reference [14].

Optical activity measurements have been performed on the smectic blue phases. Figure 3 plots the data in the temperature span of all three BP$_{\rm Sm}$. Each BP$_{\rm Sm}$ will be discussed in detail separately. First, the Iso-BP$_{\rm Sm}$3 transition has been investigated on the series of compounds nBTMHC by varying the aliphatic chain length, n. This variation allows us to change the molecular length at a "given chirality", and therefore to modulate the influence of the smectic order. Figure 4 shows that the optical activity in BP$_{\rm Sm}$3 becomes more supercritical as the molecular chain length decreases. These results are in agreement with calorimetric measurements [3] and prove that BP$_{\rm Sm}$3 behaves just like the classical BP3 as far as the optical activity is concerned [15]. Indeed, the length scale of the smectic fluctuations in BP$_{\rm Sm}$3 is not large enough to be probed by visible light. Thus, BP$_{\rm Sm}$3 and BP3, which are two amorphous phases having isotropic symmetry [10,9], are similar from an optical point of view.

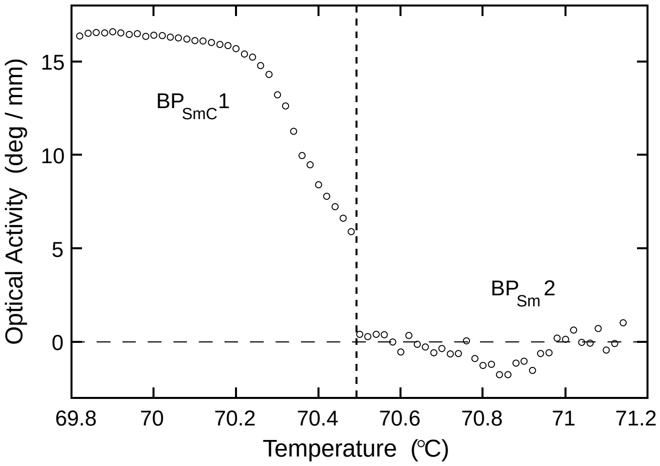

Fig. 5. Optical activity at 633 nm in the temperature range of BP$_{\rm SmC}$1 (and BP$_{\rm Sm}$2) (16FHFH-BTC1M8 compound).

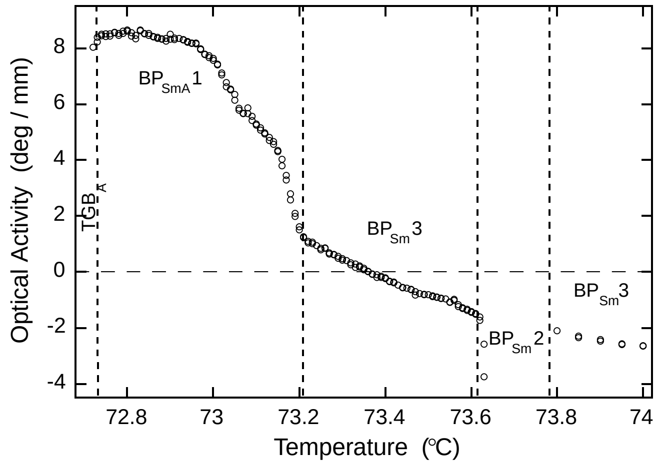

Fig. 6. Optical activity at 633 nm of the 14BTMHC compound.

Figure 5 reports the optical activity in the temperature range of BP$_{\rm SmC}$1 and BP$_{\rm Sm}$2. However, the measurements in BP$_{\rm Sm}$2 are not significant. Due to its birefringence, this phase does not produce a good minimum in the light transmission between crossed polarizers, thus giving high error estimates (around a few degrees/mm). Therefore, the values close to zero obtained in BP$_{\rm Sm}$2 certainly do not reflect the real optical activity of this phase.

The evolution of the optical activity *versus* temperature is similar both for BP$_{\rm SmC}$1 (Fig. 5) and BP$_{\rm SmA}$1 (Fig. 6). Contrary to classical BP1 (Fig. 2), the optical activity ceases to increase as the temperature decreases toward the TGB transition. This corresponds to a *saturation* of the optical activity in BP$_{\rm Sm}$1, as shown in

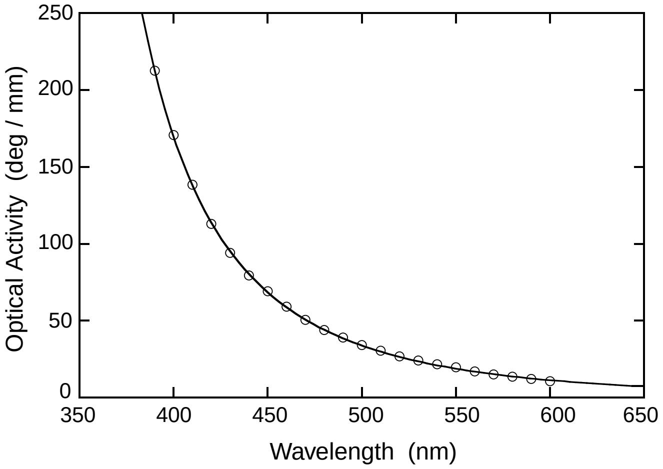

Fig. 7. Optical activity at 72.8 °C as a function of wavelength for $\mathrm{BP_{SmA}}1$ (14BTMHC compound). The solid line is a fit to equation (3).

Figure 5 and in Figure 6. These results confirm that $\mathrm{BP_{SmA}}1$ and $\mathrm{BP_{SmC}}1$ are very similar from an optical point of view, and also show that the smectic order disturbs the orientational order, as discussed at length in Section 4. Note the unusual phase sequence depicted in Figure 6 for the 14BTMHC compound: $\mathrm{TGB_A}$-$\mathrm{BP_{SmA}}1$-$\mathrm{BP_{Sm}}3$-$\mathrm{BP_{Sm}}2$-$\mathrm{BP_{Sm}}3$-Iso. The specific properties of 14BTMHC originate from the metastability of $\mathrm{BP_{Sm}}3$ as has been already reported in reference [6].

The last experiment performed deals with the wavelength dependence of the optical activity in $\mathrm{BP_{SmA}}1$. A divergence of the optical activity is expected close to the selective reflection, λ_0, as has already been seen in the cholesteric phase [16] and in the classical blue phases [17]. The data for the 14BTMHC compound are plotted in Figure 7, showing a rise of the optical activity when the wavelength decreases. This confirms that the $\mathrm{BP_{Sm}}$ lattice parameter is in the UV-range, and a fit to equation (3) represented by the solid line in Figure 7 allows for an estimation: $\lambda_0 = 320\,\mathrm{nm}$ ($P = 0.21\,\mu\mathrm{m}$ if $n = 1.5$). This value is consistent with the pitch found by the Grandjean-Cano method in the $\mathrm{TGB_A}$ phase where $P = 0.16\,\mu\mathrm{m}$ close to the $\mathrm{BP_{Sm}}$ transition [3]. Indeed, an increase of the pitch of about 30% is also observed at the transition from cholesteric to classical blue phases [17]. Note that the equation

$$\rho = (C/\lambda)/[\lambda^2({\lambda_0}^2 - \lambda^2)] \tag{3}$$

differs from the de Vries formulation (see Eq. (1)) by the wavelength dependence of $(\Delta n)^2/n$, which is proportional to $1/\lambda$. This has been already used, for instance in reference [18], to fit data in the TGB and cholesteric phases. However, in the case of the smectic blue phases, there is no *a priori* reason that this theoretical formulation works because it does not correspond to its range of application and validity. Thus, we consider the fit given by equation (3) a good "first estimate" of the selective reflection wavelength, and not a result stemming from a firm theoretical prediction.

4 Discussion

As shown in Figures 5 and 6, the first smectic blue phase ($\mathrm{BP_{SmA}}1$ or $\mathrm{BP_{SmC}}1$) behaves differently from classical blue phases. A saturation of the optical activity is observed for temperatures close to the transition in TGB($_\mathrm{A}$ or $_\mathrm{C}$) phase. This is probably due to the presence of smectic order which disturbs the $\mathrm{BP_{Sm}}$ orientational order. Two explanations, which represent two variations of the same idea, may account, at least in part, for this unusual behaviour.

The first explanation is that twist and layering are two incompatible orders, therefore generating geometrical frustration as in the TGB phases. Indeed, the main contribution to the optical activity in the classical cubic blue phases comes from the $m = \pm 2$ modes, which represent planar spiral modes. The increasing amplitude of the $m = \pm 2$ modes may be affected by the presence of smectic order, leading to a saturation in the optical activity. Indeed, a similar behaviour has already been seen just above the transition from the isotropic phase to the $\mathrm{TGB_A}$ phase [19]. The assumption of a new isotropic phase has been proposed [20], but recent work involving coupling between the smectic and orientational order fluctuations also provides an explanation [21]. Perhaps this idea can be extended to the smectic blue phases, but more theoretical work will be necessary.

There is another possible reason for the saturation of the optical activity in $\mathrm{BP_{Sm}}1$. The smectic order may "rigidify" the $\mathrm{BP_{Sm}}$ structure compared to the classical blue phases and thus "lock in" the evolution of the lattice parameter with decreasing temperature. Indeed, the wavelength of maximum selective reflection in the blue phases (and therefore the value of the pitch) increases as the temperature is lowered [17]. For wavelengths greater than the value of the selective reflection wavelength, this causes an increase in the optical activity at low temperatures. A "locking in" of the $\mathrm{BP_{Sm}}$ pitch due to the smectic order would then produce a saturation of the optical activity in the $\mathrm{BP_{Sm}}1$ range.

5 Conclusion

Even though the thickness of the smectic layers is significantly smaller than the wavelength of light, optical activity measurements are capable of revealing important similarities and differences between the classical and smectic blue phases. Similarities include the general temperature dependence of the optical activity in the various phases (except for $\mathrm{BP_{Sm}}2$) and the supercritical nature of the transition to the isotropic phase. Two differences are the existence of a non-cubic blue phase, $\mathrm{BP_{Sm}}2$, and the influence of smectic order on the temperature dependence of the optical activity in the lowest temperature $\mathrm{BP_{Sm}}$. Optical activity measurements can also be used to estimate the lattice parameter of the $\mathrm{BP_{Sm}}$ for the first time.

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References

1. S.R. Renn, T.C. Lubensky, Phys. Rev. A **38**, 2132 (1988).
2. P.P. Crooker, in *Chirality in Liquid Crystals*, edited by H.S. Kitzerow, C. Bahr (Springer-Verlag, New York, 2001).
3. M.H. Li, V. Laux, H.T. Nguyen, G. Sigaud, P. Barois, N. Isaert, Liq. Cryst. **23**, 389 (1997).
4. P.E. Cladis, T. Garel, P. Pieranski, Phys. Rev. Lett. **57**, 2841 (1986).
5. B. Pansu, E. Grelet, M.H. Li, H.T. Nguyen, Phys. Rev. E **62**, 658 (2000).
6. E. Grelet, B. Pansu, M.H. Li, H.T. Nguyen, Phys. Rev. Lett. **86**, 3791 (2001).
7. E. Grelet, B. Pansu, H.T. Nguyen, Phys. Rev. E **64**, 010703 (2001).
8. E. Grelet, B. Pansu, H.T. Nguyen, Liq. Cryst. **28**, 1121 (2001).
9. Z. Kutnjak, C.W. Garland, J.L. Passmore, P.J. Collings, Phys. Rev. Lett. **74**, 4859 (1995).
10. P. Jamée, G. Pitsi, M.H. Li, H.T. Nguyen, G. Sigaud, J. Thoen, Phys. Rev. E **62**, 3687 (2000).
11. H. De Vries, Acta Crystallogr. **4**, 219 (1951).
12. D. Bensimon, E. Domany, S. Shtrikman, Phys. Rev. A **28**, 427 (1983).
13. H.T. Nguyen, A. Bouchta, L. Navailles, P. Barois, N. Isaert, R.J. Twieg, A. Maaroufi, C. Destrade, J. Phys. II **2**, 1889 (1992).
14. T.K. Brog, P.J. Collings, Mol. Cryst. Liq. Cryst. **60**, 65 (1980).
15. J.B. Becker, P.J. Collings, Mol. Cryst. Liq. Cryst. **265**, 163 (1995).
16. S. Chandrasekhar, J. Shashidhara Prasad, Mol. Cryst. Liq. Cryst. **14**, 115 (1971).
17. P.J. Collings, Mol. Cryst. Liq. Cryst. **113**, 277 (1984).
18. B.D. Yanoff, A.A. Ruether, P.J. Collings, A.J. Slaney, J.W. Goodby, Liq. Cryst. **14**, 1793 (1993).
19. K.C. Frame, J.L. Walker, P.J. Collings, Mol. Cryst. Liq. Cryst. **198**, 91 (1991).
20. J.W. Goodby, D.A. Dunmur, P.J. Collings, Liq. Cryst. **19**, 703 (1995); J.P. Marcerou, R. Farhi, J.C. Rouillon, H.T. Nguyen, Eur. Phys. J. E **3**, 29 (2000).
21. G.M. Barretto, P.J. Collings, D. Bennemann, D. Lötzsch, G. Heppke, Liq. Cryst. **28**, 629 (2001).