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Optical activity and light scattering in the isotropic and smectic A* phases of a highly chiral smectic liquid crystal

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The results of optical activity measurements on the smectic A* phase of 1-methylheptyl 4′-[(4-*n*-tetradecyloxyphenyl)proprioloyloxy]biphenyl-4-carboxylate (14P1M7) and the chiral nematic phase of a chiral–racemic mixture of *S*-4-(2-methylbutyl)phenyl 4-decyloxybenzoate (CE6) are shown to be extremely similar. This is in full agreement with the proposed model of the A* phase as a twist-grain-boundary (TGB) phase. In addition, new light scattering measurements using circularly polarized light in a back-scattering geometry yield information on the fluctuations in the isotropic phase. Unlike in chiral nematics where only one structural mode is affected, the data show a strong deviation from the normal temperature dependence near the isotropic–smectic A* transition for two structural modes. Possible reasons for this behaviour in highly chiral smectic liquid crystals are discussed.

1. Introduction

Significant progress in our understanding of chiral liquid crystals has come from the realization that the orientational order in these systems can be described in terms of five structural modes. The orientational order of the chiral nematic (N*), blue (BP), and chiral smectic C (C*) phases can all be represented as a linear combination of these five structural modes. Fluctuations in the isotropic and smectic A phases can also be described in terms of these modes. One important result of this work is the observation that fluctuations in the isotropic phase near the transition to the blue phase increase with chirality, significantly affecting the nature of the transition (See [1] for a recent review of this work.)

Recent investigations into highly chiral smectic liquid crystals have revealed that they might behave quite differently from highly chiral nematic systems. A new phase appears below the isotropic phase, and the evidence is mounting that this is a twist-grain-boundary (TGB) phase [2–4]. In addition, thermodynamic measurements indicate that significant changes take place in the isotropic phase just above the transition to the A* phase [3, 5]. Clearly, analysis of the results of optical activity and light scattering measurements in terms of the five structural modes, which is so useful in highly chiral nematic systems, should reveal important information about these smectic liquid crystals. For example, the orientational order in the proposed TGB phase is identical to the chiral nematic phase, except that the director rotates continuously in the N* phase and discontinuously in the TGB phase. However, the

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discontinuities in the TGB phase appear to be separated by a distance much smaller than the wavelength of light, and therefore should not affect measurements in the visible. With this in mind, both the N* and A* phases can be represented in terms of the same combination of two structural modes, and thereby possess the same optical properties. This article contains results from optical activity experiments on the A* phase of 1-methylheptyl 4′-[(4-*n*-tetradecyloxyphenyl)proprioloyloxy]biphenyl-4-carboxylate (14P1M7) and a chiral–racemic mixture of *S*-4-(2-methylbutyl)phenyl 4-decyloxybenzoate (CE6) which confirm this.

In addition, the results of light scattering experiments in the isotropic phase which measure the amplitude of fluctuations in two of the structural modes are reported. Whereas such measurements on highly chiral nematic liquid crystals have revealed that a weak deviation from mean field behaviour occurs only for one structural mode, these new results on 14P1M7 show strong deviations for both modes. These deviations seems to indicate that the behaviour of these systems just above the isotropic transition is quite complex, perhaps involving interactions due to the presence of strong fluctuations of both the orientational and positional order parameters.

2. Theory

Landau–de Gennes theory uses 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. For chiral systems, it is appropriate to represent ε_{ij} as a linear combination of five basic tensors or 'structural modes' with a wavevector $\mathbf{q}$. (See [1] for a more extensive description of this theory.) The five independent elements become the amplitudes $\varepsilon_m(\mathbf{q})$ of these five modes. The $m=0$ mode is not chiral and represents a nematic-like structure. The $m=\pm 1$ modes are conical spirals and the $m=\pm 2$ modes are planar spirals. The plus and minus signs refer to a left-handed or right-handed structure, respectively. In this formulation, a right-handed chiral nematic phase can be represented as 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 [6] and later more exact calculations were performed by numerous people. These later results confirm that the de Vries equation

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

where ρ is the optical activity, λ is the wavelength, n is the average refraction index, Δn is the optical anisotropy, and $\lambda_0=nP$, where P is the pitch, holds as long as Δn is small and λ is not too close to λ_0 [7].

The orientational order in the A* phase is very similar to the N* phase, except that instead of a continuous rotation of the director, the director rotates in steps of about 17° every 24 nm or so [8]. Since this distance is much less than the wavelength of visible light, the rotation should appear virtually continuous for visible light propagating along the helical axis. To confirm this, we ran an algorithm which numerically calculated the propagation of light through such a structure [9, 10] and the results were identical to the de Vries equation in the visible part of the spectrum.

If the free energy is written as an expansion up to second order in ε_{ij} and its spatial derivatives, then each mode contributes independently to the free energy density $F(q)$,

$$F(\mathbf{q})=(1/2)\sum_m\{A-mBq_0q+[B+(C/6)(4-m^2)]q^2\}|\varepsilon_m(q)|^2. \tag{2}$$

A, B, and C are coefficients in the expansion and q_0 is the chirality $4\pi/P$. The coefficient A is temperature dependent, $A(T)=A_0(T-T^*)$, where T is the temperature and T^* is the temperature at which a second order transition would occur for a non-chiral system. The mean square fluctuations of $\varepsilon_m(q)$ in the isotropic phase can be calculated from the equipartition theorem. We find that the inverse of the mean square fluctuations of $\varepsilon_m(q)$ should be linear in T, but the fluctuations in each mode tend to diverge at a different temperature, $T^*_m(q)$,

$$\begin{aligned} T^*_{\pm 2}(q) &= T^* + (B/A_0)(\pm 2q_0 q - q^2), \\ T^*_{\pm 1}(q) &= T^* + (B/A_0)(\pm 2q_0 q - [1 - C/2B]q^2), \\ T^*_0(q) &= T^* + (B/A_0)(-[1 + 2C/3B]q^2). \end{aligned} \tag{3}$$

Here q is the scattering vector $(2k \sin\theta)$, where k is the wavevector of the light in the sample and θ is half the scattering angle. This has been recently confirmed in chiral nematics, where the difference between $T^*_2(q)$ and $T^*_{\pm 2}(q)$ ranged from 0·2 to 0·8 K [11, 12].

The effect of fluctuations on the structural modes can be obtained following the method of Brazovskii [13–15], where a first correction to $A(T)$ due to fluctuations can be made. The result is

$$\tilde{A}(T) = A(T) + L\{k_B T q_0^2/[4\pi\sqrt{(B\tilde{A}(T))}]\}, \tag{4}$$

where $\tilde{A}(T)$ is the corrected $A(T)$ and $L$is the coefficient of the fourth order term in the free energy. As can be seen from figure 1, this correction to $A(T)$ causes the inverse of the mean square fluctuations in ε_m to bend away from the normal linear temperature dependence close to the transition, which is just what is observed in light scattering experiments on highly chiral nematic liquid crystals [12].

In a transition from the isotropic phase to a smectic phase, both orientational order and smectic order are involved. Prior theoretical work on the isotropic to nematic transition [16–18] has shown that smectic fluctuations can be taken into account in

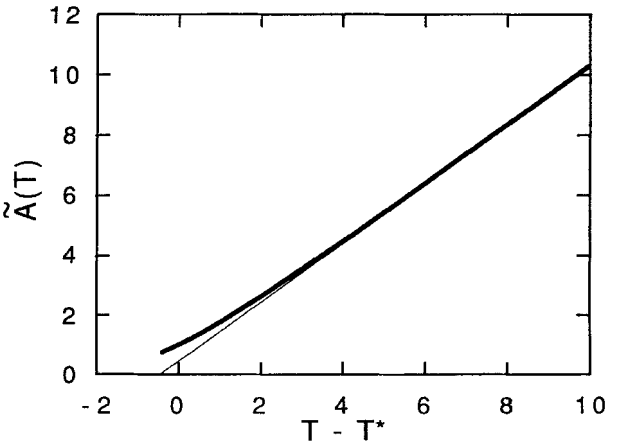

Figure 1. The correction to the coefficient $A(T)=A_0(T-T^*)$ due to orientational fluctuations in the isotropic phase using equation (4) with $A_0=1$ and $Lk_BTq_0^2/(4\pi\sqrt{B})=1$. Thick line: corrected value of $A(T)$. Thin line: Value of $\tilde{A}(T)$ according to a linear extrapolation from its behaviour significantly above T^*.

ways similar to Brazovskii's method. The result is that the inverse light scattering intensity bends down away from a linear temperature dependence due to smectic fluctuations acting through a third order term coupling the smectic and nematic order parameters. This has been verified by a number of experiments, where a smectic phase exists below a narrow nematic phase [17–19]. Certainly such effects should be even more important in the transition from the isotropic to the smectic A* phase, since it is likely that the fluctuations in both order parameters are of the same relative magnitude.

3. Experiments and results

The optical activity measurement system consisted of a 1000 W xenon lamp and a monochromater set to a bandpass of 2 nm. The polarizer in front of the sample was fixed, while the polarizer behind the sample was rotatable and controlled by a computer. Before entering the sample the light was chopped and the output of a silicon diode detector behind the second polarizer went to a lock-in amplifier. To measure the optical rotation angle, the computer would scan the second polarizer through 10° on either side of the minimum, fit the points to a second order polynomial, and determine the angle of minimum intensity. The angles measured in this way were accurate to less than one degree. The sample was located in an Instec HS-1 hot stage, with a temperature homogeneity of less than 10 mK.

The samples were (1) a 38 wt% mixture of one optical isomer of CE6 with a racemic mixture of both optical isomers of CE6 and (2) one optical isomer of 14P1M7. This particular mixture of CE6 was chosen so that it would have a pitch about equal to that of 14P1M7. Each was introduced into 10 μm glass cells, the surfaces of which had been coated with poly(1,4-butylene terephthalate) and rubbed. A planar texture in the chiral nematic phase of CE6 was obtained by slowly warming from the smectic A phase. A similar texture was obtained in the smectic A* phase of 14P1M7 by slowly cooling from the isotropic phase. Both textures contained a few defects which were visible under the microscope. To gauge what effect these defects had on the optical activity data, the experiments were repeated on several different samples. Although there were slight differences in the value of the optical activity from sample to sample (less than 10 per cent), the wavelength dependence remained virtually unchanged. In all cases, the optical activity measurements were made throughout most of the visible spectrum with the temperature held constant, after which the temperature was increased by one degree and the measurements repeated.

The chiral nematic range of CE6 and the smectic A* range of 14P1M7 are both about 4 K, therefore measurements at three different temperatures are reported for each. The results for the CE6 mixture are shown in figure 2. Since these measurements are all for wavelengths less than $\lambda_0 = nP$, it is clear that CE6 possesses a right-handed helix. These data do not follow equation (1) exactly, because the optical anisotropy and average index of refraction both decrease with an increase in wavelength. How strongly $(\Delta n)^2/n$ decreases with wavelength depends on how close to the visible the sample begins to absorb. For example, cholesteryl nonanoate begins to absorb somewhere below 200 nm, and $(\Delta n)^2/n$ decreases slower than $1/\lambda$ [20]. PAA begins to absorb at around 450 nm, and $(\Delta n)^2/n$ decreases faster than $1/\lambda$ [21]. CE6 and 14P1M7 begin to absorb at around 310 and 350 nm, respectively, so in an attempt to include this effect, the data were fitted to equation (1) with the addition that the constant containing $(\Delta n)^2/n$ was given a $1/\lambda$ dependence. Although reasonable, the validity of this is uncertain, so all results should be viewed as approximate. As can be seen from figure 2,

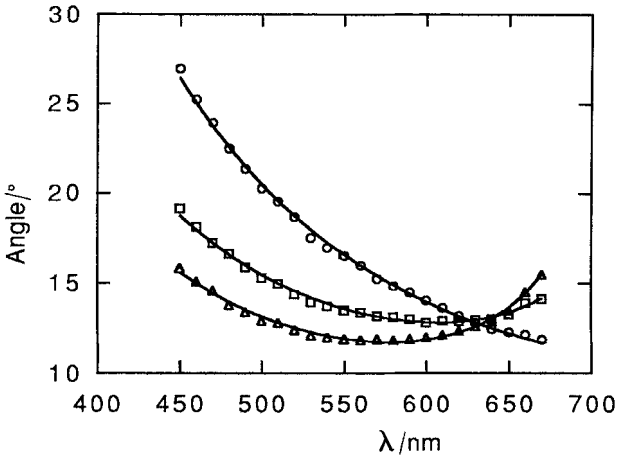

Figure 2. Angle of optical rotation as a function of wavelength at three temperatures in the chiral nematic phase of a mixture of 38 wt% CE6 and 62 wt% CE6R. The sample thickness is 10 μm. The solid lines represent least squares fits to equation (1), with $(\Delta n)^2/n$ proportional to $1/\lambda$. ○, 41·54°C; □, 42·54°C; △, 43·54°C.

Table 1. Least squares-fitted values for the optical activity of a 38 wt% mixture of the pure optical isomer of CE6 with a racemic mixture of both optical isomers using the function $\rho=(K/\lambda)\lambda_0^3/[\lambda^2(\lambda_0^2-\lambda^2)]$. The sample thickness is 10 μm.

T/°C	λ_0 nm	$K\times10^3$ ° cm^{-1} nm^2
41·54	993±8	1·928±0·005
42·54	784±1	1·464±0·004
43·54	746±1	1·213±0·004

this procedure gives good fits to the data and and allows both λ_0 and the constant containing $(\Delta n)^2/n$ to be estimated. The results are given in table 1. Notice that λ_0 decreases with increasing temperature and that the constant containing $(\Delta n)^2$ also decreases with temperature. This latter effect is most likely due to the fact that the order parameter (and hence Δn) is decreasing.

The results for 14P1M7 are shown in figure 3. This compound must possess a left-handed helix, since the optical activity is negative at wavelengths less than λ_0. The same fitting procedure was used, and again reasonable fits were obtained. The results for λ_0 and the constant containing $(\Delta n)^2/n$ are presented in table 2. Notice again that λ_0 decreases with temperature. This decrease is in close agreement whith the results of reflectivity measurements on this compound [22]. The values for λ_0 obtained from these optical activity measurements are about 5 per cent higher than those from the reflectivity measurements, but this can easily be the result of the approximate fitting procedure. A comparison of tables 1 and 2 reveals that the constant containing $(\Delta n)^2/n$ does not decrease with increasing temperature in 14P1M7 nearly as much as in CE6. This is quite understandable, since it is well known that the order parameter in smectic liquid crystals decreases much less with increasing temperature than in nematic liquid crystals.

The experimental apparatus used for the light scattering experiment was very similar to the one described in [12]. Light from a 5 mW He–Ne laser was passed

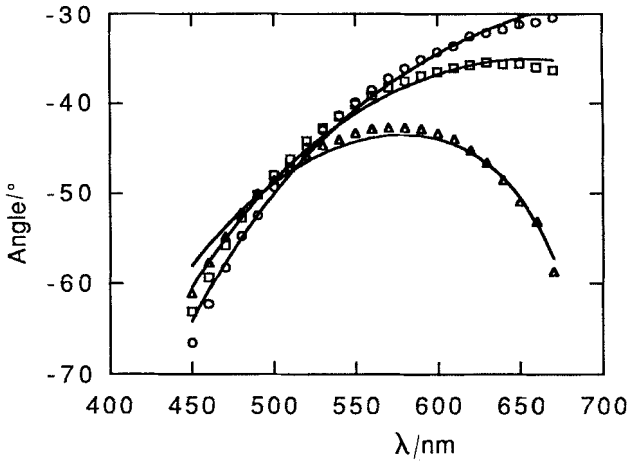

Figure 3. Angle of optical rotation as a function of wavelength at three temperatures in the smectic A* phase of 14P1M7. The sample thickness is 10 μm. The solid lines represent least squares fits to equation (1), with $(\Delta n)^2/n$ proportional to $1/\lambda$. ○, 91°C; □, 92°C; △, 93°C.

Table 2. Least squares-fitted values for the optical activity of 14P1M7 using the function $\rho=(K/\lambda)\lambda_0^3/[\lambda^2(\lambda_0^2-\lambda^2)]$. The sample thickness is 10 μm.

T/°C	λ_0/nm	$K\times10^3$ °cm^{-1} nm^2
91·00	966±12	−4·74±0·02
92·00	847±6	−4·67±0·03
93·00	747±2	−4·51±0·03

through a polarizer and quarter-wave plane before being focused on the sample. Light scattered from the sample at 165° passed through a second quarter-wave plate and second polarizer before being focused on a pinhole in front of a photomultiplier tube. The angle between the polarizers and the fast axis of the quarter-wave plates was always 45°, so the light incident on the sample was either right circularly polarized (RCP) or left circularly polarized (LCP). Likewise, the light detected by the photomultiplier tube was either RCP or LCP. In the experiment, the polarizers were in one of two positions: either RCP light was incident on the sample and RCP light was detected or LCP light was incident and LCP light was detected. The first case is only sensitive to the $m=-2$ structural mode, while the second case is only sensitive to the $m=2$ structural mode. The sample was contained between two pieces of glass separated by 100 μm and with their temperature controlled by an Instec HS-1 hot stage to better than 10 mK.

The light scattering results are shown in figure 4. The background intensity I_0 is determined by fitting the data to a $D/(T-T^*)+I_0$ temperature dependence, where D, T^*, and I_0 are fitting parameters. The fits improve as the lowest data points are dropped one by one, and the straight lines in the figure represent the fits with the lowest chi-squared per data point for the stronger scattering mode. This implies that the data do not follow the mean field temperature dependence for about a 4 K region just above the transition to the smectic A* phase. This is the same region where the optical activity behaves anomalously [23],and a broad peak shows up in DSC scans [3] and heat capacity measurements [5]. The difference between $T^*_{\frac{1}{2}}(q)$ and $T^*_{-2}(q)$ is 0·6 K, which is similar to results from measurements on chiral nematic systems [11, 12].

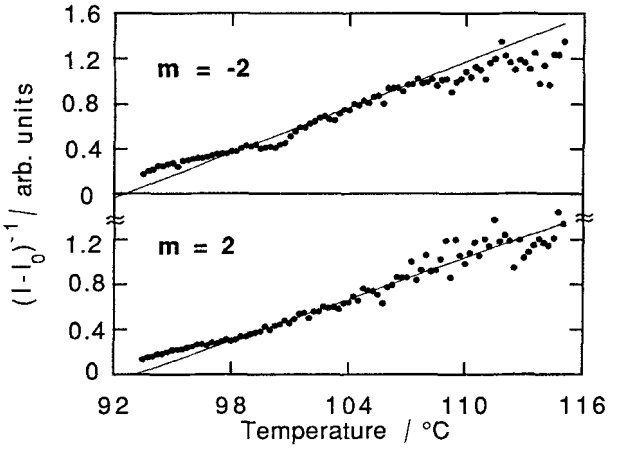

Figure 4. Inverse of the scattered light intensity versus temperature in the isotropic phase of 14P1M7 for two orientations of the polarizers. The upper data (weaker scattering) were obtained with RCP light incident on the sample and RCP light detected in the scattered light. The lower data (stronger scattering) were obtained with LCP incident light and LCP detected light. The sample thickness was 100 μm and the scattering angle was 165°. The straight lines represent the least squares fits to the function $I = D/(T - T^*) + I_0$ using only the data above 98°C.

4. Discussion

The similarity of the data in figures 2 and 3 indicates that the smectic A* phase behaves just like a chiral nematic phase as far as the optical activity is concerned. This is what we would predict given the proposed structure of the TGB phase, so these results add further support to this model. The fits to these data also point out that the order parameter in the smectic A* phase behaves like other smectic phases in that it does not decrease significantly with an increase in temperature.

The light scattering data for the isotropic phase are more difficult to interpret. If the bending up from the linear temperature dependence of the inverse scattering intensity is due to the presence of strong fluctuations, then they are strong enough to affect both structural modes, where only one was significantly affected in a nematic sample. This should not be surprising, however, since, if fluctuations are the cause of this behaviour, they must be strong enough to register on DSC scans and heat capacity measurements. The fact that the deviation does not continue to increase even more with decreasing temperature makes the behaviour even more complex. This could be explained by the presence of strong smectic fluctuations in addition to the orientational fluctuations. In a non-chiral sample, with narrow nematic range, these smectic fluctuations cause a downward bend in the inverse light scattering intensity. Perhaps the type of behaviour seen in 14P1M7 is due to the presence of both types of fluctuations, which tend to affect the inverse light scattering intensity of the isotropic phase in opposite directions. If the orientational fluctuations begin to grow strong at a higher temperature than the positional fluctuations, then data like those shown in figure 4 might result.

5. Conclusions

These optical activity measurements add one more piece of evidence for considering the smectic A* phase of 14P1M7 as a TGB phase. The evidence is mounting, especially considering the latest freeze-fracture transmission electron microscopy results [8].

The light scattering results indicate that the interactions in the vicinity of the isotropic to smectic A* transition are exceedingly complex. A few explanations involving both positional and orientational fluctuations have been suggested and seem reasonable. However, all of the data accumulated to date do not rule out the possibility of an additional, highly disordered phase in the 4 K region above the smectic A* phase of 14P1M7. Which of these is the case is a question which requires further evidence before it can be answered.

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References

[1] COLLINGS, P. J., 1992, *Mod. Phys. Lett.* B, **6,** 425.
[2] RENN, S. R., and LUBENSKY, T. C., 1988, *Phys. Rev.* A, **38,** 2132.
[3] GOODBY, J. W., WAUGH, M. A., STEIN, S. M., CHIN, E., PINDAK, R., and PATEL, J. S., 1989, *J. Am. chem. Soc.*, **111,** 8119.
[4] GOODBY, J. W., WAUGH, M. A., STEIN, S. M., CHIN, E., PINDAK, R., and PATEL, J. S., 1989, *Nature, Lond.*, **377,** 449.
[5] HUANG, C. C., LIN, D. S., GOODBY, J. W., WAUGH, M. A., STEIN, S. M., and CHIN, E., 1989, *Phys. Rev.* A, **40,** 4153.
[6] DEVRIES, H. L., 1951, *Acta crystallogr.*, **4,** 219.
[7] ONG, H. L., 1988, *Phys. Rev.* A, **37,** 3520.
[8] IHN, K. J., ZASADZINSKI, J. A. N., PINDAK, R., SLANEY, A. J., and GOODBY, J., 1992, *Science, N.Y.*, **258,** 275.
[9] BERREMAN, D. W., and SCHEFFER, T. J., 1970, *Phys. Rev.* A, **25,** 577; 1970, *Molec. Crystals liq. Crystals*, **11,** 395.
[10] BERREMAN, D. W., 1972, *J. opt. Soc. Am.*, **62,** 502; 1973, *Molec Crystals liq. Crystals*, **22,** 175.
[11] SINGH, U., and KEYES, P. H. (Private communication).
[12] WYSE, J. E., and COLLINGS, P. J., 1992, *Phys. Rev.* A, **45,** 2449.
[13] BRAZOVSKII, S. A., 1975, *Zh. éksp. teor. Fiz.*, **68,** 175; 1975, *Sov. Phys. JETP*, **41,** 85.
[14] BRAZOVSKII, S. A., and DMITRIEV, S. G., 1975, *Zh. ésp. teor. Fiz.*, **69,** 979 [1976, *Sov. Phys. JETP*, **42,** 497].
[15] BRAZOVSKII, S. A., and FILEV, V. M., 1978, *Zh. ésp. teor. Fiz.*, **75,** 1140 [1978 *Sov. Phys. JETP*, **48,** 573].
[16] POULIGNY, B., MARCEROU, J. P., LALANNE, J. R., and COLES, H. J., 1983, *Molec. Phys.*, **49,** 583.
[17] GOHIN, A., DESTRADE, C., GASPAROUX, H., and PROST, J., 1983, *J. Phys., Paris*, **44,** 427.
[18] ANISIMOV, M. A., GORODETSKII, E. E., and PODNEK, V. E., 1983, *Pis'ma Zh. teor. Fiz.*, **37,** 352 [1983, *JETP Lett.*, **37,** 414].
[19] ANISIMOV, M. A., LABKO, V. I., NIKOLAENKA, G. L., YUDIN, I. K., 1985, *Molec. Crystsls liq. Crystals Lett.*, **2,** 77.
[20] PELZL, G., and SACKMANN, H., 1973, *Z. phys. Chem.*, **254,** 354.
[21] CHATELAIN, P., and GERMAIN, M., 1964, *C.r. hebd. Séanc Acad. Sci., Paris*, **259,** 127.
[22] SRAJER, G., PINDAK, R., WAUGH, M. A., GOODBY, J. W., and PATEL, J. S., 1990, *Phys. Rev. Lett.*, **64,** 1545.
[23] FRAME, K. C., WALKER, J. L., and COLLINGS, P. J., 1991, *Molec. Crystals liq. Crystals*, **198,** 91.