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The effect of biasing electric field on the soft mode in the vicinity of the ferroelectric phase transition in liquid crystals

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The complex permittivity of a room-temperature ferroelectric liquid crystal 4-*n*-octyloxy benzoic acid 4′-[(2-methylbutyloxy)carbonyl]phenyl ester, has been measured in the vicinity of the phase transition in the frequency range 40 Hz–300 kHz. In the para-electric phase the contribution ε_s of the soft mode to the permittivity and the soft-mode relaxation frequency f_s satisfy the Curie–Weiss law. Under a biasing field E, the helicoidal structure is unwound, and ε_s and f_s can then be measured even in the ferroelectric phase. On the other hand, the phase transition is smeared under the influence of E. This smearing results in deviations from the Curie–Weiss law for both ε_s and f_s in the vicinity of the transition. On increasing E, the maximum of the permittivity, ε_{max}, is lowered and shifted to higher temperatures. Both the shift and ε_{max}^{-1} are proportional to $E^{2/3}$. From experimentally found dependences, some constants in the free energy are determined.

1. Introduction

Ferroelectric properties can appear in tilted chiral smectic mesophases (C*, I*, F*, G*, J*, H*, K*) because their local symmetry, C_2, permits a spontaneous dipole moment. It arises along the polar two-fold axis lying in the plane of the smectic layers. The ferroelectric phase can be reached by cooling either from a cholesteric phase or from a smectic A phase. From all of the possible phase transitions yielding a ferroelectric phase, only the $S_C^* \leftrightarrow S_A$ transition has been described theoretically so far [1]. It is generally considered that this transition is due to softening of the spatially inhomogeneous fluctuations of the molecular tilt with respect to the normal to the smectic layer when the transition is approached from the S_A phase. Below the transition, in the ferroelectric phase, a spontaneous tilt of the molecules appears, the directions of which precess about the smectic-layer normal, a helicoidal structure being formed. In the vicinity of the transition the soft mode gives a contribution ε_s to the permittivity. The temperature dependence of ε_s was derived [2] from the free energy [1] constructed for the $S_C \leftrightarrow S_A$ transition and obeys the Curie–Weiss law, which is truncated at the transition (owing to freezing of the helicoidal structure) before the divergence is reached. Similarly, the relaxation frequency of ε_s is a linear function of temperature near the transition [2].

In the S_A phase ε_s is the only contribution to the permittivity due to the occurrence of the phase transition [3–5]. But in the S_C^* phase ε_s is overwhelmed by the contribution ε_G from the Goldstone mode. This is a vibration of the helicoidal structure that appears below the transition [2, 3, 6]. Principally, ε_s and ε_G can be distinguished by their different relaxation frequencies f_s and f_G. But near the transition, f_s and f_G can differ by only one order of magnitude [5], i.e. ε_s can be overwhelmed by ε_G even at f_s.

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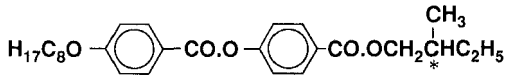
Therefore for the determination of ε_s near the transition it is necessary to unwind the helicoidal structure; then $\varepsilon_G \equiv 0$. The unwinding is achieved by decreasing the sample thickness d to a value comparable to the helicoidal pitch p [7]. In such a case, owing to the polar anchoring on the sample boundaries, a twist along the sample thickness takes place [8]. Deformations of the twist in the electric field contribute to the permittivity with a similar strength and can exhibit a similar relaxation frequency to the Goldstone mode [9]. For still thinner samples ($d \approx 1\,\mu$m), which might provide a spatially homogeneous structure [10], the smectic layers are usually tilted [11] from the sample-plane normal, which results in a complicated defect structure. Moreover, the properties of extremely thin samples are determined mostly by the boundary conditions.

Unwinding the helicoidal structure by an electric or a magnetic D.C. field in thick samples is the best way to obtain a homogeneous structure with which to determine ε_s in the vicinity of the transition in the S_C phase. On the other hand, the field considerably influences the phase transition as well as the ε_s contribution.

A study of the phase transition and the soft-mode properties under a D.C. electric field by investigating the temperature–frequency dependences of the permittivity is the aim of this paper.

2. Experimental results

The material studied was 4-*n*-octyloxy benzoic acid 4′-[(2-methylbutyloxy)-carbonyl]phenyl ester



which exhibits a ferroelectric S_C^* phase only on cooling. Its phase sequence is

$$C\ 34°C\ (S_C^*\ 32°C)\ S_A\ 56°C\ I.$$

Preliminary permittivity measurements and temperature dependences of spontaneous tilt angle and polarization have been published in [5, 6].

The samples filled the space between two glass plates separated by 25 μm with an ITO electrode area of 3 mm × 3 mm. The glass electrodes were coated with a polyimide layer rubbed with a velvet cloth to achieve planar alignment. By applying an A.C. field, 20 Hz, 4×10^3 kV m^{-1}, the alignment in the S_A phase was improved, resulting in mutually parallel smectic layers perpendicular to the glass plates. The alignment could be checked during the experiment by observation with a polarizing microscope. The permittivity measurements were performed at temperatures stabilized to within 0·01 K using a Hewlett–Packard 4192A impedance analyser controlled by micro-computer. At any temperature the frequency range 40 Hz–300 kHz was scanned in a logarithmic scale. The cooling run was repeated under a D.C. biasing field E of 4×10^2 kV m^{-1}, which ensured the unwinding of the helicoidal structure in the S_C^* phase. The polarity of the bias field was changed before every measurement to avoid compensation of the bias field by the free-charge distribution.

In the S_A phase a single relaxation mechanism contributes to the permittivity in the frequency range studied. The contribution decreases on departing from the transition and can be detected up to a temperature of $T_c + 2$ K at $E = 0$ and up to $T_c + 0{\cdot}7$ K at $E = 4 \times 10^2$ kV m^{-1}; here T_c is the transition temperature in zero field.

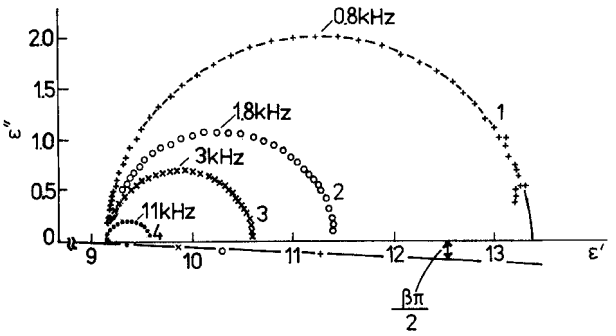


Figure 1. Cole–Cole diagrams in the S_A phase at $E = 0$. The inclination of the circular arcs from the real axis defines the value of β. The diagrams correspond to the following temperatures: (1) $T - T_c = 0{\cdot}02\,K$; (2) $0{\cdot}07\,K$; (3) $0{\cdot}15\,K$; (4) $0{\cdot}53\,K$.

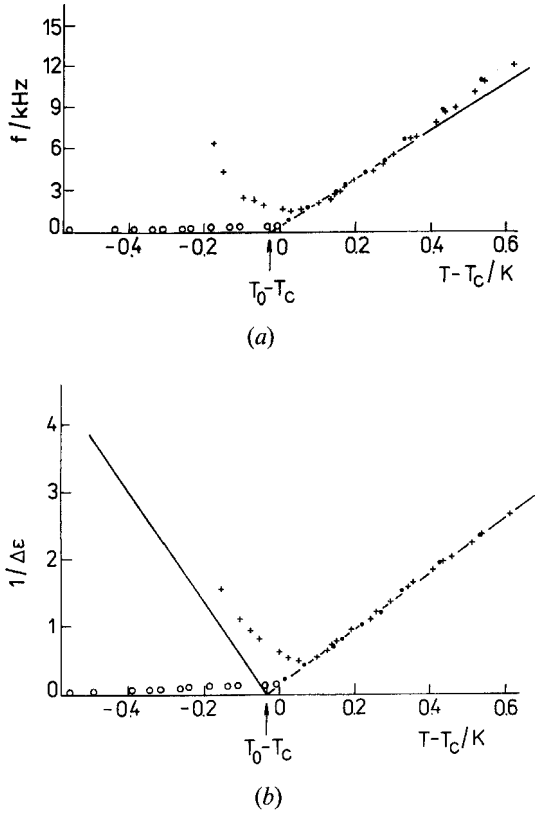


Figure 2. Temperature dependences of the soft-mode relaxation frequency (*a*) and the reciprocal of the soft-mode dielectric strength (*b*) at $E = 0$ (●) and at $E = 4 \times 10^2\,kV\,m^{-1}$ (+). The temperature dependences of the Goldstone-mode relaxation frequency (*a*) and the corresponding reciprocal dielectric strength (*b*) are denoted by open circles (○). T_0 is an extrapolated temperature; T_c is the transition temperature in zero field. For $T - T_c > 0{\cdot}3\,K$, $f(T - T_c)$ deviated from a linear dependence for both $E = 0$ and $E = 4 \times 10^2\,kV\,m^{-1}$.

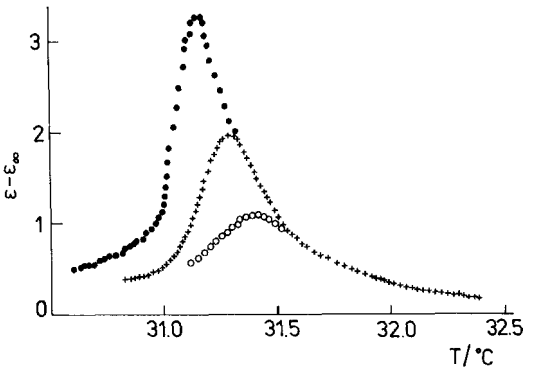


Figure 3. Temperature dependence of the permittivity at $f = 90$ Hz measured at $10\,\mathrm{kV\,cm^{-1}}$ (○), $E = 2\,\mathrm{kV\,cm^{-1}}$ (●), $4\,\mathrm{kV\,cm^{-1}}$ (+).

In these temperature ranges the permittivity obeys the Cole–Cole expression (see figure 1 for $E = 0$)

$$\varepsilon_\omega - \varepsilon_\infty \propto \frac{1}{1 + (if/f_r)^{1-\beta}}$$

with $\beta = 0{\cdot}035$ rad, thus showing a rather small departure from Debye behaviour. The relaxation frequency in the S_A phase exhibits a linear temperature dependence with critical slowing down at T_c (see figure 2 (*a*)) proving that the relaxation mechanism can be ascribed to the soft mode. The temperature dependence of the reciprocal difference $(\Delta\varepsilon)^{-1} = (\varepsilon_0 - \varepsilon_\infty)^{-1}$ determined from the Cole–Cole diagram obeys the Curie–Weiss law (see figure 2 (*b*)), as expected for the soft-mode contribution to the permittivity (see equation (6*a*) in §3).

In zero field T_c was determined optically from the change in the sample texture. On the other hand, an extrapolated temperature $T_0 < T_c$ can be determined from both $(\Delta\varepsilon)^{-1}(T)$ and $f_r(T)$ dependences (see figures 2 (*a*, *b*)), and we find $T_c - T_0 \approx 0{\cdot}03$ K.

In the S_C^* phase the contribution from the Goldstone mode prevails in zero field. The soft-mode contribution is not simultaneously distinguished, being 20 times

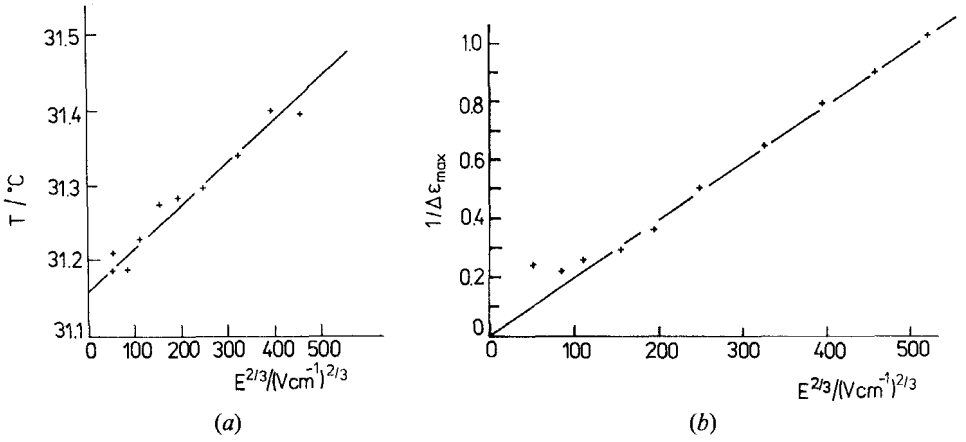


Figure 4. Field dependences of the temperature T_{max} for the maximum value of the permittivity ε_{max} (measured at a frequency of 90 Hz) (*a*), and of $(\Delta\varepsilon_{max})^{-1} = (\varepsilon_{max} - \varepsilon_\infty)^{-1}$ (*b*).

smaller, but can be measured with the structure unwound by a field of 4×10^2 kV m^{-1}. The temperature dependences of the reciprocal soft-mode contribution (see figure 2 (*b*)), and of the soft-mode relaxation frequency (see figure 2 (*a*)) are non-linear in the vicinity of T_c and in the S_C phase.

The effect of a D.C. bias field E on the phase transition was studied by monitoring the permittivity on continuous cooling from the S_A to the unwound S_C phase. The cooling run was repeated for different values of E. The cooling rate was 0·1 K min^{-1} and the measuring frequency was 90 Hz. For increasing E, the maximum ε_{max} of $\varepsilon(T)$ near T_c is lowered and becomes broader (see figure 3). The dependence of the reciprocal of $\Delta\varepsilon_{max} = \varepsilon_{max} - \varepsilon_\infty$ on E is shown in figure 4 (*b*); here ε_∞ is the high-temperature permittivity. Moreover, on increasing E, the temperature T_{max} for the maximum value of ε increases (see figure 4 (*a*)). Both of the dependences are linear functions of $E^{2/3}$.

3. Phase transition under a high D.C. electric field

For a D.C. electric field higher than a coercive field E_c the helicoidal structure in the S_C^* phase becomes unwound. The free-energy density describing the phase transition from S_C^* to S_A under $E > E_c$ is

$$g = \tfrac{1}{2}a\theta^2 + \tfrac{1}{4}b\theta^4 + \frac{1}{2\chi}P^2 + CP\theta - PE, \tag{1}$$

where $a = \alpha(T - T^*)$, $\chi = (\varepsilon_\infty - 1)/4\pi$ is the high-temperature dielectric susceptibility. Expression (1) is similar to the free-energy density derived in [2], but all of the gradient terms describing the spatial modulation of θ and P are omitted here. Minimizing g with respect to P, we obtain $P = \chi(E - C\theta)$, which, substituted into g, gives

$$g = \tfrac{1}{2}(a - \chi C^2)\theta^2 + \tfrac{1}{4}b\theta^4 + C\chi\theta E. \tag{2}$$

In this free-energy function the inverse soft-mode susceptibility is renormalized by $a - \chi C^2 = \alpha(T - T_0)$, which defines a new critical temperature, the transition temperature to the unwound structure, $T_0 = T^* + \chi C^2/\alpha$. Further minimization with respect to θ allows us to determine $\theta(E, T)$ as a solution of the equilibrium equation

$$\alpha(T - T_0)\theta + b\theta^3 + C\chi E = 0. \tag{3}$$

This equation has only one real solution for $T \geqslant T_k$ and three real solutions for $T < T_k$, where T_k is a critical temperature at which the discriminant $D = (C\chi E/2b)^2 + [\alpha(T - T_0)/3b]^3$ of equation (3) vanishes:

$$T_k = T_0 - 3\left(\frac{C^2\chi^2E^2b}{4\alpha^2}\right)^{1/3}.$$

The solution for $T \geqslant T_k$,

$$\theta = \left(-\frac{C\chi E}{2b} + D^{1/2}\right)^{1/3} + \left(-\frac{C\chi E}{2b} - D^{1/2}\right)^{1/3}, \tag{4}$$

is valid in the vicinity of T_0. It can be shown that for $T < T_k$ one solution corresponds to the maximum of the free energy (2), the other to a local minimum; the third, corresponding to the minimum of g, turns continuously into the solution (4) at T_k. Under the external electric field, θ has a non-zero value even in the high-temperature phase. Therefore the phase transition is not defined, because θ is non-zero everywhere.

From the free energy (1) the dielectric susceptibility of the soft mode can be determined as

$$\chi_s = \frac{\chi^2 C^2}{a + 3b\theta^2 - \chi C^2}, \tag{5}$$

where θ is the equilibrium value of the tilt angle. If $E = 0$, the helicoidal structure appears at T_c and expression (5) gives the same results as in [2]:

$$\chi_s = \begin{cases} \dfrac{\chi^2 C^2}{\alpha(T - T_c) + Kq^2} & (T \geqslant T_c), \quad (6a) \\ \dfrac{\chi^2 C^2}{2\alpha(T - T_c) + Kq} & (T < T_c), \quad (6b) \end{cases}$$

where K is the elastic constant, q is the wavevector of the space modulation, and $T_c = T_0 + \chi C^2/\alpha$ is the transition temperature for $E = 0$. If $E > E_c$, expression (4) should be inserted into equation (5) for $T \geqslant T_k$. To determine χ_s close to T_0, we use, for simplicity, a Taylor expansion of expression (4) around T_0:

$$\theta(T, E) \approx -\left(\frac{C\chi E}{b}\right)^{1/3} + \frac{\alpha(T - T_0)}{3b}\left(\frac{b}{C\chi E}\right)^{1/3}. \tag{7}$$

To interpret our experiments, we calculate the temperature T_{max} for which χ_s has a maximum value χ_{max} and χ_{max} itself as functions of the applied field. The condition for χ_{max} is equivalent to the condition

$$\frac{\partial \chi_s^{-1}}{\partial T} = \frac{\alpha}{\chi^2 C^2} + \frac{6b\theta}{\chi^2 C^2}\frac{\partial \theta}{\partial T} = 0. \tag{8}$$

In equation (8)

$$\frac{\partial \theta}{\partial T} = -\frac{\partial G}{\partial T}\left(\frac{\partial G}{\partial \theta}\right)^{-1},$$

where G is the left-hand side of the equilibrium equation (3); it gives

$$\frac{\partial \chi_s^{-1}}{\partial T} = \frac{\alpha^2(T - T_0) - 3b\alpha\theta^2}{\chi^2 C^2[\alpha(T - T_0) + 3b\theta^2]}.$$

Equation (8) is valid if

$$\alpha(T_{max} - T_0) - 3b\theta^2 = 0.$$

Using equation (3), we obtain an equivalent equation

$$4\alpha(T_{max} - T_0)\theta + 3C\chi E = 0. \tag{9}$$

Using the approximate expression (7) for $\theta(T, E)$, we obtain the solution of equation (9) as

$$\Delta T_{max} = T_{max} - T_0 = \frac{3}{2\alpha}(bC^2\chi^2E^2)^{1/3}. \tag{10}$$

This solution gives a temperature shift of the maximum of the soft mode susceptibility with $E > E_c$. Inserting T_{max} into expression (5), we obtain

$$\frac{1}{\chi_{max}} = \frac{9}{4\chi^2 C^2}(bC^2\chi^2E^2)^{1/3}. \tag{11}$$

4. Discussion and conclusions

The frequency dependence of the permittivity is in accord with the Cole–Cole formula at all measured temperatures and zero electric field. In the S_A phase the relaxation mechanism contributing to the permittivity corresponds to the soft mode. The temperature dependence opf the reciprocal soft-mode contribution $(\Delta\varepsilon)^{-1}$ obeys the Curie–Weiss law. This contribution is not greatly affected by the bias field except in the vicinity of the transition (see figure 2(*b*)). The extrapolation to zero of $(\Delta\varepsilon)^{-1}(T)$ defines a temperature T_0, giving $T_c - T_0 = Kq^2/\alpha \approx 0{\cdot}03\,\mathrm{K}$, the slope determines the value $\alpha/\chi^2C^2 \approx 50\,\mathrm{K}^{-1}$ and $(\Delta\varepsilon)^{-1}(T_c) = Kq^2/4\pi C^2\chi^2 \approx 0{\cdot}14$. These values allow us to estimate the constants in the free-energy function (1). Taking measured values for the high-temperature dielectric susceptibility $\chi = 0{\cdot}56$, $q = 2\pi/p$, where p is the helical pitch, $\approx 3\,\mu\mathrm{m}$, and the estimated value $K \approx 5 \times 10^{-12}\,\mathrm{N}$ [12], the coupling constant C is determined as ≈ 20 and $\alpha \approx 6{\cdot}2 \times 10^3$. The low value of $T_c - T_0 \approx 0{\cdot}03\,\mathrm{K}$ indicates that the modulation of the S_C^* structure is only a slight perturbation, which does not influence the phase transition appreciably. Similarly, the low estimated value of $T_0 - T^* = \chi C^2/\alpha \approx 0{\cdot}035\,\mathrm{K}$, which is the difference between the transition temperature T^* of the non-polar substance (i.e. the racemic mixture) and that, T_0, of the polar homogeneous substance, shows that the polar interactions are rather weak in this material. The same result was found for other chiral smectics (e.g. DOBAMBC [13]) and for a ferroelectric liquid crystal with high spontaneous polarization [14].

The constant C determines the value of the spontaneous polarization P_s originating from the bilinear interaction P and θ: $P_s = \chi C\theta$. At $T_c - T = 4\,\mathrm{K}$ the tilt angle has nearly reached its saturated value $\theta \approx 0{\cdot}26\,\mathrm{rad}$ [6]; then the calculated $P_s \approx 0{\cdot}9\,\mu\mathrm{C\,cm}^{-2}$; it is only 20 per cent of the measured P_s value [6]. The rest of P_s has to originate from the higher biquadratic coupling, not included in the free energy (1), but which becomes important far below T_c [15].

For $E > E_c$, $(\Delta\varepsilon)^{-1}(T)$ exhibits a non-linear dependence in the vicinity of T_c. This dependence reflects a broadening of the phase transition, which is not strictly defined when E is applied. At low temperatures $(\Delta\varepsilon)^{-1}(T)$ asymptotically approaches the straight line (shown in figure 2(*b*)) that crosses the temperature axis at T_0 and has slope $-\chi^2C^2/2\alpha$, in magnitude twice that in the high-temperature phase. This line represents the behaviour of a hypothetical homogeneous structure in zero field. The broadening of the phase transition is also reflected in the temperature dependence of the soft-mode relaxation frequency. It behaves similarly to $(\Delta\varepsilon)^{-1}(T)$. The gradual broadening on increasing field strength is clearly visible on deformation of the soft-mode contribution anomaly (see figure 3). The peak at the phase transition is still broader and lower and shifted to higher temperatures on increasing E. The temperature shift ΔT_{max} of the permittivity maximum ε_{max} is proportional to $E^{2/3}$, as is the reciprocal of ε_{max}. From the slope of the latter dependence (see figure 4). $(9/4\pi\chi^2C^2)(bC^2\chi^2)^{1/3} \approx 1{\cdot}94 \times 10^2\,\mathrm{V}^{-2/3}\,\mathrm{cm}^{2/3}$, the coefficient b in the free energy is estimated as $b \approx 0{\cdot}21$ c.g.s.u. The function $(\Delta\varepsilon_{max})^{-1}(E^{2/3})$ is extrapolated to zero because the permittivity of a homogeneous structure should diverge at T_0 if $E = 0$. However, in reality, such a structure does not exist when $E < E_c$, where E_c is the critical unwinding field. It is interesting to note that with solid ferroelectrics exhibiting a second-order phase transition similar field dependences $\varepsilon_{max}^{-1} \propto E^{2/3}$ and $T_{max} \propto E^{2/3}$ have been found [16].

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References

[1] INDENBOM, V. L., PIKIN, S. A., and LOGINOV, E. B., 1976, *Kristallografiya*, **21**, 632.
[2] MARTINOT-LAGARDE, PH., and DURAND, G., 1980, *J. Phys., Lett. Paris*, **41**, L32.
[3] LEVSTIK, A., ŽEKŠ, B., LEVSTIK, I., BLINC, R., and FILIPIČ, C., 1979, *J. Phys., Paris, Colloq.*, **40**, C3–303.
[4] BAHR, CH., and HEPPKE, G., 1987, *Liq. Crystals*, **2**, 825.
[5] PAVEL, J., and GLOGAROVÁ, M., 1988, *Ferroelectrics*, **84**, 241.
[6] PAVEL, J., GLOGAROVÁ, M., and DĄBROWSKI, R., 1988, *Ferroelectrics*, **81**, 1371.
[7] CLARK, N. A., and LAGERWALL, S. T., 1984, *Appl. Phys. Lett.*, **36**, 899.
[8] GLOGAROVÁ, M., and PAVEL, J., 1984, *J. Phys., Paris*, **45**, 143.
[9] GLOGAROVÁ, M., and PAVEL, J., 1984, *Molec. Crystals liq. Crystals*, **114**, 249.
[10] PAVEL, J., 1984, *J. Phys., Paris*, **45**, 137.
[11] CLARK, N. A., RICKER, T. P., and MACLENNAN, J. E., 1988, *Ferroelectrics*, **85**, 79. HIJI, N., CHANDANI, A. D. L., NISHIYAMA, S.-I., OUCHI, Y., TAKEZOE, H., and FUKUDA, A., 1988, *Ferroelectrics*, **85**, 99.
[12] MARTINOT-LAGARDE, PH., and DURAND, G., 1980, *J. Phys., Paris*, **42**, 269.
[13] MEYER, R. B., LIEBERT, L., STRZELECKI, L., and KELLER, P., 1975, *J. Phys., Paris, Lett.*, **36**, L69.
[14] BAHR, CH., and HEPPKE, G., 1987, *Molec. Crystals liq. Crystals*, **151**, 69.
[15] ŽEKŠ, B., 1984, *Molec. Crystals liq. Crystals*, **114**, 259.
[16] WIEDER, H. H., 1959, *J. appl. Phys.*, **30**, 1010.