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Quasicritical behavior of the low-frequency dielectric permittivity in the isotropic phase of liquid crystalline materials

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Results presented give evidence of the existence of *quasicritical, fluidlike* behavior in the isotropic phase of 4-cyano-4-pentyl-biphenyl (5CB) for frequencies ranging from the static to the ionic-dominated [low-frequency (LF)] region. Despite the boost of dielectric permittivity on lowering the frequency below 1 kHz, values of the isotropic-nematic transition discontinuity ($\approx$1.1 K) and the critical exponent α ($\approx$0.5) remain constant. It is shown that the contribution from residual ionic impurities is a linear function of temperature in the critical, prenematic fluctuation-dominated region. The validity of the *fluidlike* and *critical* behavior for LF dielectric permittivity confirmed results of a derivative analysis of the experimental data: $d\varepsilon/dT \propto (T-T^*)^{-\alpha}$, originally proposed for critical mixtures. Results of a preliminary test in the isotropic phase of 4-decyl-4′-isothiocyanatobiphenyl (10BT), on approaching the smectic-*E* phase, may indicate a general validity of results obtained.

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I. INTRODUCTION

In recent years the complex liquid [1–18], *fluidlike* and *critical* [1–8] nature of the isotropic phase (I) of nematic liquid crystals was shown owing to the application of experimental techniques. These included the transient grating Kerr effect [9–12], dynamic light scattering [13–16], ultrasonic birefringence [17,18], and ''*linear*'' and ''*nonlinear*'' dielectric permittivity studies [4–8]. The mentioned fluidlike description [1–8] is a point of view on the isotropic phase of nematogens whose picture was for several decades dominated by the simple mean-field description within the Landau–de Gennes [19,21] or Maier-Saupe [19–23] models. The unique feature appearing in linear and nonlinear dielectric studies is the fact that in the static case, when relaxation processes can be neglected, the same dependences are valid on approaching the nematic (*N*), smectic-*A* (Sm*A*), and smectic-*E* (Sm*E*) phases [4–8,24,25]:

$$\mathcal{E}_{\mathrm{NDE}}(T)=\frac{A_{\mathrm{NDE}}}{T-T^*}=\frac{2}{3a}\varepsilon_0\frac{(\Delta\varepsilon^0)^2}{(T-T^*)^{\gamma}}, \tag{1a}$$

$$\varepsilon(T)=\varepsilon^*+a_T(T-T^*)+A_T(T-T^*)^{1-\alpha},$$

$$T^*=T^C-\Delta T, \quad T>T^C, \tag{1b}$$

where $\mathcal{E}_{\mathrm{NDE}}=(\varepsilon^E-\varepsilon)/E^2$ is the measure of the nonlinear dielectric effect (NDE) ε denotes dielectric permittivity in a weak, measuring radio frequency electric field, ε^E is dielectric permittivity under additional strong, steady electric field, T^* is the virtual critical temperature, T^C is the clearing temperature, ΔT is the discontinuity of the isotropic-mesophase transition, $\Delta\varepsilon^0$ denotes the molecular anisotropy of dielectric permittivity in the zero-frequency limit, and a^{-1} is the susceptibility amplitude.

When discussing these dependences it is noteworthy that they can also be derived from relations for the homogeneous phase of critical mixtures, in agreement with the fluidlike and critical description [4,6–8]. Particularly noteworthy is the fact that the reciprocal of the static NDE is a linear function from $T_x \approx T^C+40\,\mathrm{K}$ up to T_C, without any distortions [6,8]. The temperature T_x can be recognized as a point where fluctuations shrink to two or three molecules [6,9–12]. This allowed for a precise estimation of ΔT [4,6,8,24,25]. Regarding dielectric permittivity, relation (1b) describes experimental data even 100 K away from T_C [6,8,24,25]. This behavior may be associated with the fact that the static dielectric permittivity is not directly coupled to pretransitional fluctuations. It originates from cancellation of permanent dipole moments due the prenematic arrangement. This occurs only if the permanent dipole moments are predominantly parallel to the long axis of the rodlike molecule [20,21]. The behavior of the static dielectric permittivity suggests that prenematic ordering may occur also for $T>T_x$, but the number of arranged molecules is too small to be recognized as a fluctuation by fluctuation-sensitive methods [6]. It has to be stressed that $\varepsilon(T)$ studies in the static region (1–100 kHz) allowed for an unequivocal estimation of the exponent $\alpha = 0.5 \pm 0.02$ [4,7,8,24,25]. Such a reliable estimation was difficult in density or heat capacity measurements previously applied. Pretransitional anomalies of these properties are weak, limited only to a few degrees from [26–32].

Decreasing the frequency below $f=1$ kHz dielectric permittivity boosts the value as a result of the influence of residual ionic impurities [20,21]. The behavior of the dielectric permittivity in the low-frequency (LF) region is still a puzzling problem. There have been several phenomenological attempts to parametrize dielectric permittivity at lower frequencies mainly in terms of space charge polarization [33–43]. The majority of those studies were conducted for *n*-pentylcyanobiphenyl (5CB) which is considered as a model material. They concentrated on parametrization of the frequency or time evolution of the dielectric permittivity for a few temperatures in the isotropic or nematic phase.

To the best of the authors' knowledge, there have been no studies taking into account the possible influence of complex liquid structures on results and there have been no attempts to portray the temperature evolution of dielectric permittivity at lower frequencies.

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Results discussing both these factors are presented in this paper. They show the essential influence of premesomorfic fluctuations on the behavior of dielectric permittivity even remote from T^C. Studies were conducted in the isotropic phase of 4-cyano-4-pentyl-alkylbiphenyl (5CB), especially purified to reduce residual ionic impurities [21]. In LF dielectric studies 5CB is used as the classical, basic material. The *I-N* transition in 5CB characterizes the smallest value of ΔT in the *n*-cyanobiphenyl series [8,25], and hence it exhibits particularly pronounced pretransitional effects [5,8,25]. To test the range of the general validity of the results obtained, preliminary investigations were also conducted for the I-SmE transition in 4-decyl-4′-isothiocyanatobiphenyl (10BT), the material with the smallest discontinuity $\Delta T \approx 5.6\,\mathrm{K}$ in the *n*BT homologous series [25].

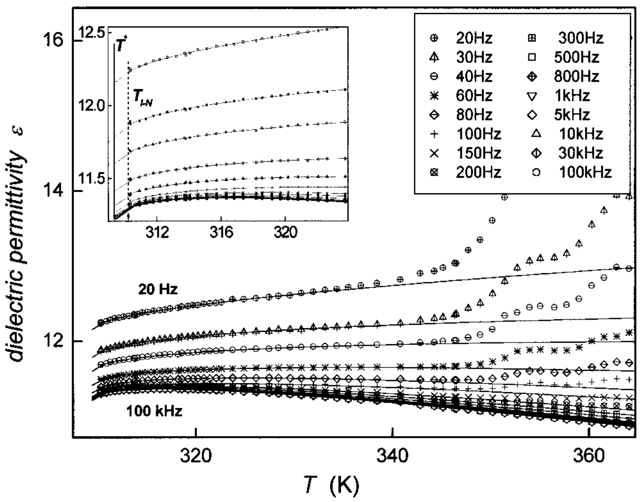

FIG. 1. Results of dielectric permittivity measurements in the isotropic phase of 5 CB. The dashed arrow indicates the nematic clearing temperature. Solid curves are parametrized by relation (1b) with the parameters given in Table I.

II. EXPERIMENT

The sample of 5CB ($T_{I\text{-}N} \approx 308.4\,\mathrm{K}$) was synthesized in the Technical Military Academy in Warsaw (Poland) and obtained due to the courtesy of Krzysztof Czupryński and Roman Dąbrowski. Prior to measurements, the sample was carefully degassed. The sample was placed in a measurement capacitor made from Invar: the gap of the capacitor was $d = 0.5\,\mathrm{mm}$, diameter $2r = 20\,\mathrm{mm}$, and hence $C_0 = 7.55\,\mathrm{pF}$. A quartz ring was used as the spacer so that the sample was only in contact with the Invar, quartz, and Teflon. The capacitor was placed in a specially designed thermostatted jacket fed from the Julabo FP45 HD thermostat with external circulation. It made changes of temperature with resolution ±0.01 K possible. Temperature was measured by means of a miniature platinum resistor (DIN 43 260) placed in one of the covers of the capacitor and a Keithley 195A multimeter. Additionally, the temperature gradient between the covers of the capacitor was scanned by a copper-Constantan thermocouple. Dielectric permittivity was measured using a Solartron 1260A impedance analyzer with voltage $U = 1$ V and averaging over 100–1000 periods, which gave a permanent 5-digit resolution. Data were analyzed by means of Origin 3.5 and 5.0 software.

III. RESULTS AND DISCUSSION

The temperature dependences of dielectric permittivity for a series of tested frequencies are shown in Fig. 1. On decreasing the frequency below $f = 1\,\mathrm{kHz}$, the influence of ionic impurities boosts the value of the dielectric permittivity. Despite this fact, Eq. (1b) remains valid even for $f = 20\,\mathrm{Hz}$ (see Table I and solid lines in Fig. 1). It is particularly noteworthy that for all frequencies the critical exponent $\alpha \approx 0.5$ and the discontinuity ΔT are the same, within the limit of experimental error. The fact that the fluidlike, critical equation (1b) remains valid also in the ionic-dominated region confirms the distortion-sensitive derivative analysis of experimental data (Fig. 2):

$$\frac{d\varepsilon}{dT} = a_\varepsilon + A_\varepsilon (1-\alpha)(T-T^*)^{-\alpha}, \quad \alpha \approx 0.5. \qquad (2)$$

Such a dependence was originally proposed by Mistura [44] for critical mixtures to show the relationship between the anomaly of dielectric permittivity with that of the specific heat. Only recently were its first successful experimental tests made: in critical [7,45] and isotropic phases of mesogens [6–8,25]. The latter finding additionally supported the mentioned fluidlike hypothesis [3,6].

However, in correlation length units (ξ) the distance (l) at which mobile ions are moved by the electric field is $[l(f)/\xi(T)]_{T\to T^*} \to 0$. Figure 3 presents an analysis aimed at resolving the boost of the value of $\varepsilon(T)$ on decreasing the frequency. There are shown temperature dependences of

TABLE I. Results of fitting temperature dependences of dielectric permittivity in the isotropic phase of 5CB compounds by means of relation (1b). An asterisk denotes that the value of the exponent was fixed.

Frequency	ε^*	$a_\varepsilon(\mathrm{K}^{-1})$	$A_\varepsilon(\mathrm{K}^{1-\alpha})$	$T^*(\mathrm{K})$	$\phi = 1-\alpha$
20 Hz	12.162	−0.003	0.09	309.4	0.5*
30 Hz	11781.	−0.004	0.10	309.4	0.5*
40 Hz	11.598	−0.006	0.098	309.4	0.5*
60 Hz	11.41	−0.0084	0.096	309.4	0.5*
80 Hz	11.31	−0.094	0.1045	309.4	0.49
100 Hz	11.262	−0.0141	0.1003	309.4	0.48
150 Hz	11.241	−0.0171	0.106	309.45	0.51
200 Hz	11.233	−0.0185	0.1084	309.41	0.48
300 Hz	11.230	−0.019	0.110	309.44	0.49
500 Hz	11.218	−0.0206	0.113	309.50	0.48
800 Hz	11.220	−0.0206	0.112	309.42	0.50
1 kHz	11.219	−0.0207	0.112	309.44	0.50
5 kHz	11.217	−0.021	0.112	309.42	0.50
10 kHz	11.216	−0.0212	0.113	309.42	0.50
30 kHz	11.215	−0.0213	0.113	309.42	0.50
100 kHz	11.214	−0.0212	0.113	309.42	0.50

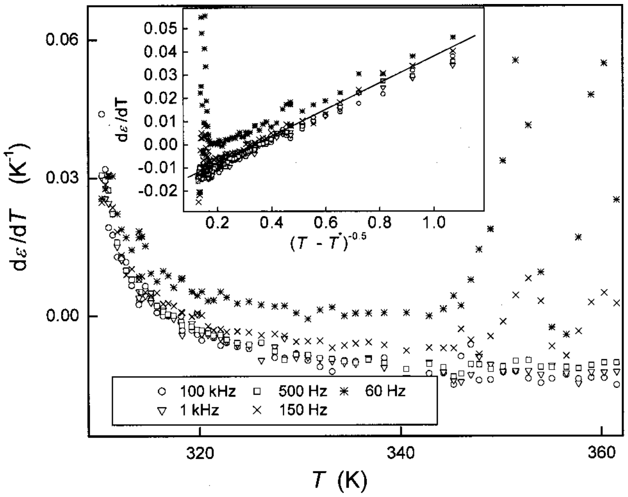

FIG. 2. The derivative of $\varepsilon(T)$ experimental data from Fig. 2 for several chosen frequencies in the static and ionic regions. The inset presents the same data in a way showing the value of the critical exponent $\alpha\approx0.5$.

$\Delta\varepsilon(T)=\varepsilon(f)-\varepsilon(100\,\mathrm{kHz})$: the data for $f=100\,\mathrm{kHz}$ are taken as a ''*static*'' and ''*nonionic*'' reference background. It is visible that $\Delta\varepsilon(T)$ can be well portrayed by linear functions, with an increasing slope on frequency decrease. The extent of the linearity shrinks on lowering the frequency, but even for $f=20\,\mathrm{Hz}$ it is still as large as $T-T^C\approx15\,\mathrm{K}$. This behavior may suggest that the pretransitional ''*bending down*'' associated with the term $A_\varepsilon(T-T^*)^{1-\alpha}$ in Eq. (1b) is extracted. It is only possible if for $T\rightarrow T^*$ the amplitude A_ε has a constant value, which may suggest also the results in Table I. Hence one may conclude that the ionic LF contribution of mobile ionic dopants seems to contribute only to the linear term in Eq. (1b). It was mentioned that in the static domain equation (1b) portrays experimental data also for $T\gg T_X$. However, it is apparent that the LF dielectric permittivity region of Eq. (1b) follows experimental data only for temperatures lower than T_x, which suggests that it becomes directly coupled to prenematic fluctuations as in the case of the NDE. One may put forward a hypothesis that on approaching the clearing point ionic impurities are caught in quasicritical, prenematic fluctuations and next polarize them. At a given frequency the ability of mobile ions to polarize fluctuations disappears at T^* where the correlation length is infinite. Based on the linear dependence visible in Fig. 3 and on the fact that Eq. (1b) remains valid in the ionic region, the linear term in relation (1b) may be presented as the sum of two linear terms as is shown in Fig. 4. It is noteworthy that neither the power term $A_\varepsilon(T-T^*)^{1-\alpha}$ nor the linear term $\varepsilon^*+a_\varepsilon(T-T^*)$ does not describe the experimental data

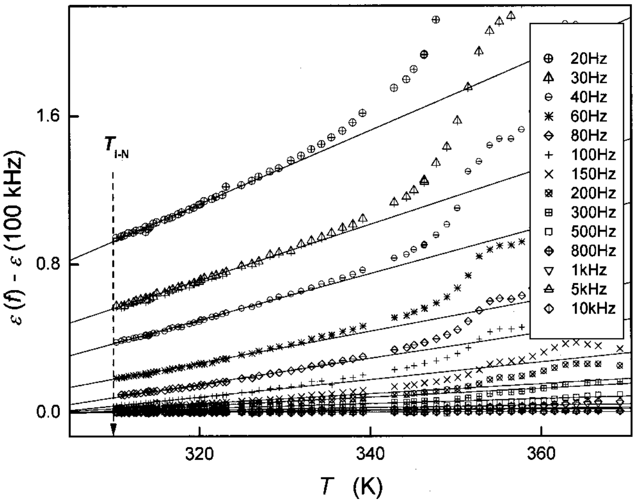

FIG. 3. The ''*difference*'' analysis: $\Delta\varepsilon(T)=\varepsilon(f)-\varepsilon(100\,\mathrm{kHz})$ for experimental data taken from Fig. 2. The frequencies f are shown in the figure.

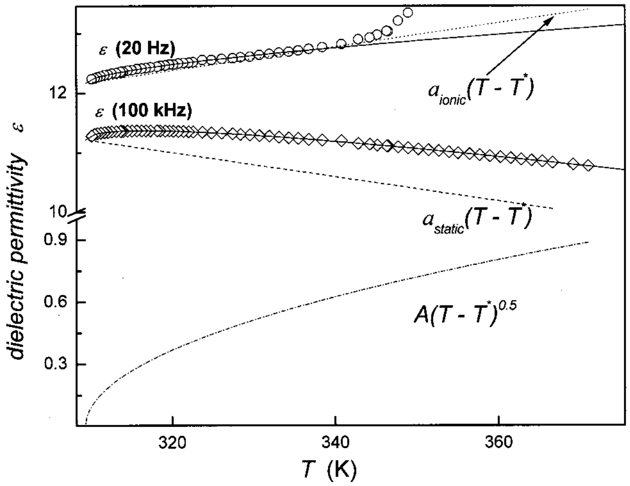

FIG. 4. The analysis of the $\varepsilon(T)$ pretransitional behavior in the isotropic phase for $f=100\,\mathrm{kHz}$ (static region) and $f=20\,\mathrm{Hz}$ (ionic region). The parameters describing solid curves [Eq. (1a)] are given in Table I. The lower dashed, ''*static*'' line is parametrized by: $\varepsilon(T)=11.217-0.0204(T-T^*)$. The upper dotted, ''*ionic*'' line describes equation $\varepsilon(T)=12.167+0.020(T-T^*)$ and the bottom dot-dashed curve $\varepsilon(T)=0.113(T-T^*)^{0.5}$.

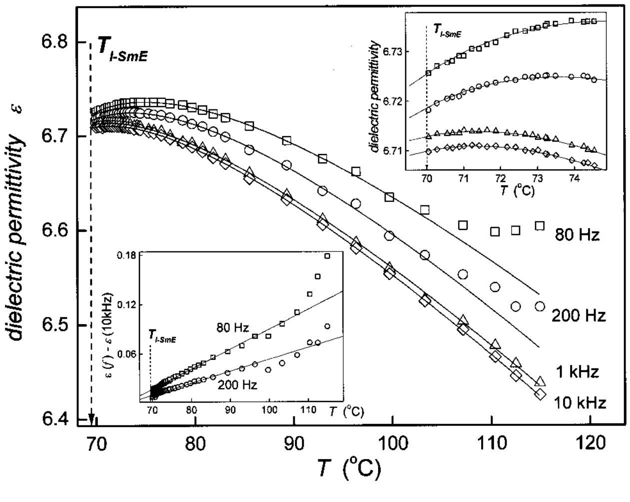

FIG. 5. Results of measurements in the isotropic phase of 10BT (I-SmE transition) for ''*static*'' and ''*ionic*'' frequencies. Insets show the behavior in the immediate vicinity of the I-SmE transition and results of the ''*difference*'' analysis, as in Fig. 3 for 5CB.

separately at any distance from T^*. Consequently, the linear term in Eq. (1b) cannot be treated as a background effect, describing data remote from $T_{I\text{-}N}$.

Concluding, the results obtained show that the appearance of prenematic fluctuations in the isotropic phase may have a dominant influence on the behavior of the low-frequency dielectric permittivity also in the low-frequency region. Results presented in Fig. 5 for 10BT on approaching the ''*soft crystal*'' smectic-*E* phase [20] may suggest that the discussed behavior may be general. The *fluidlike* and *critical* description [1–8] remains valid in the static domain [4–8,24,25] and in the ionic region, with the same value of the critical exponent $\alpha\approx0.5$ and the discontinuity ΔT of the isotropic-mesophase transition.

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[1] P. K. Mukerjee and T. B. Mukherjee, Phys. Rev. B **52**, 9964 (1995).
[2] P. K. Mukherjee and M. Saha, Phys. Rev. E **51**, 5745 (1995).
[3] P. K. Mukherjee, J. Phys.: Condens. Matter **10**, 9191 (1998).
[4] A. Drozd-Rzoska, S. J. Rzoska, and J. Zioło, Phys. Rev. E **54**, 6452 (1996).
[5] A. Drozd-Rzoska and S. J. Rzoska, Mol. Cryst. Liq. Cryst. **330**, 25 (1999).
[6] A. Drozd-Rzoska, Phys. Rev. E **59**, 5556 (1999).
[7] A. Drozd-Rzoska, S. J. Rzoska, and J. Zioło, J. Phys.: Condens. Matter **12**, 6135 (2000).
[8] A. Drozd-Rzoska, S. J. Rzoska, and J. Zioło, Acta Phys. Pol. B **98**, 431 (2000).
[9] J. J. Stankus, R. Torre, C. D. Marshal, S. R. Greenfield, A. Sengupta, A. Tokmakoff, and M. D. Fayer, Chem. Phys. Lett. **194**, 213 (1992).
[10] J. Stankus, R. Torre, and M. D. Fayer, J. Phys. Chem. **97**, 9478 (1993).
[11] A. Sengupta and M. D. Fayer, J. Chem. Phys. **102**, 4193 (1995).
[12] R. Torre, F. Tempestini, P. Bartolini, and R. Righini, Philos. Mag. B **77**, 645 (1998).
[13] J. Fuchs and W. Burchard, J. Phys. II **4**, 1551 (1994).
[14] R. S. Miller and R. A. MacPhail, Chem. Phys. Lett. **241**, 121 (1995).
[15] T. Ueno, K. Sakai, and K. Takagi, Phys. Rev. E **54**, 6457 (1996).
[16] T. Shibata, T. Matsuoka, S. Koda, and H. Nomura, J. Chem. Phys. **109**, 2038 (1998).
[17] T. Matsuoka, K. Yasuda, S. Koda, and H. Nomura, J. Chem. Phys. **111**, 1580 (1999).
[18] H. Nomura, S. Koda, and T. Matsuoka, Mem. School Engn, Nagoya Univ. **51**, 107 (2000).
[19] P. G. de Gennes, *The Physics of Liquid Crystals* (Clarendon, Oxford, 1974); P. G. de Gennes and J. Prost, *The Physics of Liquid Crystals* (Claredon, Oxford, 1993).
[20] *Fundamentals*, Vol. 1 of *Handbook of Liquid Crystals*, edited by D. Demus, J. Goodby, G. W. Gray, H. Spiess, and V. Vill (Wiley-VCH, Weinheim, 1998).
[21] G. Vertogen and W. H. DeJeu, *Thermotropic Liquid Crystals: Fundamentals*, Springer Series in Chemical Physics (Springer-Verlag, Berlin, 1988).
[22] W. Maier and R. Saupe, Z. Naturforsch. A **14**, 882 (1959).
[23] G. S. Attadand and G. R. Luckhurst, Liq. Cryst. **2**, 441 (1987).
[24] A. Drozd-Rzoska, S. J. Rzoska, and J. Zioło, Phys. Rev. E **61**, 5349 (2000).
[25] A. Drozd-Rzoska, S. J. Rzoska, and K. Czupryński, Phys. Rev. E **61**, 5355 (2000).
[26] E. Gulari and B. Chu, J. Chem. Phys. **62**, 795 (1975).
[27] G. Koren, Phys. Rev. A **13**, 1177 (1976).
[28] G. S. Armitage and F. P. Price, Mol. Cryst. Liq. Cryst. **38**, 229 (1977).
[29] E. A. S. Lewis, H. M. Strong, and G. H. Brown, Mol. Cryst. Liq. Cryst. **53**, 89 (1979).
[30] J. Thoen, R. Kindt, and W. Van Daael, Phys. Rev. A **26**, 2886 (1982).
[31] R. A. Orwoll, V. J. Sullivan, and G. C. Campbell, Mol. Cryst. Liq. Cryst. **149**, 121 (1987).
[32] R. Kiefer and G. Baur, Mol. Cryst. Liq. Cryst. **188**, 12 (1990).
[33] G. J. Sprokel, Mol. Cryst. Liq. Cryst. **22**, 249 (1973).
[34] N. Ashcroft and N. D. Mermin, *Solid State Physics* (Holt, Rinehart and Winston, New York, 1976).
[35] G. Derfel and A. Lipiński, Mol. Cryst. Liq. Cryst. **55**, 89 (1979).
[36] W. Leśniak, W. Labno, W. Szwajczak, and A. Szymański, Mol. Cryst. Liq. Cryst. **61**, 241 (1980).
[37] W. Otowski and T. K. Bose, Mol. Cryst. Liq. Cryst. **265**, 463 (1995).
[38] H. Mada and M. Ryuzaki, Jpn. J. Appl. Phys., Part 2 **34**, L1134 (1995).
[39] H. Mada, S. H. Endoh, and M. Fukuro, Jpn. J. Appl. Phys., Part 2 **35**, L1114 (1996).
[40] A. Sawada, Y. Nakazono, K. Tarumi, and S. Naemura, Mol. Cryst. Liq. Cryst. **318**, 22 (1998).
[41] W. L. Szymański and M. Kużma, Mol. Phys. Rep. **23**, 194 (1999).
[42] A. V. Kovalchuk, in *Proceedings of the Dielectric and Related Phenomena Conference, Spala, Poland* (unpublished).
[43] M. Kuźma, A. Blahut, W. L. Szymański, and A. B. Szymański, in *Proceedings of the Dielectric and Related Phenomena Conference* [42].
[44] L. Mistura, J. Chem. Phys. **59**, 4563 (1974).
[45] A. Drozd-Rzoska, S. J. Rzoska, M. Górny, P. Habdas, and J. Zioło, in *Proceedings of the Dielectric and Related Phenomena Conference* [42].