High-pressure studies of the low-frequency nonlinear dielectric effect in the isotropic phase of octyl- and dodecylcyanobiphenyls

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(Received 30 September 1996)

Results are presented for high-pressure, isothermal studies of the low-frequency nonlinear dielectric effect (LF NDE) in the isotropic phase of n-octylcyanobiphenyl (8CB, isotropic-nematic liquid crystal phase transition) and n-dodecylcyanobiphenyl (12CB, isotropic–smectic-A phase transition). In both cases a linear pressure dependence of reciprocals of LF NDE, with no distortions near the clearing point, was found. This behavior is in agreement with classical relations derived from the Landau–de Gennes model. The pressure dependence (up to 100 MPa) of clearing temperatures and temperatures of extrapolated, hypothetical, continuous phase transitions were determined. For 8CB isothermal pressure and isobaric temperature pretransitional effects have been superimposed on one scaling curve. This makes it possible to investigate the pretransitional effects under high pressure from temperature measurements carried out under atmospheric pressure. [S1063-651X(97)09302-1]

PACS number(s): 64.70.Md, 77.22.Ch.

INTRODUCTION

Studies of the isotropic-nematic (I-N) phase transition have a long history and are still of considerable interest [1–4]. Basic experimental facts are derived from measurements in the isotropic phase of such physical properties as the Kerr effect (KE), Cotton-Mouton effect (CME), light scattering (I) [5–7], turbidity (t) [8], and nonlinear dielectric effect (NDE) [9–11]. They exhibit the same classical pretransitional anomaly in the isotropic phase. Their phenomenological description made possible the application of the Landau–de Gennes (LdG) model ([5] and references therein). In the case of low-frequency NDE (LF NDE), applied in this paper, the appropriate relation has the form [10,11]

$$\mathcal{E}_{\mathrm{NDE}}=\frac{A_T^{\mathrm{NDE}}}{(T-T^*)^{\gamma}}=\frac{2}{3}\,\epsilon_0(\Delta\epsilon^0)^2 a_T^{-1}(T-T^*)^{-\gamma} \qquad (1)$$

with $\gamma=1$, $T>T_C$, and $T_C-T^*=\Delta T$, where $\mathcal{E}_{\mathrm{NDE}}=(\epsilon^E-\epsilon^0)/E^2$ is a measure of NDE, and ϵ^E and ϵ^0 are dielectric permittivities in a strong and in a weak electric field E, respectively. $\Delta\epsilon^0$ is a molecular anisotropy of dielectric permittivity in the zero frequency limit. ΔT is a value of the discontinuity of the phase transition. a_T denotes the constant amplitude of the second-rank term in the LdG series. $T_{I\text{-}N}$ and T^* are the clearing temperature (I-N, in this case) and the extrapolated temperature of the hypothetical, continuous phase transition. For the LF NDE [10,11]: $f^{-1}/\tau \ll 1$ up to the clearing point, f is the NDE measuring frequency, and τ denotes relaxation time of pretransitional processes in the isotropic phase.

Recent investigations of the series of n-cyanobiphenyls (from 6CB to 12CB) [10] point to a unique feature of LF NDE: starting from $T-T_C\approx 50$ K the reciprocal of the effect remains linear up to the clearing temperature. Additionally, such behavior occurs for both the isotropic-nematic (I-N) and isotropic–smectic-A (I–Sm-A) phase transition. For the I-N phase transition a good quantitative agreement with relation (1) was ascertained [10,11].

It is well known that the hydrostatic pressure strongly influences both properties of the liquid crystalline phases [12–19] and the phase transition behavior [7–9,12–20]. For the I-N transition one could expect the pressure to influence such important parameters as T_C, ΔT, or a_T. It also poses the question regarding differences in the pretransitional behavior when the phase transition is approached by change of temperature changes or isothermal density changes. Unfortunately, pressure studies of physical quantities mentioned above are very scarce [8,9,20]. This is undoubtedly due to serious technical problems encountered at the high pressures [21].

This paper presents results of high pressure (up to 100 MPa) LF NDE studies in the isotropic phase of two liquid crystalline n-octylcyanobiphenyl (8CB, I-N phase transition) and n-dodecylcyanobiphenyl (12CB, I–Sm-A phase transition). Apart from addressing the problems mentioned above we discuss the possibility of scaling of pressure and temperature pretransitional effects.

EXPERIMENT

NDE measurements were performed using an apparatus with frequency modulation of an LC generator described in detail in our previous papers [10,11]. The parameters of the weak measurement field were: $f=250$ kHz and $U=3$ V. The additional, strong, steady electric field was applied in the form of a rectangular pulse of the length 4 ms, repeatability 3 s, and voltage $U=300$–900 V. The sample was placed in a specially designed flat-parallel capacitor (gap 0.6 mm, $C_0\approx 4$ pF) which was a modified construction presented in [21]. The capacitor contained 0.8 cm^3 of a sample. The tested liquid was only in contact with stainless steel, quartz, and Teflon. The pressure was exerted on the sample by the deformation of 40 μm thick Teflon membrane. The pressure chamber, within the capacitor was placed, was constructed

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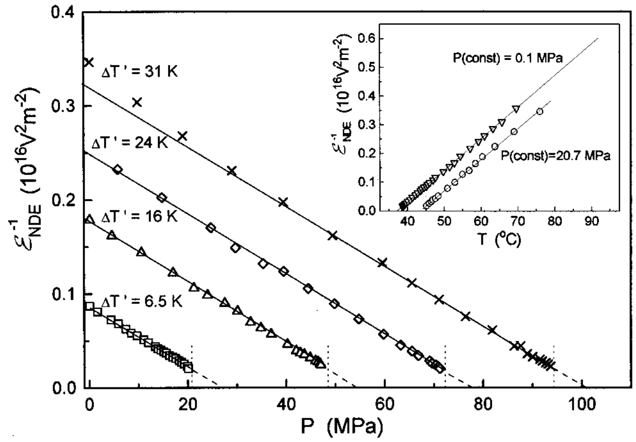

FIG. 1. Reciprocals of measured LF NDE in the isotropic phase of 8 CB, for few isotherms, denoted on the figure in relation to the clearing temperature under atmospheric pressure [$\Delta T' = T$(measurement)$- T_C(P \approx 0.1$ MPa)]. The inset shows results of temperature measurements under atmospheric pressure and for $P = 20.7$ MPa.

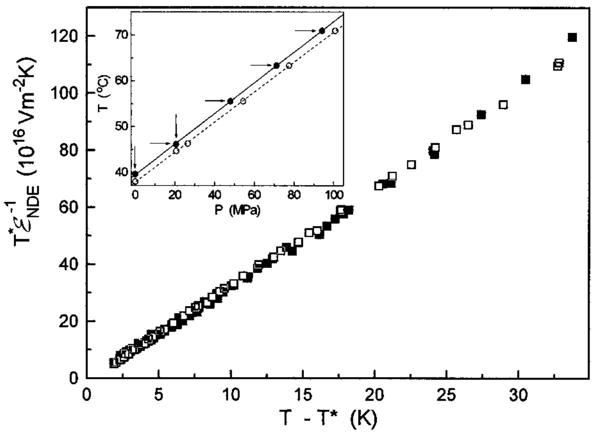

FIG. 2. The scaling behavior of isothermal pressure and isobaric temperature pretransitional LF NDE effects in 8CB. The plot contains all experimental data from Fig. 1. The solid squares are for isobaric temperature data and open squares are for the transformed pressure, isobaric data. The inset demonstrate the pressure dependence of the $T_{I\text{-}N}$ (full circles) and T^* (full circles). Solid and broken lines are fits according to relation (3). Arrows show directions of approaching the clearing point applied in this research.

by UNIPRESS, Warsaw, Poland and Experimental Workshops of the Institute of Physics, Silesian University. The pressure was transmitted from its source (special chamber with a piston under hydraulic press) through a mixture of octane and silicone oil. On approaching the phase transition point the applied high voltage was decreased to keep the response of the sample in the same range, from 5 to 30 fF. At each measurement point the fulfillment of the condition $(\epsilon^E - \epsilon) \propto E^2$ was tested. The temperature was measured by means of Keithley 195A multimeter using a platinum resistor (A1 class, DIN 43 760) located in the jacket of the sample and a copper-constantan thermocouple placed inside the pressure chamber. The temperature was stabilized with precision higher than 0.02 K/h. The pressure was measured by a Nova Swiss tensometric pressure meter with accuracy ± 0.1 MPa. Studies were conducted in the isotropic phase of 8CB ($T_{I\text{-}N} = 40.15$ °C) and 12CB ($T_{I-\text{Sm-}A} = 58.6$ °C), prepared by the Dąbrowskii group from the Military Technical Academy, Warsaw. Each sample was degassed prior to measurements. Data were analyzed by means of the ORIGIN 3.5 software (Microcal Inc.). Errors are given as three standard deviations.

RESULTS AND DISCUSSION

Results of isothermal, pressure measurements in the isotropic phase of 8CB are shown in Fig. 1. The inset in Fig. 1 demonstrates the isobaric temperature measurements at atmospheric pressure and for $P = 20.7$ MPa. In both cases reciprocals of NDE remain a linear function of pressure or temperature up to the clearing point. Noteworthy is the range in which this simple classical behavior holds: $P_C - P \approx 70$ MPa and $T - T_C \approx 50$ K, respectively. Applying the LdG model [5–7,10] and the Landau [22] suggestion of the equivalence of pressure and temperature in this series one can easily derive a relation for the isothermic, pretransitional effect:

$$\mathcal{E}_{\mathrm{NDE}} = \frac{A_p^{\mathrm{NDE}}}{P_C - P} = \frac{2}{3}\,\epsilon_0 (\Delta\epsilon^0)^2 a_p^{-1} (P_C - P)^{-1} \qquad (2)$$

with $P < P_C$, $P^* - P_C = \Delta P$, $T = $const, where A_p^{NDE} is the pretransitional amplitude for the isothermal, pressure studies. P_C and P^* denote pressure coordinates of the clearing point and of the hypothetical, continuous phase transition. ΔP denotes pressure value of the discontinuity of the I-N phase transition. a_p is the constant amplitude for the second-rank term in the (isothermal) LdG series. The obtained value of pretransitional amplitudes are constant, within the limit of the experimental error, for isothermal and isobaric paths. Their average values are

$$A_P^{\mathrm{NDE}} = 310 \pm 3 \times 10^{-16}\ \ \mathrm{m^2\,V^{-2}\,MPa} \quad \text{and}$$

$$A_T^{\mathrm{NDE}} = 92 \pm 1 \times 10^{-16}\ \ \mathrm{m^2\,V^{-2}\,K}.$$

The $T_C(P)$ and $T^*(P)$ lines, presented in the inset of Fig. 2, are governed by linear relations:

$$T^* = 37.8(\pm 0.2) + [0.327(\pm 0.006)]P \quad (\mathrm{°C}),$$

$$T_c = 39.4(\pm 0.2) + [0.334(\pm 0.006)]P \quad (\mathrm{°C}), \qquad (3)$$

where $dT^*/dP = 0.327 \pm 0.006$ K MPa^{-1} and $dT_C/dP = 0.334 \pm 0.006$ K MPa^{-1}. These dependencies predict that the discontinuity of the phase transition increases with pressure from $\Delta T \approx 1.6$ K for $P = 0.1$ MPa to $\Delta T \approx 2.3$ K for $P = 100$ MPa. A similar trend of $\Delta T(P)$ was observed in MBBA, yet is based on turbidity measurements [8].

Figure 2 shows that the obtained isothermal pressure and isobaric temperature pretransitional effects can be superimposed on one curve, plotting $(T^*/\mathcal{E}_{\mathrm{NDE}})$ as a function of $(T - T^*)$ with pressure data converted into the temperature scale by the relation:

$$P^* - P \rightarrow T - T^*(P) = \left(\frac{dT^*}{dP}\right)(P^* - P), \qquad (4)$$

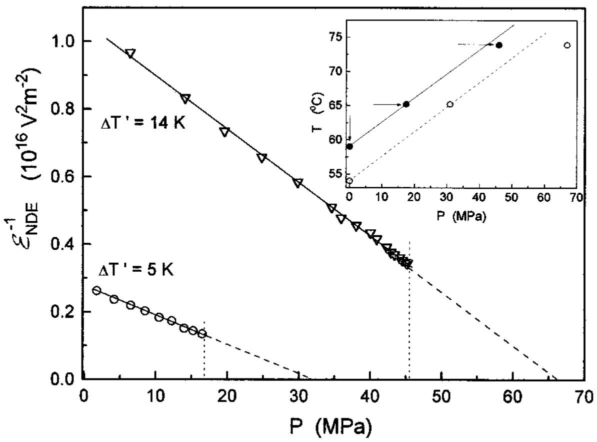

FIG. 3. Reciprocals of LF NDE on approaching the I–Sm-A transition in 12CB. Studies were carried out for two isotherms, denoted on the figure in relation to the clearing temperature under atmospheric pressure ($\Delta T'$). The inset shows the pressure dependence of $T_{I-\text{Sm-}A}$ (open circles) and T^* temperatures (full circles). The slope of the solid line is $dT_C/dP \approx 0.38$ K MPa^{-1}. Arrows show directions of approaching the clearing point applied in this investigation.

where $T^*(P)$ and dT^*/dP are taken from relations (3). Scaling behavior, presented in Fig. 2, offers the possibility of determining the properties under higher pressures from temperature measurements under atmospheric pressure.

Figure 3 enables comparison of the results presented above with the properties of I–Sm-A transition in 12CB. The LF NDE pretransitional effects in the isotropic phase also exhibit classical behavior [relation (2)] but amplitudes A_P^{NDE} are definitely different for the two tested isotherms:

$$A_P^{\text{NDE}} = 115 \pm 2 \times 10^{-16}\ \text{m}^2\,\text{V}^{-2}\,\text{MPa}^{-1} \quad \text{and}$$

$$A_P^{\text{NDE}} = 64 \pm 2 \times 10^{-16}\ \text{m}^2\,\text{V}^{-2}\,\text{MPa}^{-1}$$

for the lower and upper isotherm, respectively. The $T^*(P)$ and $T_C(P)$ dependencies are nonlinear (inset in Fig. 3).

CONCLUSIONS

The presented results suggest the equivalence (isomorphism) of temperature and pressure paths on approaching the I-N phase transition for the LF NDE. Taking into account the recently postulated critical character of pretransitional effects [2,3,11] in the isotropic phase of nematogens this equivalence may be regarded as a consequence of the isomorphism postulate of critical phenomena [7]. The classical behavior of the pretransitional effect holds also for I–Sm-A phase transition in 12CB.

Basing on the well-known solution of the Landau model [7,22] one can rewrite relations (1) and (2) in the following form:

$$\mathcal{E}_{\text{NDE}} = \text{const} \times (\Delta \epsilon^0)^2 \chi^*, \tag{5}$$

where the term χ^* denotes the generalized susceptibility (for the weakly discontinuous I-N transition), i.e., the isothermal compressibility χ_T^*, for P=const, and thermal expansion coefficient (''isobaric compressibility'') χ_p^*, for T=const. Relation (4) is similar to that applied in critical, binary, solutions. Indeed, recent theoretical and experimental studies [2,3,11,23] pointed out the close relationship between the pretransitional behavior in the isotropic phase of nematogens and in the homogeneous phase of critical solutions. Relations (1), (2), and (5) for the isothermal and the isobaric approaching the (T^*,P^*) point, gives

$$\frac{\mathcal{E}_{\text{NDE}}(T)}{\mathcal{E}_{\text{NDE}}(P)} = \frac{a_T^{-1}(T-T^*)}{a_P^{-1}(P^*-P)} = \frac{\chi_T^*}{\chi_p^*} = \frac{(\partial V/\partial p)^*_{T\to T^*}}{(\partial V/\partial T)^*_{p\to p^*}} = \frac{dT^*}{dp^*}. \tag{6}$$

This relation (''equation of state'') shows that the scaling behavior of LF NDE, presented in Fig. 3, reflects the relationship between susceptibilities χ_T^* and χ_p^*. Note that differences in pretransitional effects in 8CB and 12CB may arise from dependence $T^*(p)$. Noteworthy is also an increase of the discontinuity of the phase transition with pressure, particularly taking into account the disagreement between experimental (under atmospheric pressure) [4–10] and theoretical values of ΔT ([2–4] and references therein).

ACKNOWLEDGMENT

The presented research was supported by the Polish Committee for Scientific Research (KBN), Project No. 2 P302 081 06.

[1] R. Tao and P. Sheng, Phys. Rev. Lett. **70**, 1271 (1993).
[2] P. K. Mukherjee, T. R. Bose, D. Ghose, and M. Saha, Phys. Rev. E **51**, 4570 (1995).
[3] P. K. Mukherjee and T. B. Mukherjee, Phys. Rev. B **51**, 9964 (1995).
[4] E. I. Ryumtsev, M. A. Osipov, T. A. Rotinyan, and N. P. Yevlampieva, Liq. Cryst. **18**, 87 (1995).
[5] P. G. de Gennes and J. Prost, *Liquid Crystals* (Oxford University Press, Oxford, 1994).
[6] G. Vertogen and W. H. de Jeu, *Thermotropic Liquid Crystals—Fundamentals*, Springer Series in Chemical Physics Vol. 45 (Springer, Berlin, 1988).
[7] M. A. Anisimov, *Critical Phenomena in Liquids and in Liquid Crystals* (Gordon and Breach, Reading, MA, 1992).
[8] W. J. Lin, P. H. Keyes, and W. B. Daniels, J. Phys. (Paris) **41**, 633 (1980).
[9] S. J. Rzoska and J. Zioło, Liq. Cryst. **17**, 629 (1994).
[10] A. Drozd-Rzoska, S. J. Rzoska, and J. Zioło, Liq. Cryst. **21**, 273 (1996).
[11] A. Drozd-Rzoska, S. J. Rzoska, and J. Zioło, Phys. Rev. E **54**, 6452 (1996).
[12] T. E. Faber and R. G. Horn, Proc. R. Soc. London A **368**, 199 (1979).
[13] G. M. Schneider, A. Bartelt, J. Friedrich, H. Reisig, and A.

Rother, Physica **139&140B**, 616 (1986).
[14] R. Shashidhar, Physica **139&140B**, 609 (1986).
[15] V. K. Piershin, Zhurn. Fiz. Khimii **LX**, 2540 (1986).
[16] C. Rein and D. Demus, Liq. Cryst. **16**, 323 (1994).
[17] H. G. Kreul, S. Urban, and A. Wuerflinger, Phys. Rev. A **45**, 8624 (1992).
[18] S. Urban, T. Brueckert, and A. Wuerflinger, Z. Naturforsch. Tiel A **49**, 552 (1994).
[19] S. Urban, Z. Naturforsch. Tiel A **50**, 8268 (1995).
[20] E. Demikhov, J. Hollmann, and P. Pollmann, Europhys. Lett. **21**, 581 (1993).
[21] P. Urbanowicz, S. J. Rzoska, M. Paluch, B. Sawicki, A. Szuls, and J. Zioło, Chem. Phys. **201**, 575 (1995).
[22] L. D. Landau and E. M. Lifshitz, *Statistical Physics* (Nauka, Moscow, 1976) (in Russian).
[23] S. J. Rzoska, Phys. Rev. E **48**, 1136 (1993).