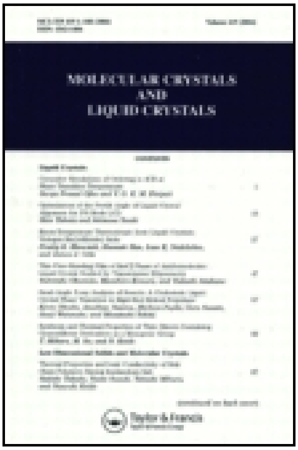

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The Influence of High Pressure on the Discontinuity of the Isotropic - Nematic and the Isotropic – Smectic A Phase Transitions Studied by the Low-Frequency Nonlinear Dielectric Effect Measurements

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Results are presented for isothermal, pressure studies of the low frequency nonlinear dielectric effect in the isotropic phase of 8CB (isotropic – nematic (I-N) transition) and 12CB (isotropic – smectic(I-SmA transition). This made possible to determined the pressure dependence of the nematic and smectic clearing temperatures as well as the extrapolated temperatures of a hypothetical continuous phase transition up to $P = 200$ MPa. In the case of the I-N transition the discontinuity of the transition (ΔT) increases systematically with pressure while for the I-SmA transition ΔT decreases with rising pressure.

Keywords: clearing point; nematic; smectic; high pressures; nonlinear dielectric effect

INTRODUCTION

The increase of the nematic clearing temperature (T_c) with rising pressure (P) has been predicted theoretically [1-3] and observed in experiments [4,5]. The obtained $T_C(P)$ dependencies are often parametrized by a second-order polynomial (P2) [4,5]. The same number of fitted parameters has the Simon-Glatzel (SG) relation [6]:

$$T = T_C^{atm.} \times \left(1 + \frac{P}{b}\right)^a \qquad (1)$$

Recently Rein and Demus[7] derived its modified version for describing strongly nonlinear evolution of phase transition temperatures (SG-RD relation):

$$T = T_C^{atm.} \times \left(1 + \frac{P}{b}\right)^a \exp(cP) \qquad (2)$$

where a, b, c are constant parameters.

The applicability of equations (1) and (2) is extensively discussed in refs.[7,8]. The basic methods in experimental studies of liquid crystals under pressure are differential thermal analysis [4,8] and dielectric spectroscopy[5]. Unfortunately these methods do not deliver information on the temperature of a hypothetical continuos phase transition (T^*) and the discontinuity of the transition ($\Delta T = T_C - T^*$). They can be determined by means of measurements of physical properties particularly sensitive to fluctuations, as the Kerr effect (KE), Cotton - Mouton effect (CME) or the intensity of the scattered light (I) [9]. Unfortunately pressure studies of such properties are very scarce. This is undoubtedly due to technical problems encountered at high pressures. In 1976 Lin et al. [10] determined the evolution of $T^*(P)$ and $\Delta T(P)$ for MBBA and EBBA by means of turbidity (t) measurements. Recently, similar results were obtained in 8CB using the low-frequency nonlinear dielectric effect (LF-NDE)[11]. For both mentioned studies, conducted up to $P \approx 100$ MPa, a systematic increase of ΔT with increasing pressure was found. In 8CB additionally scaling behaviour of LF-NDE pretransitional effects was shown [11]. The presented below results has been also obtained using the LF NDE method. This magnitude describes the shift of dielectric permittivity $\Delta\varepsilon^E = \varepsilon^E - \varepsilon$ induced by a strong electric field E (ε^E, ε are dielectric permittivities in a strong and weak electric field, respectively). In the isotropic phase of nematogens NDE exhibits the same, classical pretransitional behaviour as KE, CME, I or t [11-14].

$$\frac{\Delta\varepsilon^E}{E^2} = \frac{A^T_{NDE}}{T - T^*} = \frac{2}{3a_T}\varepsilon_0\frac{\Delta\varepsilon^0\Delta\varepsilon^f}{T - T^*}\ ,\ T^* = T_C - \Delta T\ ,\ T > T_C,\ (\text{for } P = \text{const}) \tag{1}$$

$$\frac{\Delta\varepsilon^E}{E^2} = \frac{A^P_{NDE}}{P^* - P} = \frac{2}{3a_p}\varepsilon_0\frac{\Delta\varepsilon^0\Delta\varepsilon^f}{P^* - P},\ P^* = P_C + \Delta P\ ,\ P < P_C,\ (\text{for } T = \text{const}) \tag{2}$$

where $\Delta\varepsilon^E/E^2$ is the measure of NDE, a_T , a_P , are constant amplitudes in the second rank term in the Landau - de Genness (LdG) (isobaric or isothermic) expansion [9]. $\Delta\varepsilon^0$, $\Delta\varepsilon^f$ are molecular anisotropies of dielectric permittivity in the zero-frequency limit and for the measurement frequency.

For the frequency of the weak measuring field low enough $\Delta\varepsilon^0 \approx \Delta\varepsilon^f$. In such case following condition between time scales introduced by the measurement frequency f and the relaxation time (τ) of pretransitional processes takes place: $f^{-1} >> \tau$ (LF NDE). This causes that the influence of relaxational processes on results is negligible and the reciprocal of total, measured NDE is a linear function of temperature from T_C to $T \approx T_C + 40K$, with no distortions in the immediate vicinity of T_C. The unique feature of the LF NDE is that the same type of behaviour occurs both for the isotropic - nematic (I-N) and isotropic smectic A (I-SmA) phase transitions. Additionally the reciprocal of experimental data of LF NDE is a linear function of pressure up to T_C + (30÷40 K) without the necessity of taking into account an additional "background term" and without any discrepancy in the immediate vicinity of T_C [11-14].

This paper presents results of high pressure (up to 200 MPa) studies in the isotropic phase of n-octylcyanobiphenyl (8CB) with $T_{I-N} \approx 35$ °C) and n-dodecylcyanibiphenyl (12CB, $T_{I-SmA} \approx 58.6$ °C).

The paper discuss the behaviour of $T_C(P)$, $T^*(P)$, $\Delta T(P)$ and A^P_{NDE} in a wide range of pressure, up to $P \approx 200$ MPa.

EXPERIMENTAL

NDE measurements were performed using a measurement set - up, described in details in ref.[12]. The parameters of the weak measurement field was f = 70 kHz and the voltage U = 3 V. The strong electric filed was applied in the form of a rectangular DC pulses of the length 8 ms - 16 ms, repeatability 3 s and voltage 100 - 700 V. At each measurement point the condition $\Delta\varepsilon^E \propto E^2$ was fulfilled. The sample was placed in a specially designed flat - parallel capacitor (gap 0.25 mm, $C_0 \approx 7$ pF). The capacitor contained only 0.8 cm^3 of the sample, which was totally isolated from the medium exerted the pressure (silicone oil). The pressure was transmitted to the sample due to the deformation of the 50 μm Teflon film. The temperature was measured using a thermocouple inside the chamber and a platinum resistor in the jacket of the pressure chamber. The pressure was measured using a tensometric pressure meter. The tested materials was obtained from Military Technical Academy due to the courtesy of Prof. Dąbrowski and Prof. Czupryński. Data were analysed by means of ORIGIN 3.5 software.

RESULTS AND DISCUSSIONS

Figure 1 shows results of measurements of the LF NDE in the isotropic phase of 8CB. Measurement data obtained in the isotropic phase of 12CB are presented in Fig. 2. In both cases reciprocals of NDE are linear functions of pressure from P_C to about P_C - 100 MPa, in an agreement with relation (2) The multiplication of the range of validity of equation (2) (100 MPa)by given below values of dT^*/dP gives 30 K

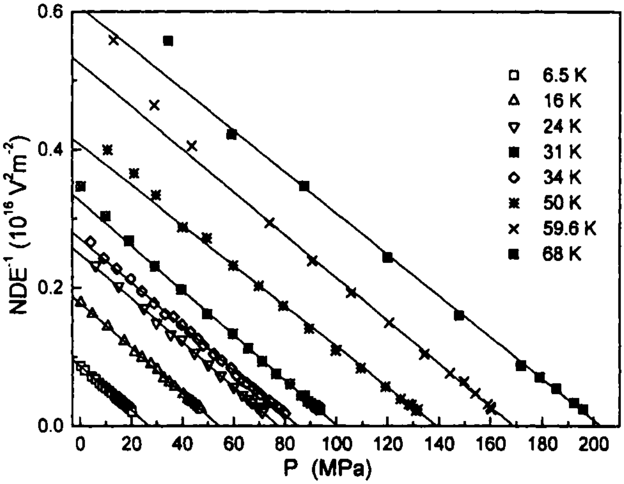

FIGURE 1 Reciprocals of measured LF-NDE in the isotropic phase of 8CB for isotherms denoted on the figure in relation to the clearing temperature under atmospheric pressure: $\Delta T = T(meas.) - T_C(0.1MPa)$. Data for $T = 6.5$, 16, 24 and 31 K are taken from ref.[11].

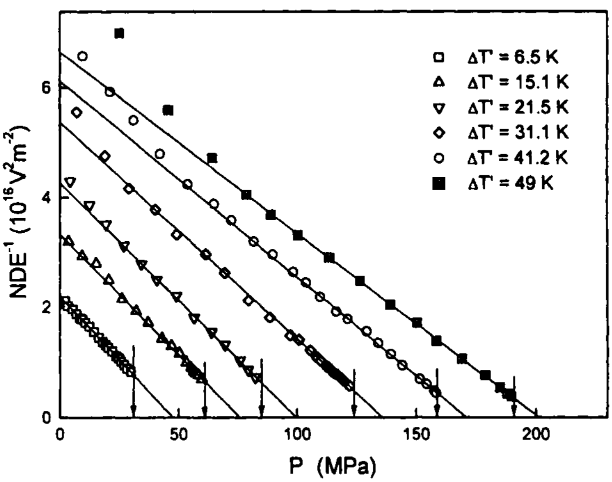

FIGURE 2 Reciprocals of measured LF-NDE in the isotropic phase of 12CB for isotherms denoted on the figure in relation to the clearing temperature under atmospheric pressure.

This value close to that found in previous LF NDE at atmospheric pressure [13, 14]. Figure 3 shows $T^*(P)$ and $T_C(P)$ dependencies determined on the basis of solid lines fitted in Fig 1. It is clearly visible that in 8CB up to relatively high pressure both characteristic temperatures are linear functions of pressure:

$T_C(P) = 313.2 + 0.32 \times P$ and $T^*(P) = 312.6 + 0.31 \times P$

In the case of the I-SmA phase transition $T^*(P)$ and $T_C(P)$ are slightly nonlinear and can be parametrized by P2, SG or SG-RD functions. All these functions follows the same solid lines in Fig. 4:

$T_C(P) = 330.5 + 0.3 \times P - 0.00017 \times P^2$ and

$T^*(P) = 324.5 + 0.28 \times P - 0.00013 \times P^2$ or

$T_C(P) = 330.5 \times (1 + P/515)^{0.44}$ and $T^*(P) = 324.5 \times (1 + P/420)^{0.4}$ or

$T_C(P) = 330.5 \times (1 + P/370)^{0.25} \times \exp(-0.00013P)$ and

$T^*(P) = 324.5 \times (1 + P/633)^{0.8} \times \exp(-0.0003P)$.

Insets in Fig. 3 and 4 show the pressure evolution of discontinuities of investigated phase transitions. The discontinuity increases, approximately linearly, with pressure for 8CB (I-N) but decreases for 12CB (I-SmA). For the latter even more complicated evolution of the discontinuity seems to be possible at higher pressures.

In the tested range of pressures pretransitional amplitudes A^P_{NDE} (reciprocals of solid lines in Figs. 1 and 2) are approximately constant for 8CB and systematically increases for 12CB. This behaviour is closely related with $T^*(P)$ dependence. Basing on the scaling relation proposed in ref.[11] following "scaling" relation can be written:

$$\frac{A^P_{NDE}(\Delta T_1')}{A^P_{NDE}(\Delta T_2')} = \frac{(dT^*/dP)_{\Delta T'}}{(dT^*/dP)_{\Delta T'}} \qquad (3)$$

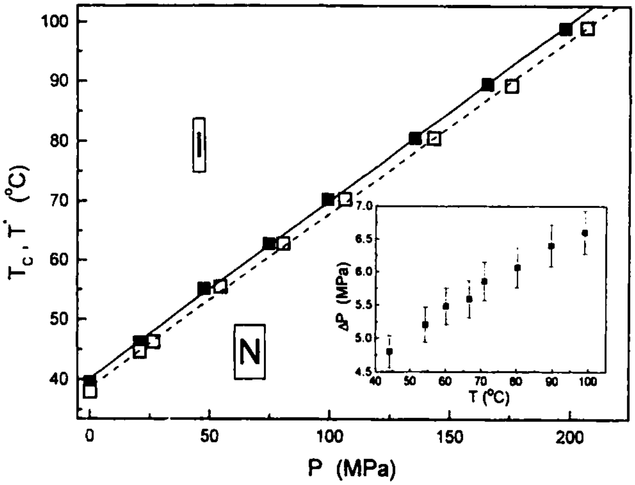

FIGURE 3 The pressure dependencies of the clearing temperature (full squares, solid line) and the extrapolated temperature of the continuous phase transition (open squares, dashed line) in 8CB. The inset shows the experimental dependence of the transition discontinuity.

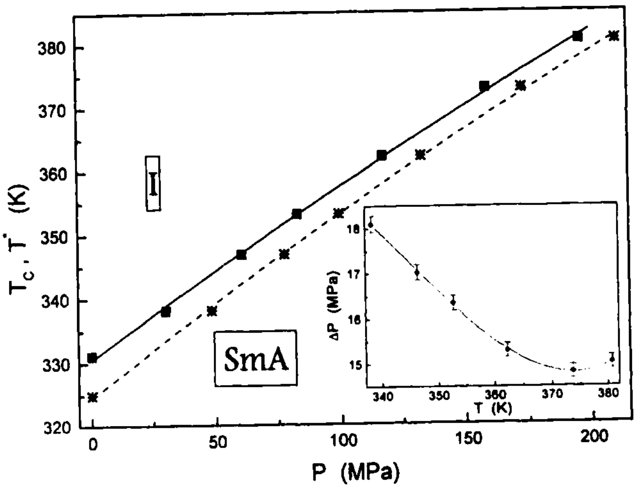

FIGURE 4 The pressure dependencies of the clearing temperature (full squares, solid line) and the extrapolated temperature of the continuous phase transition (open squares, dashed line) in 12CB. The inset shows the experimental dependence of the transition discontinuity.

The constant slopes of the solid lines describing NDE pretransitional effects for different isotherms in 8CB (Fig. 1) reflects the linear dependence of $T^*(P)$. The opposite situation takes place in 12CB (Fig. 2).

Concluding the results presented show that pressure may influence some of parameters describing the nematic and smectic clearing point in a definitively different way. The decrease of the discontinuity of the transition with rising pressure for the smectic clearing point has been not yet observed, to the best of the authors knowledge. Noteworthy is relation (3) which made possible to determine the value of A^P_{NDE} for different isotherms basing on the known $T^*(P)$ dependence. Alternatively, it is possible to determine $T^*(P)$ relation basing on values of pretransitional amplitudes. The mentioned specific features of the LF NDE causes that such studies may be conducted even relatively remote from the clearing point.

Acknowledgements

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