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Critical behaviour at the isotropic–nematic and nematic–smectic A phase transitions of 4-butyloxyphenyl 4'-decyloxybenzoate liquid crystal from refractive index data

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We present new high-resolution experimental data on the temperature dependence of the refractive index in the isotropic (I), nematic (N) and smectic A (SmA) phases of the 4-butyloxyphenyl 4'-decyloxybenzoate (10O4) liquid crystal. From an analysis of the data, using both the Vuks and Neugebauer models for the internal electric field, information on the orientational order parameter $S(T)$ was derived. From a fitting procedure consistent with mean-field theory and the first-order character of the N–I transition, we obtain a value of 0.246 ± 0.06 for the exponent β describing the critical behaviour of $S(T)$ at the N–I transition, which is in good agreement with the tricritical value $\beta=0.25$. In a temperature range of about 4 K above and below the N–SmA transition temperature, pre-transitional evidence for the coupling between the nematic and smectic order parameters was observed. We show, for the first time, that the temperature derivative of the $S(T)$ curve below and above the N–SmA transition has the same power law behaviour as the specific heat capacity with an effective critical exponent of 0.23 ± 0.01 .

1. Introduction

Different liquid crystalline mesophases can be formed in a certain temperature range by some large anisotropic organic molecules. Within the nematic (N) mesophase, formed by rod-like molecules, long-range orientational order of the long molecular axes along a director is observed, without any long-range positional order. In smectic phases, in addition to long-range orientational order, partial positional order is also present. In the smectic A (SmA) phase, of relevance here, a one-dimensional layering, with the normal to the layers parallel to the director, also occurs.

Due to its orientational ordering, a nematic liquid crystal behaves like an optically uniaxial crystal and its physical properties become anisotropic [1, 2]. As pointed by de Gennes [1], any anisotropic physical quantity may be a measure of orientational ordering in the nematic phase. Since it is known that the dimension of the order parameter is a key parameter in the identification of the universality class to which the phase transition belongs, its behaviour at the phase

transition can be used to establish the order of the phase transition, namely first or second order. In literature one can find numerous data which concern the temperature dependence of the nematic order parameter, $S(T)$, of uniaxial liquid crystals [3, 4]. However, there really is no experimental method that provides unambiguously absolute values for the orientational order parameter of uniaxial liquid crystals. This is related to the fact that the theory relating the measured property to the molecular orientational order is not exact and/or that there are unknown parameters in the theory. The values for these parameters can often only be determined by fitting the data to a model for the order parameter [4]. Theoretically it is expected that the critical exponent, β , characterizing the asymptotic temperature dependence of the order parameter $S(T)$ should indicate the membership of one of the possible universality classes of liquid crystal (LC) critical behaviour at the nematic–isotropic (NI) transition [1–5]. β values of 0.5 or 0.25 are consistent with mean-field results for a critical point or tricritical point, respectively, whereas $\beta=0.325$ corresponds to the 3D Ising universality class [1, 6, 7]. Previously reported values for β extracted from the measurement of the anisotropy of

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some macroscopic quantities, such as the dielectric constant [5, 8], the magnetic susceptibility [9] and the thermal conductivity [10], seem to confirm a value of 0.25. Until recently [11], the Haller approximation [12] was used for the analysis of the order parameter $S(T)$ from refractive index data, resulting in β values between 0.16 and 0.19 that do not match any of the predicted theoretical values. In fact the Haller approximation is incompatible with the weakly first-order nature of the nematic–isotropic (N–I) transition [8, 13]. On the basis of recent measurements of the refractive index of four compounds ($n=5$ –8) of the alkylcyanobiphenyl (n CB) homologous series and an analysis compatible with the first-order character of the N–I transition resulted in β exponent values consistent with the tricritical value of 0.25 [11]. The possibility for tricritical exponent values was proposed by Keyes [6] and Anisimov *et al.* [7, 14]. According to the conjectures of Keyes, two competing nematic order parameters (the uniaxial and the biaxial one) are expected to exhibit diverging fluctuations near T_{NI} even though the biaxial order parameter is zero in the nematic phase. Anisimov *et al.* argued that the N–I behaviour looks like that near a tricritical point because of the smallness of the coefficient of the fourth-order term in the Landau–de Gennes order parameter expansion [1].

The number of high-resolution refractive index or optical birefringence studies near the N–SmA phase transitions is very limited. Lim and Ho [15] measured the optical birefringence in 4-cyano-4'-octyloxybiphenyl to study in detail the orientational order parameter near the N–SmA transition. They did not find a measurable discontinuity in the birefringence, indicating the second-order character of the transition, and pointing out that improvements beyond mean-field molecular and phenomenological theories are necessary to account for the fluctuations induced pre-transitional temperature dependence of the birefringence above and below the transition. Gramsbergen and de Jeu [16] measured the birefringence near the N–SmA transition of mixtures of two compounds ($n=7$ and $n=8$) of the homologous series of the terminally non-polar p,p' -dialkylazoxybenzenes (n AB). The birefringence was used to probe the orientational order parameter and its coupling with the translational smectic order parameter. A tricritical nematic–smectic A transition (resulting from the order parameter coupling) was found for a mole fraction near 0.5 of 8AB in the mixture. For the second-order transitions (at lower mole fractions), the critical exponent x for the variation of nematic order parameter across the N–SmA phase transition increased with decreasing 8AB concentration from $x=0.51$ for the near tricritical mixture of mole fraction 0.464 to $x=0.64$ for

pure 7AB. Unfortunately, because of the absence of calorimetric information it was not possible to test the theoretically expected [17] relation $x=1-\alpha$, with α the critical exponent for the specific heat capacity (see further).

In the present work, we present new experimental data on the temperature dependence of the refractive index in the isotropic, nematic and smectic A phases of 4-butyloxyphenyl 4'-decyloxybenzoate ($C_{10}H_{21}OC_6H_4COOC_6H_4OC_4H_9$, $\overline{10}O\overline{4}$). The motivation for this investigation was twofold. First, we wanted to verify the results and analysis of the previous study in our group of the nematic order parameter in the n CBs which have large terminal dipoles, by investigating a compound where such a dipole is absent. Moreover, n CBs exhibit strong antiparallel coupling between dipoles, resulting in a so-called partially bilayer smectic A_d , with d around 1.5 times the molecular length [18]. The $\overline{n}O\overline{m}$ compounds do not exhibit such antiparallel coupling and have a normal monolayer smectic A phases [18]. Secondly, we wanted to investigate near the N–SmA transition the effect of the coupling between the nematic and smectic A order parameters on the refractive index and compare its critical (N–SmA) behaviour with that of the specific heat capacity results recently obtained in our group [19].

2. Theoretical considerations

2.1. Isotropic to nematic transition

A quantitative description of the ordering in the case when elongated nematic molecules behave like rotatory ellipsoids or rigid rods can be obtained using the scalar order parameter in the Maier–Saupe theory [1, 2, 20]:

$$S = \frac{1}{2} \langle 3 \cos^2 \theta - 1 \rangle, \quad (1)$$

where θ is the angle between the long molecular axis of a molecule and the optical axis. The average angle θ depends strongly on temperature, T . The brackets denote averaging over all directions of the long molecular axes in a small uniformly aligned macroscopic volume.

In the case of optical measurements, the square of the refractive index is equivalent to the high-frequency permittivity. A crucial role in modelling optical and electrical properties of a LC is played by the correct estimation of the local field E_i surrounding the molecule. Two models for the local field have been extensively applied to uniaxial materials. The first one, namely the Vuks–Chandrasekhar–Madhusudana (VCM) model [21, 22] assumes that E_i is isotropic even

in the anisotropic N phase, and it leads to the result:

$$K_V = \frac{\Delta n^2}{\langle n \rangle^2 - 1} = \frac{\Delta \alpha}{\langle \alpha \rangle} S(T) \quad (2)$$

where $\Delta n^2 = n_e^2 - n_o^2$ is the anisotropy of the square of the refractive index, and the tensorial average $\langle n \rangle^2$ is given by

$$\langle n^2 \rangle = \frac{1}{3} (n_e^2 + 2n_o^2) \quad (3)$$

where n_o and n_e are the ordinary and extraordinary refractive indices, respectively. The polarizability anisotropy is given by $\Delta \alpha = \alpha_l - \alpha_t$ with α_l and α_t the longitudinal and transverse polarizabilities relative to the long molecular axis, respectively. The mean polarizability (an intrinsic temperature independent molecular property) is defined similarly to equation (3), i.e. $\langle \alpha \rangle = (1/3)(\alpha_l + 2\alpha_t)$.

The second model, proposed by Neugebauer–Maier–Saupe (NMS) [23–25], allowing for an anisotropic distribution of neighbours around each molecule, gives

$$K_N = \frac{9}{4B} \left[\left(B^2 - \frac{10}{3}B + 1 \right)^{1/2} + \frac{B}{3} - 1 \right] = \frac{\Delta \alpha}{\langle \alpha \rangle} S(T) \quad (4)$$

where B is given by

$$B = \frac{\langle n \rangle^2 - 1}{\langle n \rangle^2 + 2} \left(\frac{n_e^2 + 2}{n_e^2 - 1} + 2 \frac{n_o^2 + 2}{n_o^2 - 1} \right). \quad (5)$$

It should be noted that the difference between the VCM and NMS models arises from the differences in the approximate description of the electric field of a light wave in the nematic medium.

The polarizability, being a molecular property, does not depend on temperature. The temperature dependence of the order parameter in the nematic phase can be approximated with a four-parameter expression consistent with mean-field theory for a critical as well as a tricritical point for a weakly first order transition [5, 13, 14, 26]. The temperature dependence of the order parameter can be written as

$$S(T) = S^{**} + A \tau^\beta \quad (6)$$

where β is the critical exponent and $\tau = 1 - T/T^{**}$ is the reduced temperature difference. T^{**} is the effective second-order transition temperature, i.e. the absolute limit of the superheating of the nematic phase and is slightly higher than the observed transition temperature T_{NI} . At $T = T^{**}$, $S(T^{**}) = S^{**}$, which is positive. Provided equation (6) is valid down to $T = 0$, a quite reasonable scaling condition for the order parameter is given by $S(0) = 1$ at $T = 0$, which implies $S^{**} + A = 1$. As elsewhere [11], we used for the fits the following

expression derived from equations (2), (4) and (6):

$$K_{N,V} = \frac{\Delta \alpha}{\langle \alpha \rangle} \left[S^{**} + (1 - S^{**}) \left(1 - \frac{T}{T^{**}} \right)^\beta \right]. \quad (7)$$

This expression contains four parameters $\Delta \alpha / \langle \alpha \rangle$, S^{**} , T^{**} and β . Note that temperatures are expressed in K. For more details, see Chirtoc *et al.* [11].

Previous attempts to fit the temperature dependence of the order parameter assumed a smaller number of free parameters for the fitting procedure. The Haller approximation [12] consists of determining $\Delta \alpha / \langle \alpha \rangle$ and β from expressions similar to equations (4) and (6) in which $S^{**} = 0$ and $T^{**} = T_{NI}$, which is not consistent with the first-order character of the N–I transition [8, 13, 14].

2.2. Nematic to smectic A transition

In liquid crystals exhibiting a smectic A phase as well as a nematic phase it is expected that the occurrence of the smectic layering enhances the orientational order of the long molecular axes, the enhancement depending on the strength of the coupling between the orientational (N) and positional (SmA) order parameters. For the coupling of the nematic order parameter S with the smectic order parameter Ψ , de Gennes [27] introduced in a mean-field approach the relationship $S - S_0 \propto \langle |\Psi|^2 \rangle$ for $T < T_{NA}$. Here S_0 is the hypothetical nematic order parameter in the absence of smectic ordering. With the inclusion of short-range SmA ordering fluctuations in the nematic phase, this form has to be modified [15] into $S - S_0 \propto \langle |\Psi|^2 \rangle$. From rather general arguments it follows as a consequence of the Landau–de Gennes free energy [17, 27, 28] that

$$\langle |\Psi|^2 \rangle = L \pm M^\pm |t|^x \quad (8)$$

where $t = (T - T_{NA})/T_{NA}$ and $x = 1 - \alpha$, with α the critical exponent for the specific heat capacity. \pm indicates above and below T_{NA} , respectively. Although, as obvious from section 2.1, the relation between Δn and S is complicated by the internal field problem, one can assume to first approximation that they are proportional. Thus, assuming the relation $S - S_0 \propto \langle |\Psi|^2 \rangle$ one can determine the exponent x in equation (8) from $\Delta n(T)$ data near the N–SmA transition and verify the theoretical relation $x = 1 - \alpha$ by comparison with the α value from specific heat capacity data when available.

A relationship between the exponents x and α can also be inferred via the Lorenz–Lorentz relationship between the refractive index and the density ρ . Indeed, in going from the N phase to the SmA phase, the increase in $\Delta n(T)$ and $S(T)$ is accompanied by a similar increase of $\rho(T)$ with decreasing temperature [29, 30]. In

other words, the increase of the nematic order parameter is associated with a better (smectic layering induced) packing of the molecules and an associated density effect. The critical variation of the density with temperature or the volume thermal expansion coefficient should, on the basis of the generalized Pippard relations, have the same power law divergence at a second order phase transition as that of the specific heat capacity [31], thus with a critical exponent α .

3. Experimental

We measured the refractive indices of the $\overline{10}O\overline{4}$ LC material, which was purchased from Soyushim Reactive Inc., Russia, as a function of temperature with two refractometers based on the same principle: determination of the critical angle by back reflection. The prisms of the refractometers were treated to induce the desired orientation of the $\overline{10}O\overline{4}$ sample. For planar alignment, which yields n_o , a film of polyvinyl alcohol (PVA) was deposited on one of the prisms, then the prisms were subsequently rubbed with a velvet cloth. For homeotropic alignment, which yields n_e , the other prism was treated with a hexadecyltrimethylammonium bromide (HTAB) solution in ethanol. The sample layer between the main prism and the secondary prism was 0.2 mm thick, which is similar to the value used previously [11]. The cell was loaded with the $\overline{10}O\overline{4}$ sample at $T > T_{NI}$ in order to avoid flow alignment. Refractive index measurements were performed whilst decreasing temperature.

The ordinary refractive index, n_o , was measured on an Atago–Abbe type 1130 refractometer. By visual interpolation of the position of the boundary line between the dark and light fields, one may reach an ultimate resolution of 5×10^{-5} . An automatic instrument model GPR 11–37 produced by Index Instruments was used to measure the extraordinary index, n_e , with a resolution of 10^{-4} . The wavelength of the light sources of both instruments was 589.3 nm.

The temperature of both refractometers was controlled by the same Neslab EX-221 programmable circulator thermostat. The temperature stability was about 0.04 K. The refractometers were connected in series by silicon rubber tubes insulated by larger rubber foam tubes. So in one run it was possible to measure both refractive indices, n_o and n_e , simultaneously. A HP 2850 quartz crystal thermometer (based on a temperature–frequency calibration curve) with a resolution of 0.01 K was positioned in the circulating water close to the prism of the Atago instrument. Details have been given previously [11]. We considered the N–I transition temperature, T_{NI} , to be the lowest temperature of a measured point in the I phase. The observed transition

temperature was 358.51 K. Note that before starting measurements on a $\overline{10}O\overline{4}$ sample, we made some measurements on 5CB and 8CB liquid crystal samples in order to check our ability to obtain reproducible results for the refractive indices like those reported previously [11].

4. Results and discussion

4.1. Temperature dependence of the nematic order parameter

Experimental values of the refractive indices n_o and n_e in the N phase and of $n(T)$ in the I phase are displayed in figure 1 for the temperature interval $-8 \text{ K} < T - T_{NI} < 5 \text{ K}$. In the N phase, n_o and n_e values were averaged over the results obtained in three runs. The quantities K_V and K_N were calculated from the experimental results for $n_o(T)$ and $n_e(T)$. In the N phase, the typical noise level per point for the K_V function was about 10^{-4} . It is worthwhile noting that repetition of the measurements and averaging of the data is necessary for successful fitting to equation (7) [11]. For the fitting procedure we used a nonlinear multi-parameter fitting program, using a subroutine of MatlabTM, based on the conjugated gradient method [11]. The optimization criterion is the minimization of the reduced χ_r^2 error function which is given by the ratio between the variance of the fit s^2 and the variance of the data σ^2 [32]. The starting values of the parameters appearing in equation (7) were: $\Delta\alpha/\langle\alpha\rangle = 0.51$, $S^{**} = 0.1$, $T^{**} = T_{NI} + 0.44$, $\beta = 0.24$.

Table 1 presents the fit results of the K_V (VCM) and K_N (NMS) models. In order to check the consistency of the fit results range shrinking was applied. It consists of eliminating gradually from the fit the points situated at each end of the data set, while observing the stability of the fit results. At the high temperature end some points (very close to T_{NI} and probably in the two-phase region) had to be eliminated. The $\overline{10}O\overline{4}$ compound exhibits a nematic–smectic A (N–SmA) transition at about $T_{NA} = 77^\circ\text{C}$ and its influence is present in the nematic phase. At the low temperature end of the N phase, range shrinking showed that only a 5.28 K data range was available for the fitting procedure. Thus, the pre-transitional smectic behaviour continues up to 3.4 K above T_{NA} . A similar situation was observed for the 8CB compound, where the pre-transitional smectic behaviour continues up to 4 K above T_{NA} [11]. Figure 2 shows the extrapolated fit results and the residuals of the fitting procedure for both the K_V and K_N models. The pre-transitional smectic behaviour is clearly seen in figure 2.

Figure 3 presents the profiles of the χ_r^2 error functions which correspond to the fits of K_V and K_N data. They

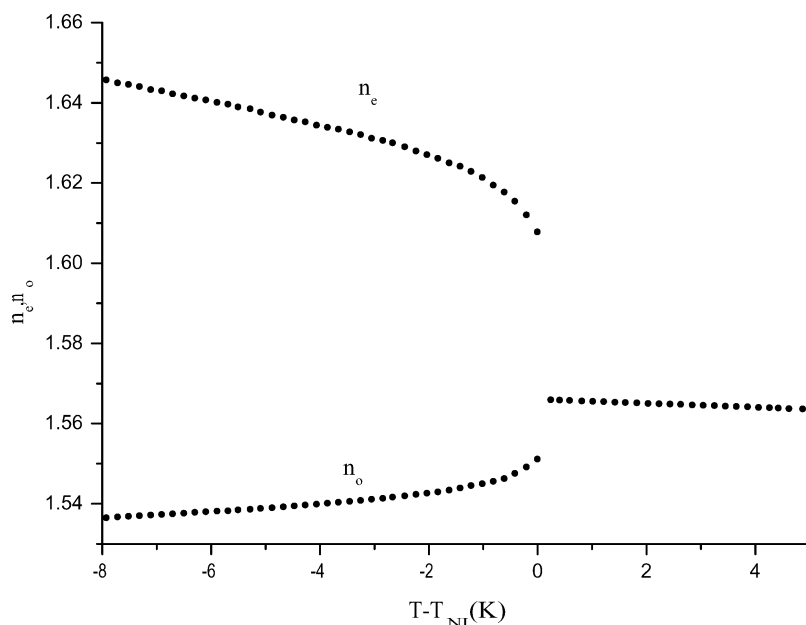


Figure 1. Refractive indices, n_o and n_e , in the nematic phase of $\overline{10O4}$ and n in the isotropic phase as a function of $T - T_{NI}$.

Table 1. Results of fitting in the nematic phase of $\overline{10O4}$ using equation (7). Parameter values in square brackets indicate that the parameter was held constant at the quoted value. The molar mass, M , of $\overline{10O4}$ is $426.602 \text{ g mol}^{-1}$ and $T_{NI} = 358.51 \text{ K}$.

$\Delta\alpha/\langle\alpha\rangle$	S^{**}	T^{**}/K	β	χ_r^2	Fitting model
0.496 ± 0.044	0.107 ± 0.073	358.67 ± 0.17	0.241 ± 0.061	1.07	K_V
0.410 ± 0.036	0.118 ± 0.064	358.66 ± 0.16	0.251 ± 0.059	0.67	K_N
0.504 ± 0.003	0.115 ± 0.004	358.66 ± 0.02	[0.25]	0.98	K_V
0.409 ± 0.003	0.117 ± 0.004	358.66 ± 0.02	[0.25]	0.64	K_N

were determined by varying β in steps of 0.02 during the fitting procedure. The average value of the critical exponent is found to be $\langle\beta_{opt}\rangle = 0.237 \pm 0.014$. In table 1 fits with β a free parameter also are given in addition to fits with β fixed to 0.25. All these values are consistent with a value of 0.25 for β . Thus, it should be concluded that, within the limit of experimental error, the critical exponent of the nematic order parameter of this compound is in accordance with the value predicted by the tricritical hypothesis (TCH) i.e. $\beta = 0.25$ [6, 7]. This result, for a compound without a terminal dipole and with a normal monolayer smectic A phase, is also within experimental resolution the same as that obtained [11] for four compounds of the nCB homologous series with strong terminal dipoles and partial smectic bilayer phases.

Figure 4 displays the correlation between the parameters β and S^{**} along the degenerate river on the χ_r^2 surface (details of the fitting procedure are provided elsewhere [11]). The trajectories of fits for both models follow a curved path so that there is an absolute maximum $S^{**}_{max} = 0.145$ on average. From Figure 4 it

is clear why in the Haller approximation ($S^{**} = 0$ assumed) the obtained β values are systematically low, namely $\beta < 0.20$. Furthermore, $\Delta\alpha/\langle\alpha\rangle$ is lower as well by 14–15% and χ_r^2 values are larger by a factor of 2.3 in comparison with four-parameter fitting results. It should be noted that, not only for a fixed value of $\beta = 0.25$ but also for four-parameter fitting, the corresponding S^{**} takes a value of 0.11 on average. Note that large uncertainties in S^{**} fit values are due to the low sensitivity of $S(T)$ to this parameter. The smallest uncertainty (less than $\pm 0.2\%$) is observed for T^{**} due to the high sensitivity of $S(T)$ to it. An average $\langle T^{**} - T_{NI} \rangle = 0.16 \pm 0.04 \text{ K}$ is observed. Note that in previous work for the nCB series $\langle T^{**} - T_{NI} \rangle = 0.21 \pm 0.04 \text{ K}$ was found [11].

In an alternative analysis we also used, as fitting equation, the derivative of equation (7) given by

$$\frac{dK_{V,N}}{dT} = C \left(1 - \frac{T}{T^{**}} \right)^{\beta-1}, \quad (9)$$

where C is a constant, in order to find β and T^{**} values. The derivatives of the quantities K_V and K_N with respect

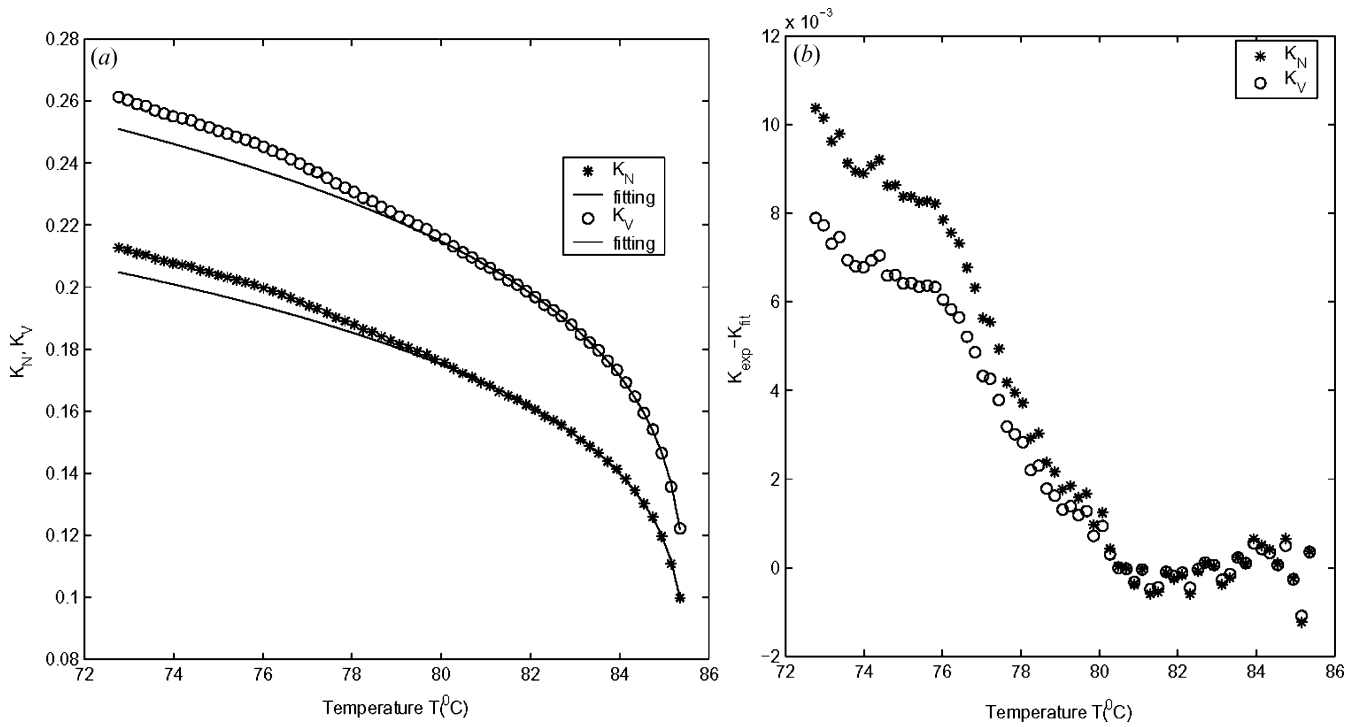


Figure 2. (a) The quantities K_V [equation(2)] and K_N [equation(4)] as a function of temperature. Solid lines are the fits to equation(7). Note that the smectic A phase is included in the temperature range. (b) Temperature dependence of the quantity $K(T) - K_{fit}(T)$ (see text) near the N-SmA transition. Pre-transitional behaviour above and below $T_{NA} = 77.03^\circ\text{C}$ is clearly seen in both figures.

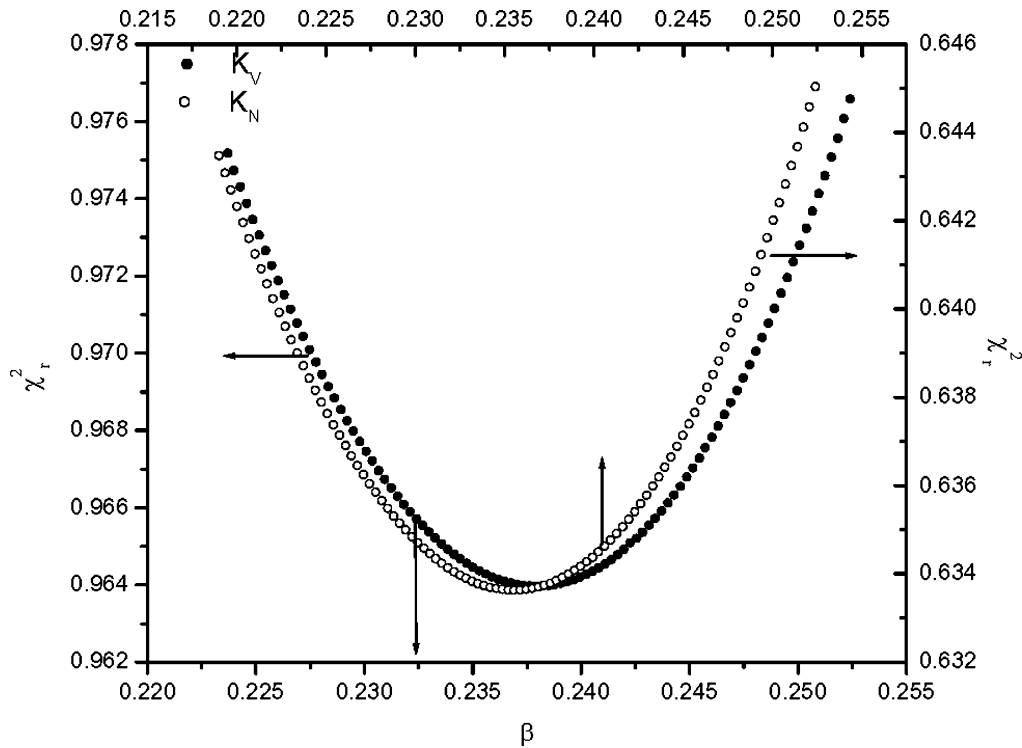


Figure 3. Profiles of the error function, χ_r^2 , obtained from three-parameter fitting and stepwise variation of β .

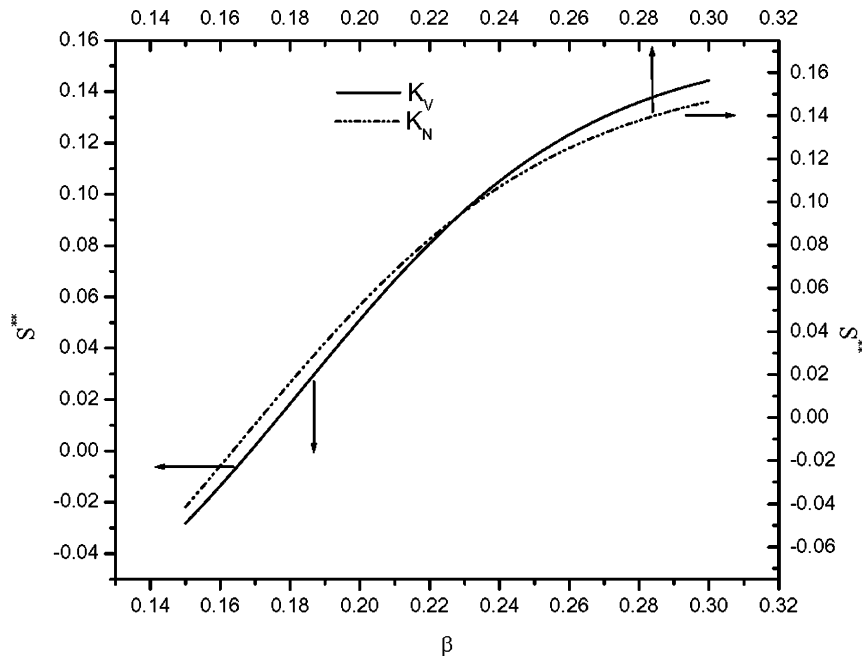


Figure 4. Correlation of four-parameter fit results in the (β, S^{**}) plane around the optimal values.

to temperature were fitted to the double logarithmic form of equation (9). The values of $\log C$ and β have been calculated by the linear regression method. The parameter T^{**} was adjusted to get the best correlation coefficient of the linear regression. β and T^{**} values determined by this method are listed in table 2. Figure 5 shows the results of derivative analysis on log-log scale. As can be seen in table 2, both β and T^{**} values are quite close to the ones presented in table 1. It should be noted that when fitting to the K_N model, the parameters S^{**} , T^{**} , and β remained practically the same as those of table 1, but the polarizability anisotropy decreased by a factor 1.21. Similarly, the parameter C appearing in equation (9), which is related to the polarizability anisotropy, decreased by a factor 1.24 when fitting to the K_N model. On the other hand, as seen in figure 3 for the K_N model, the error function χ_r^2 was somewhat lower than the one for K_V model fits.

4.2. Coupling between the nematic and smectic order parameters

In figure 2 a one can clearly see that there is an increase in the nematic order parameter $S(T)$ induced by the

Table 2. Parameter values from the fits with the double logarithmic form of equation (9).

β	T^{**}/K	$\log C$	Fitting model
0.255 ± 0.042	358.75 ± 0.13	-1.578 ± 0.094	K_V
0.252 ± 0.042	358.75 ± 0.13	-1.675 ± 0.094	K_N

occurrence of smectic layering both above and below $T_{NA} \approx 77^\circ C$. Also shown, in figure 2 b, is the difference $K_{exp} - K_{fit}$, with K_{fit} from the fits in the nematic range above $T_{NA} + 3.4 K$ extrapolated down to lower temperatures. From the temperature dependence of this quantity, one observes there is an anomalous increase in $P(T) = -dK/dT$ both above and below T_{NA} . One could try to numerically differentiate the data of figure 2 b, but this is, however, not very accurate because of the scatter in the data. Instead we introduced a new quantity $Q(T) = -[K(T) - K_{NA}]/(T - T_{NA})$. It can easily be shown that in the case where $P(T)$ follows a power law with a given critical exponent z , the limiting behaviour of $Q(T)$ also follows a power law with the same critical exponent. This quantity, $Q(T)$, is similar to the quantity $C(T) = [H(T) - H_{NA}]/(T - T_{NA})$, with $H(T)$ the enthalpy as a function of temperature obtained in adiabatic scanning calorimetry [33]. $C(T)$ obeys a power law with the same critical exponent α as the specific heat capacity $C_p = dH/dT$ [34]. The quantity $Q(T)$ has a large (regular) background contribution coming from the temperature dependence of K_{fit} . The anomaly in $Q(T)$ can be seen more clearly by looking at

$$Q(T) - Q_b(T) = -\frac{K(T) - K(T_{NA})}{T - T_{NA}} + \frac{K_{fit}(T) - K_{fit}(T_{NA})}{T - T_{NA}} \tag{10}$$

As shown in figure 6, the temperature dependence of the quantity $Q(T) - Q_b(T)$ clearly exhibits critical

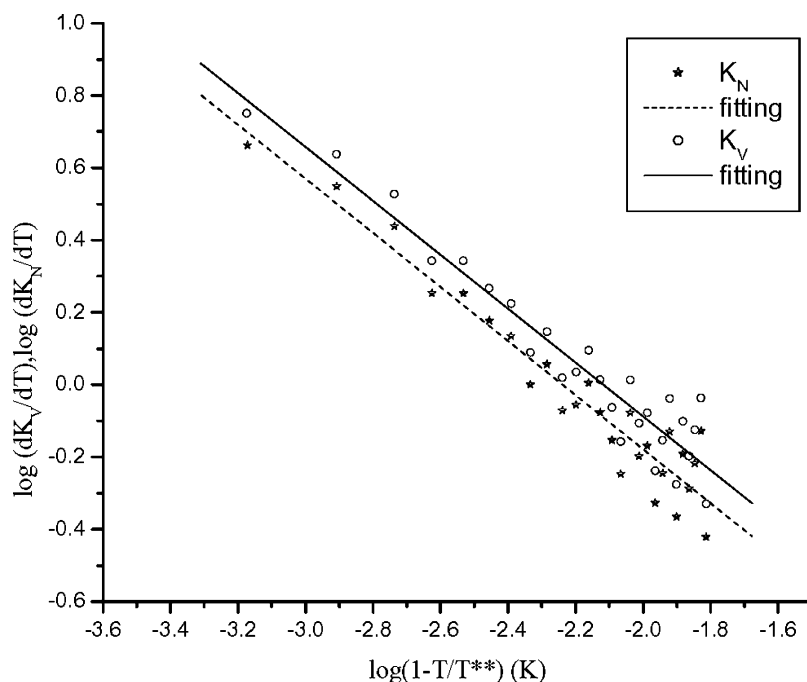


Figure 5. Derivative analysis of experimental data for the quantities K_V and K_N in the nematic phase of $\overline{10}O\overline{4}$ on a log-log scale. Solid and dashed lines are the fits to the double logarithmic form of equation (9).

behaviour near T_{NA} . As argued in section 2.1, we think that the critical exponent z describing this behaviour should be the critical exponent α describing the critical behaviour of the specific heat capacity and the volume

thermal expansion coefficient. Thus, one expects $z = \alpha = 1 - x$. The increase of the nematic order parameter $S(T)$, and thus also of $K(T)$, is, indeed, associated with a better packing of the molecules and an associated

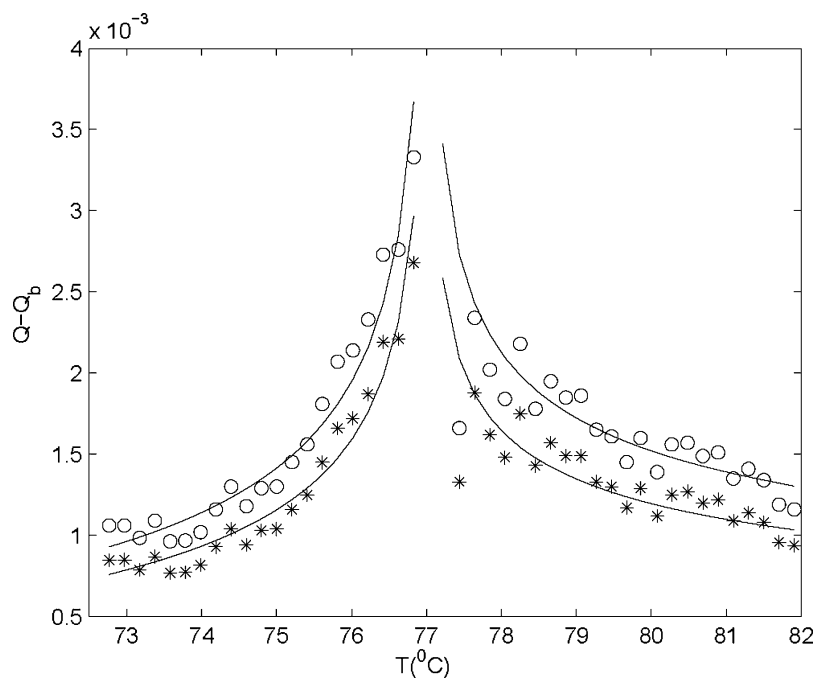


Figure 6. The quantity $Q - Q_b$ defined in equation (10) near the N-SmA phase transition temperature ($T_{NA} = 77.03^\circ\text{C}$). Circles are for K_V and stars for K_N . Solid lines are fits using equation (11).

density effect. The critical variation of the density with temperature or the volume thermal expansion coefficient should, on the basis of the generalized thermodynamic Pippard relations, have the same power law divergence at a second order phase transition as that of the specific heat capacity [31]. In order to obtain a value for the exponent z we used the following fitting expression:

$$Q(T) - Q_b(T) = A^\pm \left| \frac{T - T_{NA}}{T_{NA}} \right|^{-z} + B, \quad (11)$$

with critical amplitudes A^+ and A^- above and below T_{NA} and a background term B .

Figure 7 gives χ_r^2 results of simultaneous fits of the $Q - Q_b$ above and below the transition (at $T_{NA} = 350.18$ K) as a function of z from fits with three adjustable parameters (A^+ , A^- and B). Both for K_V and K_N , the minimum is found for a z value between 0.23 and 0.25. In a recent experiment we also carried out adiabatic scanning calorimetry (ASC) measurements on this compound and found the N-SmA transition to be second order and obtained a value $\alpha = 0.23 \pm 0.01$ in the power law for the critical specific heat capacity divergence [19]. Thus, there is excellent agreement between the z value obtained here and the α value obtained from ASC.

The temperature dependence of the mean-square smectic order parameter, $\langle |\Psi|^2 \rangle$, can also be obtained from the measurement of the integrated X-ray scattering intensity as a function of temperature [28]. From fits

of this quantity with equation (8) it is thus also possible to obtain values for the critical exponent x in equation (8) in an alternative way. Such measurements have been carried out by Chan *et al.* [28] for a series of compounds with a large variety of temperature ranges of the nematic phase between the isotropic and smectic A phases. For compounds with small nematic ranges and close to the tricritical point ($\alpha = 0.5$), x values close to $1 - \alpha$ were obtained. However, for compounds with (very) wide nematic ranges, where one has α values close to the 3D-XY universality class value $\alpha = -0.02$, it was found that x was not equal to $1 - \alpha$ and substantially smaller than 1. This disagreement raised the question concerning the quantitative validity of the Landau-de Gennes free energy [28]. Here, however, from our analysis of the refractive index for a compound with an effective α value intermediate between the tricritical and the 3D-XY value, we find that within experimental resolution $z = \alpha$. Whether such agreement between z and α would also be observed for a series of compounds with widely different ranges of the nematic phase, is not clear at the moment and remains to be investigated.

5. Conclusions

We have presented new experimental data on the temperature dependence of the refractive index in the isotropic, nematic and smectic A phases of the 4-butyloxyphenyl 4'-decyloxybenzoate ($10O4$) liquid crystal. From the analysis of the data, using both the Vuks and Neugebauer models to account for the internal

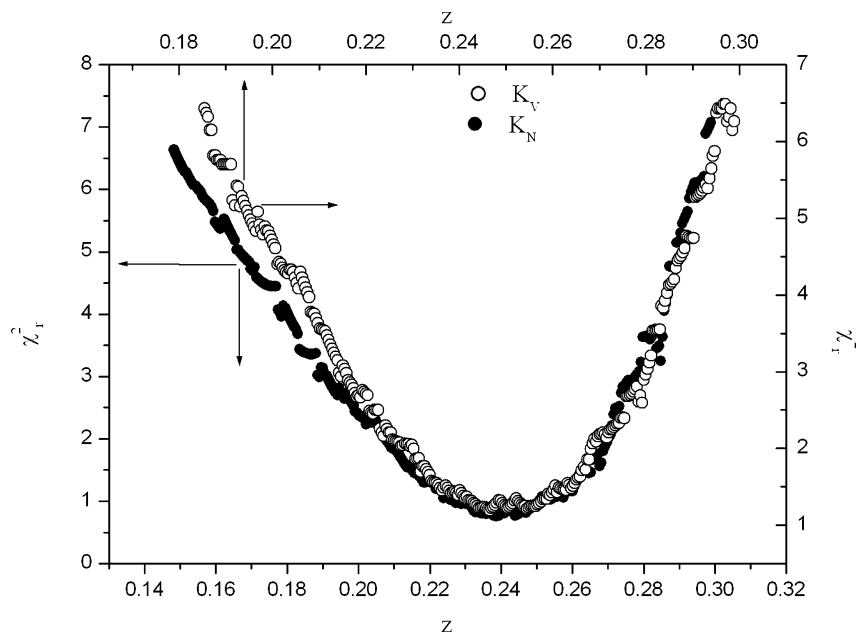


Figure 7. Profiles of the error function χ_r^2 obtained from fits of $Q(T) - Q_b(T)$ with equation (11) and stepwise variation of the critical exponent z .

electric field, information on the temperature dependence of the orientational order parameter, $S(T)$, was obtained. From the data in the nematic phase sufficiently far away from the nematic–smectic A transition temperature T_{NA} , we determined, using a four-parameter fitting expression consistent with mean-field theory, the exponent β describing the critical behaviour of $S(T)$ at the N–I transition. The average value of the critical exponent β for the orientational order parameter was found to be 0.246 ± 0.06 (table 1). A derivative analysis resulting in three-parameter fitting confirmed this β value (table 2). The obtained β value in this non-polar compound is within experimental resolution the same as previously obtained values for four members of the strongly polar n CB homologous series [11], and is in good agreement with the tricritical hypothesis, $\beta=0.25$. In a temperature range of about 4 K above and below the N–SmA transition temperature, pre-transitional evidence for the coupling between the nematic and smectic order parameters was observed. From the analysis of our refractive index data above and below the N–SmA transition temperature we found that the variation of the temperature dependence of the nematic order parameter near T_{NA} shows a power law divergence with a critical exponent z between 0.23 and 0.25. This value is, within experimental resolution, the same as the value of α (0.23 ± 0.01) obtained by adiabatic scanning calorimetry [19] for the specific heat capacity. As far as we know this is the first time that this equality between z and α has been demonstrated and it remains to be investigated for other compounds.

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