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Preliminary communication

Positive dipole correlation at the I/B₂ transition in the isotropic phase

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The first evidence of a positive dipole correlation in the isotropic phase near to the I/B₂ transition is given.

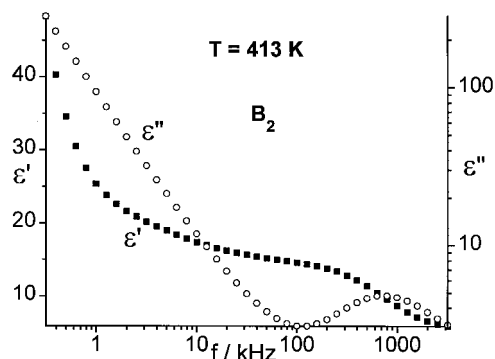
Pre-transitional effects in the isotropic phase near to the transformation into a mesophase are known and can be observed up to more than 10 K above the clearing temperature. Thus, the formation of nematic clusters can be clearly seen as unexpectedly high values of the Kerr constant [1]. Dielectric measurements prove the existence of such clusters by a strong deviation of the static dielectric constant from the linear slope in a ϵ_0/T diagram. In this case, the antiparallel correlation of the molecular dipoles reduces the ϵ_0 values increasing on approaching the phase transition from the isotropic phase. Two molecular interpretations are invoked to account for the antiparallel dipole correlations: (i) an interaction of strong molecular dipoles detected first by Bradshaw and Raynes [2] and (ii) a steric interaction as observed at the isotropic–nematic phase transition of a sample consisting of wedge-shaped swallow-tailed molecules [3]. In the latter case the strong steric interaction results in a maximum of the dielectric constant 5 K above the clearing temperature.

Particularly in the latter case, a further decrease of the mean dielectric constant in the nematic phase is observed on further cooling, pointing to the fact that the effective dielectric constant of the mesophase is

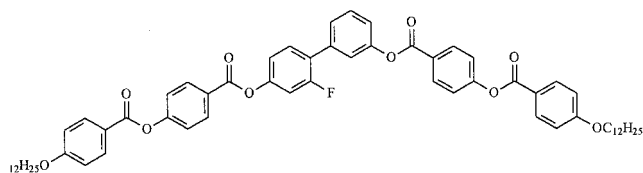
additionally reduced by the nematic order. With respect to this result, one may expect for phases in which a local ferroelectric order is present, an increase of the dielectric constant on approaching the phase transition from the isotropic state. This effect is new and provides further evidence for the positive dipole correlation mentioned already, or for short range ferroelectric order in the mesophase.

For these investigations a sample showing the I/B₂ transition was chosen. In this case the banana-shape molecules are packed in layers in which the direction of bend alternates from layer to layer. Thus, the ferroelectricity of the first layer is compensated and an antiferroelectric order is established [4]. Dielectric measurements in the B₂ phase prove the strong increase of the static dielectric constants ϵ_0 and the appearance of an additional dielectric relaxation range [5]. The increase of ϵ_0 is observed for two reasons: (i) an additional low frequency relaxation which disappears in the isotropic phase (see also figure 1, $\epsilon_0 - \epsilon_1$) and (ii) reorientation about the long molecular axes which results in the dielectric increment $\epsilon_1 - \epsilon_2$. This relaxation range can be observed in the isotropic phase with much lower intensity [5]. By interpretation of the much higher dielectric constant ϵ_1 in the B₂ phase as result of the ferroelectric short range order, one should also detect this in the pre-transitional range.

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Figure 1. Dielectric data of the B₂ phase.

For these experiments a chemically stable compound with a relatively low clearing temperature is necessary in order to measure an extended isotropic range without chemical decomposition which may occur at higher temperatures. For this reason compound **1** [6] was investigated:



1 Cr 376 B₂ 418 I; cooling I 415 B₂ 321 Cr (K)

The experimentally obtained dielectric constants are presented in figures 1 and 2. For the given compound the two discussed absorption ranges in the B₂ phase were detected.

The calculation of the characteristic data used equation (1),

$$\varepsilon^* = \varepsilon_2 + \frac{\varepsilon_0 - \varepsilon_1}{1 + (i\omega\tau_1)^{1-\alpha_1}} + \frac{\varepsilon_1 - \varepsilon_2}{1 + (i\omega\tau_2)^{1-\alpha_2}} - \frac{iA}{f} + \frac{B}{f^N} \quad (1)$$

which consists of two Cole–Cole mechanisms (terms 2 and 3), a conductivity contribution (term 4) and

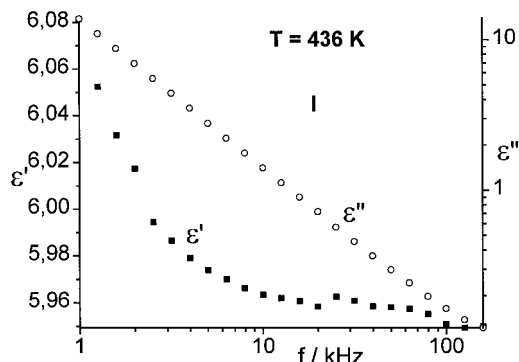


Figure 2. Dielectric data of the isotropic state.

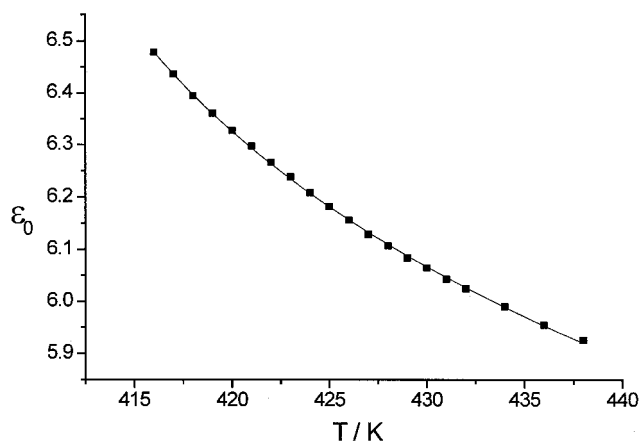
(term 5) a description of the capacitance of the electrical double layer at low frequencies where ε_i are the low and high frequency limits of the dielectric constant, $\omega = 2\pi f$ (f is frequency), τ_i are the relaxation times, and α_i are Cole–Cole distribution parameters. In this way the following parameters of the B₂ phase of **1** were calculated from the points given in figure 1: $\varepsilon_0 = 19.9$, $\varepsilon_1 = 15.4$, $\tau_1 = 1.2 \times 10^{-5}$ s, $\alpha_1 = 0.05$, $\varepsilon_2 = 4.7$, $\tau_2 = 1.9 \times 10^{-7}$ s, $\alpha_2 = 0.08$, $A = 9.2 \times 10^4$ s⁻¹, $B = 8.4 \times 10^4$ s^{-N}, $N = 1.33$.

The relaxation times in the isotropic phase are much higher than 1 MHz. Thus, relaxation effects, by calculation of the dielectric constant in the isotropic phase, can be excluded by choosing a proper frequency range as shown in figure 2. Furthermore there is no possibility of avoiding the influence of the double layer at the surface to the metal capacitor which increases the ε values at low frequencies. This effect can only be excluded by fitting the experimental data to the first and last terms of equation (1). In this case, ε_2 in equation (1) has the meaning of ε_0 for the isotropic phase. The experimental data were always taken from the same frequency range in order to reduce the minimal errors of the equipment. The dielectric constants so obtained are shown in figure 3. It should be mentioned that similar behaviour was also measured during heating.

The experimentally obtained static dielectric constant increases with decreasing temperature in a critical-like behaviour. For this reason the data were fitted to the expected linear behaviour and a 'critical' term:

$$\varepsilon_0 = A + BT + C(T - D)^E. \quad (2)$$

The mathematical analysis of the problem results in a mutual dependence of the parameters A , B , C , D and E . The reason for this is that the measurements could not be extended to the linear region because of the expected problem of chemical decomposition. Nevertheless plausible parameters could be extracted by choosing good starting

Figure 3. Static dielectric constants of **1** in the isotropic phase.

parameters for $A=9.0$ and $B=-0.008$. Then $C=8.23 \pm 1.35$, $D=(398.2 \pm 1.1)$ K and $E=(-0.80 \pm 0.04)$ were calculated. The related curve is also shown in figure 3.

From the dielectric measurements in the isotropic state near to the I/B_2 transition it can be concluded that there is a positive dipole correlation which increases the dielectric constant especially close to the phase transition. This is evidence for ferroelectric clusters in the pretransition range and of course, on further cooling, in the B_2 phase also.

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