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STUDY OF ELASTIC PROPERTIES NEAR A NEMATIC-SMECTIC-*A* TRANSITION*

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Measurements of the splay and bend elastic constants of octyl-cyano-biphenyl near the nematic-smectic-*A* transition are presented. The pretransitional increase of K_3 obeys the relation $\delta K_3 \sim (T-T_{SN})^{-\nu}$, with $\nu = 1$.

1. *Introduction*

In the last few years a large number of substances have been synthesized, which exhibit second order or weakly first order nematic-smectic-*A* transition. Near transitions of these types pretransitional phenomena are observed in the nematic range, which are due to the presence of small clusters in which the smectic order has already developed.

A typical pretransitional effect is the temperature dependence of the Frank-elastic constants near the transition. While the splay elastic constant (K_1) does not show any sharp change, the twist (K_2) and bend (K_3) elastic constants increase rapidly as the transition temperature is approached. This fact is explained by the structure of the smectic-*A* phase; in this phase only splay is allowed, twist and bend are forbidden. The gradual appearance of cybotactic groups with smectic order in the nematic phase leads to the increase of K_2 and K_3.

A number of measurements of the bend and twist elastic constants near nematic-smectic *A* transitions have been reported recently. The data are usually interpreted by assuming that the increment of K_3 or K_2 is proportional to some power of $T-T_{SN}$ (T_{SN} transition temperature):

$$\delta K_3 \sim (T-T_{SN})^{-\nu}. \tag{1}$$

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Different authors have found different values for ν; e. g. P. Cladis on CBOOA $\nu = 0.52$ [1]; Pindak et al. also on CBOOA $\nu = 0.68$ [2]; Cheung and Meyer on p-butoxybenzylidene-p'-β methylbutylaniline, which has a weakly first order nematic-smectic A transition, have found $\nu = 1$ [3]. These data indicate the necessity of further experiments in order to clarify the situation.

In the present paper we report measurements of K_1 and K_3 on octyl-cyano-biphenyl (OCB). The material, synthesized in our laboratory, has a weakly first order nematic-smectic A transition at 304.1°, the nematic-isotropic transition was found to be at 310.8°.

The elastic constants have been determined by measuring the amplitude of the splay deformation, induced by an electric field in a homogeneously aligned sample. In the measurements the field has been kept constant and the temperature scanned. As described in detail in Section 2, this method gives a precise determination of the transition temperature, and a check whether the transition is of first or of second order. The measurements provide the anisotropy of the refractive indices also. The results are analysed in Section 3.

In Section 4 we describe the structures obtained in the smectic phase by cooling down the sample in a deformed state.

2. *Experimental method*

In the experiments homogeneously aligned sandwich-cells have been used (director parallel to the boundaries of the cell). OCB has a large positive dielectric anisotropy, thus the alignment can be deformed by an electric field. The theory of deformation in electric field has been published in [4].

The deformation starts at a threshold voltage

$$V_{cr} = \pi \sqrt{\frac{K_1}{\Delta\varepsilon}}. \tag{2}$$

For small deformation the angle between the director and the boundaries (θ) is

$$\theta = \theta_m \sin \frac{\pi}{L} Z, \tag{3}$$

where L is the sample thickness. θ_m and the applied voltage, V, are related as

$$\tfrac{1}{4}\,\theta_m^2 = \frac{1}{\Delta\varepsilon/\varepsilon_\perp + K_3/K_1}\,\frac{V - V_{cr}}{V_{cr}}. \tag{4}$$

In the experiments θ_m has been determined by measuring the optical phase difference ($\Delta\phi$) between the ordinary and extraordinary components of a laser beam. For small deformations

$$\tfrac{1}{4}\,\theta_m^2 = \frac{n_0^2}{n_e(n_e + n_0)}\,\frac{\Delta\phi_0 - \Delta\phi}{\Delta\phi_0}, \tag{5}$$

with

$$\Delta\phi_0 = \frac{2\pi}{\lambda} L(n_e - n_0).$$

Thus measuring $\Delta\phi$ as a function of V, K_1 and K_3 can be determined. From the measurement of $\Delta\phi_0$, $\Delta n = n_e - n_0$ can be calculated. (In principle n_e and n_0 should be known separately for the calculation of K_3. However the factor $n_0^2/n_e(n_e+n_0)$ changes little with the change of n_0, and n_0 itself changes little with the temperature. In the calculation we have put $n_0 = 1.5$.) The dielectric data are taken from [5].

The approximation for small deformations presented above works well only for $K_3/K_1 \sim 1$. For higher K_3/K_1 ratios (>3) it is hard to measure in the limit where this approximation is valid. Thus near the transition, where K_3/K_1 increases rapidly, the elastic constants were determined by comparing the measured data with exactly calculated $\Delta\phi(V)$ curves.

The measurements have been carried out on a 80 µm thick cell. The planar orientation was obtained by evaporating a thin SiO film in an oblique direction, on the cell surfaces. The sample was placed in a copper-block, the temperature of which has been regulated by an ultra-thermostat. The temperature has been measured by a thermocouple, placed in close contact with the sample. The accuracy of temperature measurements is 0.02°.

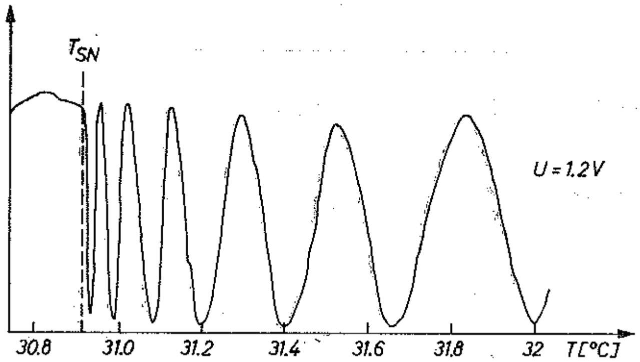

Fig. 1. Intensity of the laser beam as a function of temperature. The sample is placed between crossed polarisators

In the actual measurements the applied voltage has been fixed and the temperature has been decreased with a rate of ~ 0.05°/min. The intensity of the laser beam which gives $\Delta\phi$ is recorded on an X–Y recorder as the function of the temperature. A typical plot is given on Fig. 1. As it can be seen, this method gives a precise determination of the transition temperature, T_{SN}. T_{SN} has been reproduced in different runs within 0.02°.

Another advantage of this method is that it provides a sensitive check, whether the transition is of second or of first order. At a strictly second order transition K_3 goes to infinity, consequently θ_m becomes zero, i. e. $\Delta\phi = \Delta\phi_0$. In our measurements a small difference was found between $\Delta\phi$ and $\Delta\phi_0$ at the transition when field has been applied. This fact clearly demonstrates the first-order character of the transition.

3. *Results and discussion*

On Fig. 2 the anisotropy of the refractive indices (Δn) is presented in the nematic and smectic phase. Δn has a small discontinuity ($\sim 1\%$) at T_{SN}, which indicates again that the transition is weakly first order.

The anisotropy of the refractive indices is in good approximation proportional to the orientational order parameter. The shape of the Δn curve presented here agrees qualitatively with McMillan's calculation of the order parameter [7]. However a deviation is found also; the curve has an inflexion at about the same temperature where the pretransitional effects appear. From this fact we conclude that the presence of small smectic regions has an observable influence on the orientational order parameter already in the nematic phase. This influence is neglected in McMillan's theory.

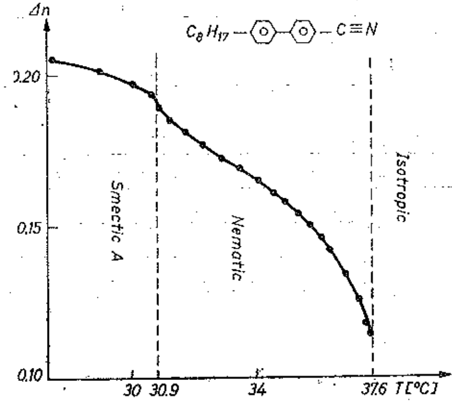

Fig. 2. The anisotropy of the refractive indices as a function of temperature. $\lambda = 0.63$ μm

On Fig. 3 the splay elastic constant is presented near the transition temperature. There is a slight increase of K_1, however, as expected, no divergence has been found.

On Fig. 4 the K_3/K_1 ratio is shown. The pretransitional increase of this ratio starts at about 1° above the transition. Although the transition is of first order, K_3/K_1 becomes very large at the transition. From the $\Delta\phi - \Delta\phi_0$ values, measured at the transition temperature we estimate $K_3/K_1(T_{SN}) \approx 30$.

To make an analysis of the data in terms of a power-law, we estimate the part of K_3/K_1, which is due to the nematic order, to be 1.2. On Fig. 5 $\delta(K_3/K_1) = K_3/K_1 - 1.2$ is plotted against $T - T_{SN}$ on logarithmic scale. As the figure shows, $\delta(K_3/K_1)$ can be approximated near the transition with a power-law of the form $(T - T_{SN})^{-\nu}$ with ν nearly 1.

Our results agree with that of Cheung and Meyer [3], who measured also on a material with weakly first order transition. This suggests that for first order transitions it is a general rule that $\nu = 1$. (We note that as K_1 does not show any divergence, $\delta(K_3/K_1)$ should increase with the same power as δK_3.)

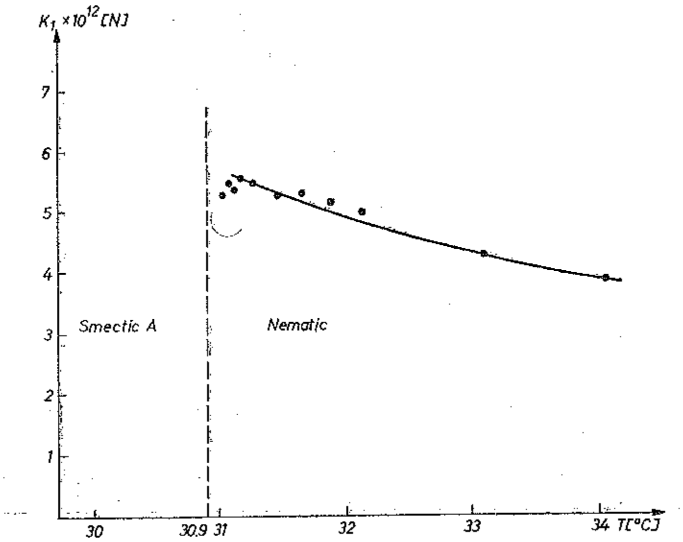

Fig. 3. Variation of the splay elastic constant near the transition

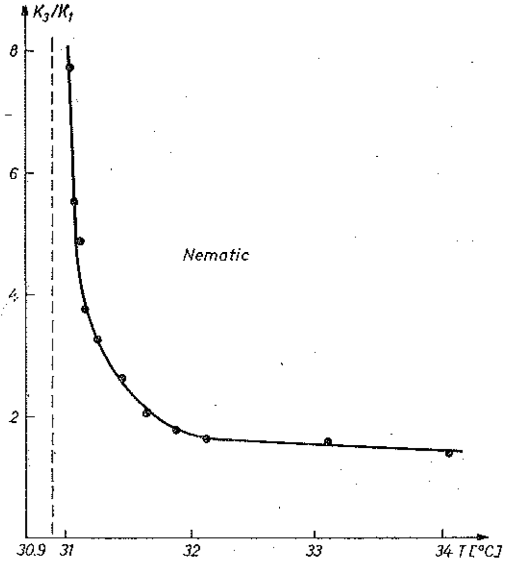

Fig. 4

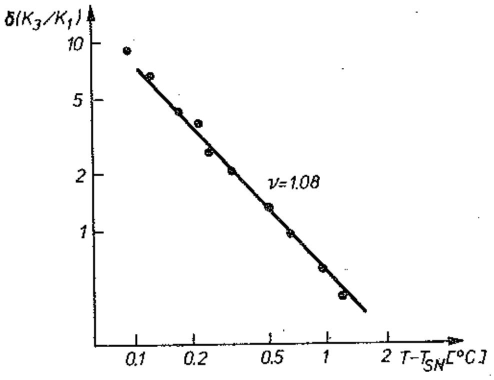

Fig. 5

Fig. 4. The K_3/K_1 ratio near the transition

Fig. 5. $\delta(K_3/K_1)$ against T-T_{SN} on logarithmic scale

4. *"Frozen in" structure in smectic phase*

As mentioned in the previous Sections, when the sample is cooled in the presence of a deformation, induced by an electric field, the deformation does not disappear when the transition temperature is reached. At the transition we have

$$\theta = \theta_m(V, T_{SN}) \sin \frac{\pi}{L} Z.$$

It has been found that this deformation freezes in if θ_m is not too large, i. e. it remains unchanged in the smectic phase even after the field is suppressed. This effect has been deduced from the birefringent measurements; the optical phase difference follows the same temperature dependence as $\Delta\phi_0$, but it is shifted with the value $\Delta\phi_0(T_{SN}) - \Delta\phi(T_{SN})$. It is confirmed by conoscopic observations also; the hyperbolae are shifted when the phase transition is passed in a deformed state.

The arrangement of the smectic planes in the undeformed ($\theta_m = 0$) and deformed ($\theta_m \neq 0$) states are shown on Fig. 6. The deformation is mainly splay, however a weak bend is also present (proportional to θ_m^2). Such a structure can be stabilised by formation of edge dislocations [6]. A relaxation to the homogeneous orientation is not possible, as it would imply a hydrodynamic motion in which the planes had to split.

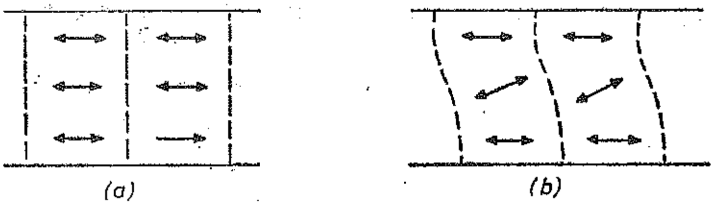

Fig. 6. Undeformed (a) and deformed (b) smectic planes. ←→ director; - - - planes

Observations of this type give an independent check of the first order character of the transition, which can be used for other materials also.

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