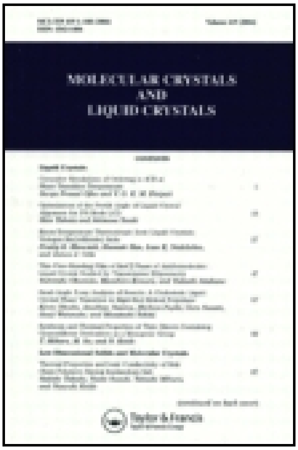

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Relations Between Liquid Crystal Order Parameter and Macroscopic Physical Coefficients-Experimental Proof

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Relations Between Liquid Crystal Order Parameter and Macroscopic Physical Coefficients-Experimental Proof

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In this paper, we relate how we have determined the order parameter by measuring the diamagnetic susceptibilities of the nematic phase, and of the ordered solid state obtained by freezing a nematic "monocrystal." Moreover, we have measured dielectric and refractive indices anisotropies, and elastic coefficients; and we have verified the theories giving the relations between the order parameter and all this physical macroscopic coefficients.

1 INTRODUCTION

The temperature has an important effect on the variations of the order parameter of liquid crystals, mainly near the nematic isotropic transition temperature. Moreover, the macroscopic physical parameters as dielectric and refractive indices anisotropies, and elastic coefficients are directly related to the order parameter. An important point is the understanding of the collective molecular organisation phenomena related to the electro-optic applications.

The order parameter temperature dependence has been measured and discussed by some authors (1 to 6) on some nematic liquid crystals by

N.M.R, I.R spectrum, U.V spectrum, optical measurements. The originality of this paper consists in the fact that we have determined the order parameter temperature dependence by measuring the diamagnetic susceptibility anisotropy, first in the nematic phase, second in the ordered solid state obtained by freezing a nematic "monocrystal", orientation of which is given by a magnetic field ($0 \leq H \leq 150$ KOe). From our measurements, we can say that this last one is independent of the temperature in the solid state, below the solid-nematic transition. Materials used are:

MBBA:	Methoxy Benzilidene Butyl Aniline
MPT:	Methoxy Pentyl Tolane
ABABN:	Alkoxy Benzilidene Amino Benzonitrile

2 MAGNETIC SUSCEPTIBILITY TEMPERATURE DEPENDENCE: ORDER PARAMETER DETERMINATION

The variations of the magnetic susceptibilities as a function of the reduced temperature of MBBA, ABBABN, and MPT have been measured with a translation balance.[8] The reduced temperature is defined by $\tau = T - T_{N,I}/T_{N,I}$, where $T_{N,I}$ is the nematic-isotropic transition temperature. For MBBA (Figure 1) our results are in good agreement with Gasparoux and all estimations.[9] For MPT and ABABN (Figure 2) we obtained similar curves.[10]

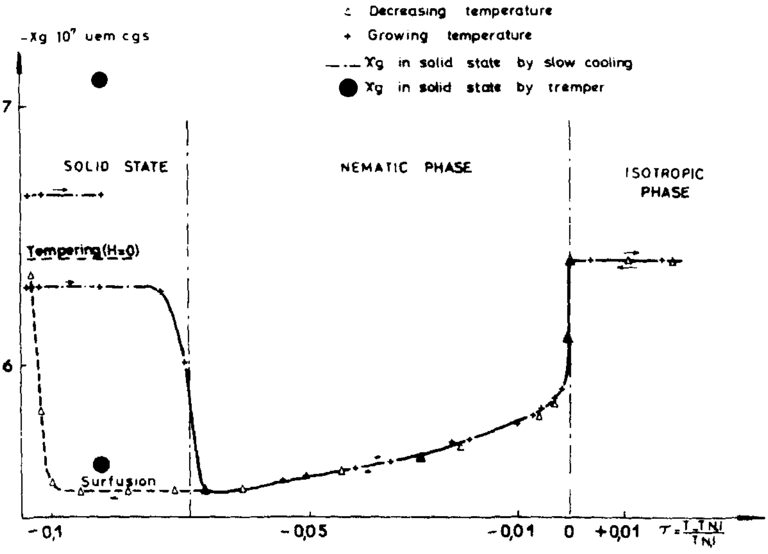

FIGURE 1 M.B.B.A.

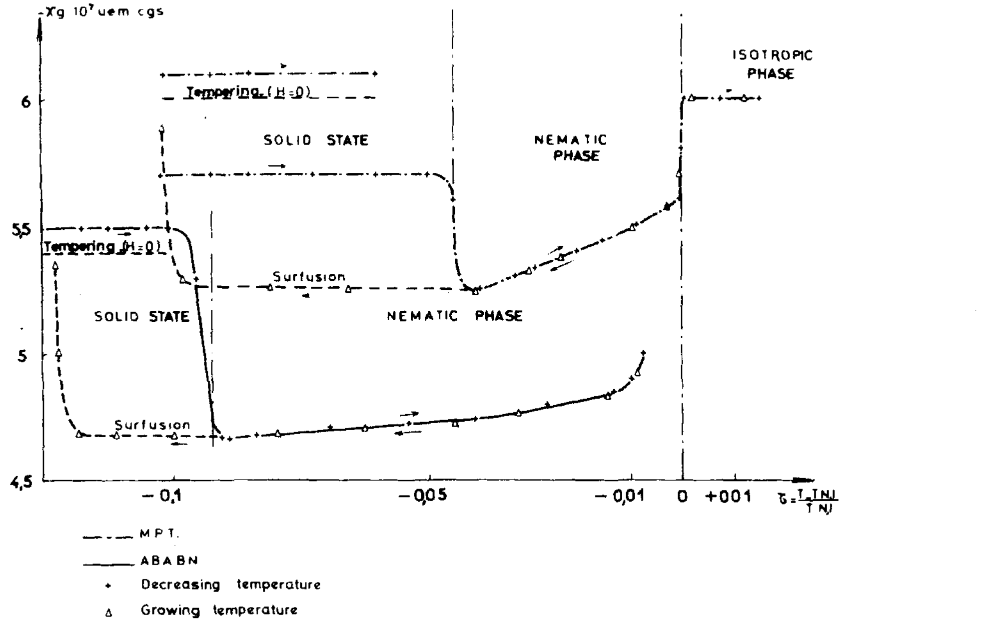

FIGURE 2

In the isotropic phase, far from the transition, we have a disorganized state and the magnetic susceptibility average $\bar{\chi}$ is measured. In the nematic phase, the long molecular axis remains parallel to the measuring magnetic field direction, and the susceptibility parallel to magnetic field is measured $(\chi_{\parallel}^{N})$.

Our apparatus permit also to measure a magnetic anisotropy in the solid state.[8] So, we have tremped in liquid nitrogen the nematic phase oriented by a magnetic field. An oriented solid is obtained, in which the average direction of the long molecular axis remains parallel to the orienting field direction.[10]

When the measuring and orienting fields are parallel together, we measure the magnetic susceptibility along the long molecular axis $\chi_{\parallel}^{S}$ in the solid state. Then the oriented sample rotation, in the measuring field, leads to the determination of $\chi_{\perp}^{S}$ when the previous directions are perpendicular $(|\chi_{\parallel}^{S} < |\chi_{\perp}^{S})$. These measurements have been made at different temperatures in the solid state, and we have noted no change of the diamagnetic anisotropy with temperature.

The oriented solid magnetic anisotropy value $\Delta\chi_S = \chi_{\parallel}^{S} - \chi_{\perp}^{S}$ is dependent upon the solidification kinetics. The maximum values were obtained in the previous kinetic. On the contrary, a slow cooling gives a lower value for $\Delta\chi_S$ and we think that two phenomena occur together; solidification growing according to either the random direction of the wall container, and the direction imposed by the magnetic field. By tremping, we can neglect the container contribution, therefore only the magnetic field contributes to the orientation of the forming solid. We have thought the $\Delta\chi_S$ value is connected with the orienting magnetic field magnitude. We have oriented our samples in magnetic field varying from 0 to 150 KOe. For $H = 0$ we have always $\Delta\chi_S = 0$; then for $0 \leq H \leq 1$ KOe, $\Delta\chi_S$ increases lineary with the magnetic field, and for $1 \leq H \leq 150$ KOe, $\Delta\chi_S$ remains at its maximum value. However, by a slow cooling, the minimum value $(\chi_{\parallel}^S)$ of the diamagnetic susceptibility depends upon the magnitude and the angle φ between the orienting and the measuring magnetic field. For orienting field taking the value 150, 42, 20 and 5 KOe, the angle φ has respectively the values 0, 10, 15, 25°; by tremping, this value $(\chi_{\parallel}^S)$ is always obtained for $\varphi = 0$.

From the measurements of $\chi_{\parallel}^N$ and $\bar{\chi}$ versus temperature, we derive the magnetic anisotropy $\Delta\chi_N$ in the nematic phase:[9]

$$\Delta\chi_N = \chi_{\parallel}^N - \chi_{\perp}^N = \tfrac{3}{2}(\chi_{\parallel} - \bar{\chi}) \tag{1}$$

In the nematic phase, if we define the order parameter by extracting the anisotropic part of the magnetic susceptibility:[6]

$$Q_{\alpha\beta} = \chi_{\alpha\beta} - \frac{1}{3}\delta_{\alpha\beta}\sum_{\gamma}\lambda_{\gamma\gamma}. \tag{2}$$

where α, β, γ are reference axis linked to the laboratory, and $Q_{\alpha\beta}$ is called the order parameter tensor which can be written[6]

$$Q_{\alpha\beta} = cA_{ij}S_{\alpha\beta}^{ij} \tag{3}$$

i, j, k are three orthogonal axis linked to the molecule, and c is the number of molecules per volume unit, A_{ij} is derived from a study of the diamagnetism in the crystalline solid state. The temperature dependence of A_{ij} is expected to be low, as we have experimentally proved it. So, Saupe and Maier[7] have used a simplified model, in which the order parameter reduced to

$$S \sim \frac{\chi_{\parallel}^N - \chi_{\perp}^N}{A_{\parallel} - A_{\perp}} = \frac{\Delta\chi_N}{\Delta\chi_S} \tag{4}$$

The curves of Figure 3 give the temperature dependence of the diamagnetic anisotropy of MBBA, ABABN, MPT. Moreover, the previous formula 4 allows to determine the order parameter versus temperature.[11] These curves are similar to the ones obtained for PAA by N.M.R,[12] I.R absorption spectrum,[13] U.V absorption spectrum.[14] Near the transition $(\tau = 0)$ the curves present a region where the order parameter $S = 0.45$, result in good agreement with the previous measurements.

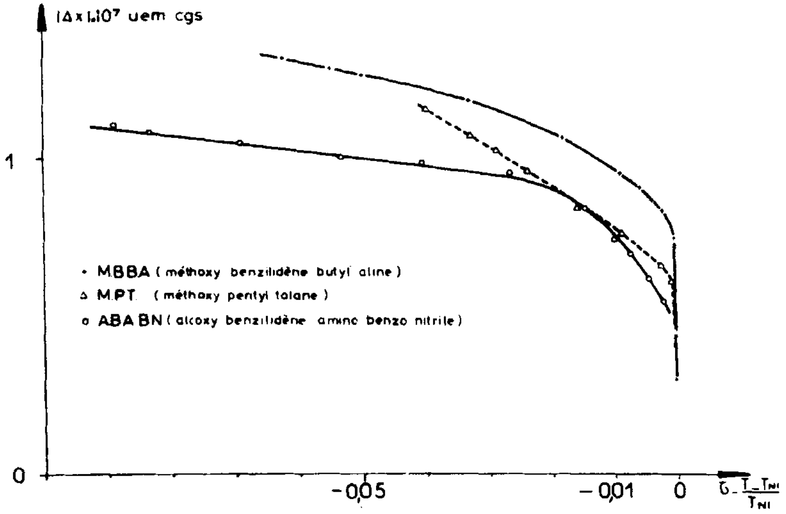

FIGURE 3 Diamagnetic anisotropy versus reduced temperature.

Our former experimental curve will be used as reference for the temperature dependence of the order parameter S.

3 DIELECTRIC CONSTANTS TEMPERATURE DEPEDENCE

The dielectric anisotropy is obtained by a capacity measurement. The liquid crystal is sandwiched between two sealed flat ceramic plates. The faces in contact with the liquid crystal are coated with chromium and gold. The cell is thermostated better than 0.1° C and placed in a 10 KOe magnetic field. The measuring electric field can be parallel or perpendicular to that orienting magnetic field and allows to measure the dielectric anisotropy $\varepsilon_{\parallel} - \varepsilon_{\perp}$, $\varepsilon_{\parallel}$ is the dielectric constant in a molecule direction parallel to the magnetic field, $\varepsilon_{\perp}$ the dielectric constant in an orthogonal direction. The cell was tested with pure C_6H_{12} and C_6H_6 liquids. With a 1615A General Radio Bridge, the cell capacity is measured versus temperature for different frequencies. The curves of Figure 4 give the dielectric anisotropy variations versus temperature for a 10 KHz frequency. A study of the dielectric anisotropy versus frequency will be published in a separate paper. This apparatus allows to have an measurement accuracy better than 1 %.

The Figure 5 shows the proportionality between the dielectric anisotropy and the order parameter, in good agreement with the Maier and Saupe Theory.[15]

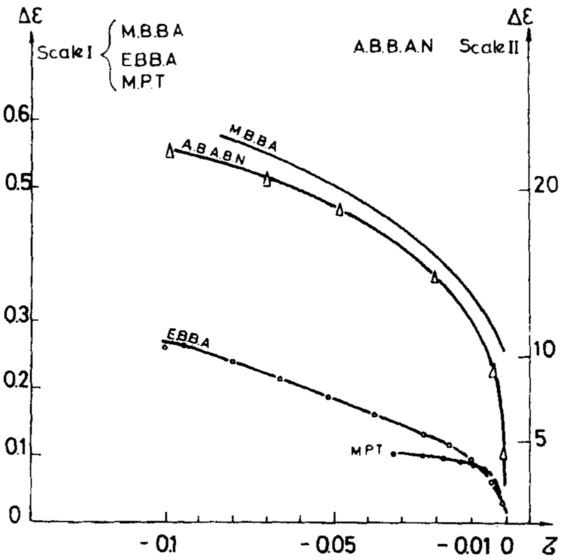

FIGURE 4 Dielectric anisotropy versus reduced temperature.

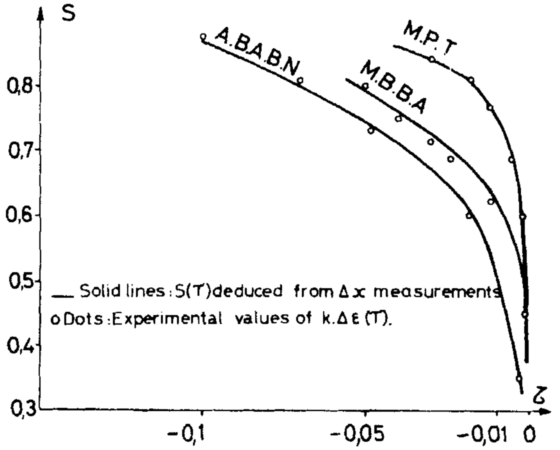

FIGURE 5 Comparison of reduced temperature dependence of the dielectric anisotropy and order parameter variations.

4 REFRACTIVE INDICES TEMPERATURE DEPENDENCE

The refractive indices have been measured with the prism method. The prism is made of two flat electrodes inclined at a small angle. The electrodes are rubbed parallel to the prism ridge, in order to induce a wall orientation effect. The incident beam is orthogonal to the enterring electrode and then refracted. It gives two deflected directions connected with the ordinary and extraordinary refractive indices. In this configuration Descarte's laws are applied. The prism is into an oven regulated at better than 0.1° C, placed on a goniometer plate. For MBBA; our measurements are in good agreement with the Brunet-Germain[16] results. ABABN and MPT give similar temperature dependence curves, and we observe a discontinuity at the transition temperature. Our measurements have been made for five wavelengths: 0.436μ, 0.506μ, 0.579μ, 0.639μ, 0.675μ. The reproductibility of the measurements shows that the accuracy is better than $5\ 10^{-3}$. From these measurements we derive the temperature dependence of the refractive indices anisotropy (Figure 6). For $\tau = 5460$ Å, we have verified that the curve $\Delta n = f(\tau)$ are independent of the transition temperature and in good agreement with Haller's measurements.[17] The Figure 7 gives a comparison between Δn and S, the accuracy on the proportionality is better than 1%. Our results are in good agreement with Madhusudana *et. al.*[18] results. Moreover we have

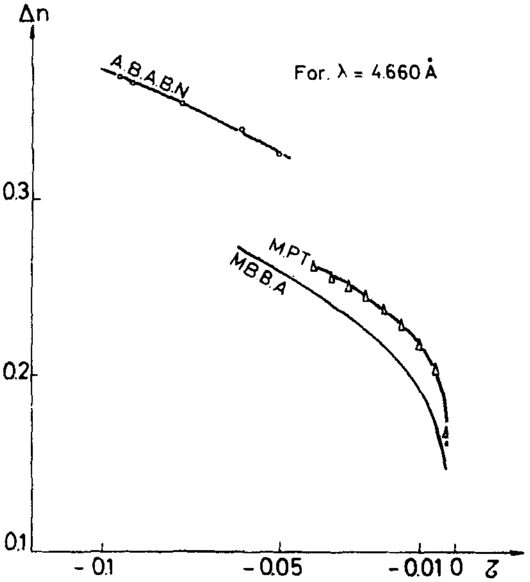

FIGURE 6 Refractives indices anisotropy versus reduced temperature.

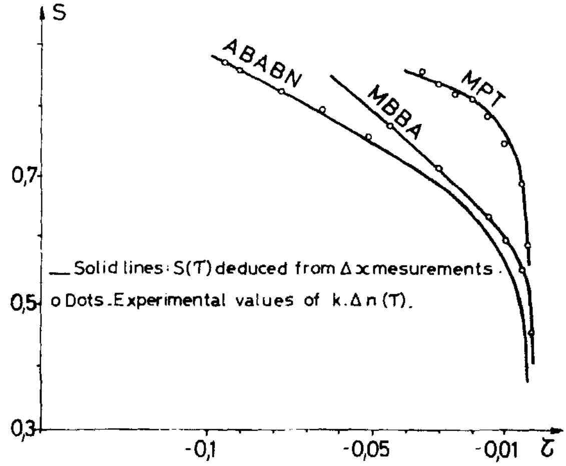

FIGURE 7 Comparison of reduced temperature dependence of the birefringence and order parameter variations.

shown that the temperature dependence of the proportionality coefficient A is neglect:[19]

$(0.344)_{21^\circ\mathrm{C}} \leq A \leq (0.346)_{47^\circ\mathrm{C}}$ for MBBA
$(0.3477)_{53^\circ\mathrm{C}} \leq A \leq (0.3479)_{60^\circ\mathrm{C}}$ for MPT
$(0.344)_{63.4^\circ\mathrm{C}} \leq A \leq (0.345)_{80^\circ\mathrm{C}}$ for ABABN

If α_e and α_0 are respectively the principal nematic continuum polarizabilities, related to the principal molecular polarizabilities $\gamma_\parallel$ and $\gamma_\perp$ by[6,20,21]

$$\begin{aligned} \alpha_e &= \bar{\gamma} + \tfrac{2}{3}(\gamma_\parallel - \gamma_\perp)S \\ \alpha_0 &= \bar{\gamma} - \tfrac{1}{3}(\gamma_\parallel - \gamma_\perp)S \end{aligned} \tag{5}$$

and n_e and n_0 the extraordinary and ordinary refractive indices given by:[22]

$$\begin{aligned} \frac{n_e^2 - 1}{\bar{n}^2 + 2} &= 4\pi v \alpha_e. \\ \frac{n_0^2 - 1}{\bar{n}^2 + 2} &= 4\pi v \alpha_0. \end{aligned} \tag{6}$$

A is easily given by:

$$A \simeq \frac{3(n_e + n_0)}{4\pi(\bar{n}^2 + 2)} \tag{7}$$

5 ELASTIC COEFFICIENTS TEMPERATURE DEPENDENCE

The elastic coefficients dependence of the order parameter is connected to the elastic energy of the continuum which is described in the Frank's hydrostatic approximation[4,5,23] by:

$$2f = K_{11}(\operatorname{div} n)^2 + K_{22}(n \operatorname{rot} n)^2 + K_{33}(n \times \operatorname{rot} n)^2 \tag{8}$$

Where n is the director describing the molecular orientation, and K_{ii} the three main elastic constants respectively related to the splay, twist and bend deformation in a liquid crystal. Lubinsky[3] has considered that f is a quadratic form of the tensor order parameter Q and his spatial derivatives (instead of n and ∇n). Hence, the free energy appears to be proportional to the square of the order parameter S. Moreover, the comparison between the different terms of the Frank's expression and the equivalent ones given by the nematic liquid crystal molecular theory from Maier and Saupe[24] shows that:[25]

$$K_{ii} = C_{ii} V_m^{-7/3} S^2 \tag{9}$$

where C_{ii} is a constant, and V_m the molar volume.

Experimentally, we have investigated the case of negative dielectric anisotropy, the liquid crystal being sandwiched between two parallel and conductive plates with the mean angular position of the molecules perpendicular to these plates. In this case, the equation giving the free elastic and electric energy of the system is:

$$F = \frac{1}{2}\int_{-1/2}^{1/2}\left[(K_{11}\sin^2\varphi + K_{33}\cos^2\varphi)\dot{\varphi}_z^2 + \frac{\varepsilon_a D_z^2}{4\pi\varepsilon_{\|}}\frac{\sin^2\varphi}{1-\frac{\varepsilon_a}{\varepsilon_{\|}}\sin^2\varphi}\right]\mathrm{d}z \tag{10}$$

ε_a being the dielectric anisotropy, D_z the electrical induction pointing along the z axis and φ the angular position of molecules versus a normal direction to the plates.

The static state is defined when the free energy is minimum. The resolution of equation 10 leads to the angular distribution $\varphi(z)$ in the cell for an applied voltage V. With the $\varphi(z)$ distribution, we can determine the birefringence variation Δn versus applied voltage.[26,27] Using a computer, we plot the theoretical curves Δn versus V. Theoretical curves have been drawn for MBBA parameters:

$$n_0 = 1.545,\ n_e = 1.755,\ \varepsilon_{\|} = 4.72,\ \varepsilon_{\perp} = 5.28$$

the threshold voltage is given by:

$$V_{th} = 2\pi\sqrt{\pi\frac{K_{33}}{\varepsilon_a}} \tag{11}$$

The fitting between theoretical curves and experimental dots leads to the determination of elastic constants K_{11} and K_{33} if ε_a is known. So, to determine the temperature dependence of these elastic coefficient; we have to know the temperature dependence of dielectric anisotropy and refractive indices. We have studied the cooperative molecular alignment of a nematic sample of MBBA in an A.C electric field, with birefringence measurements.

The sample is sandwiched between two conducting transparent glass plates coated with indium oxide. Indium oxide coating suitabily cleaned and rubbed gives, without surfactant, an homeotropic structure for MBBA. Distance between the two plates is adjusted with mylar spacers. The output monochromatic radiation intensity when the cell is placed between crossed polarizers allows to determine the birefringence variation versus applied voltage. Electric field necessary to tilt molecules has to be alternative or pulsed. In order to avoid ions migration, the frequency of the voltage was about 5 KHz and for our pure products, the relaxation time of ions deduced from mobility measurements was about 500 Hz. So, we can neglect the space charge effects. Then K_{33} is deduced from the threshold voltage, and K_{11} from the fitting between experimental and theoretical curves. The accuracy on K_{33} depends on the accuracy of the threshold voltage measurements that can be better than 2%. For K_{11}, the accuracy is better than 5%. K_{33} and K_{11} variations with temperature are given on Figure 8. The curves given on Figure 9 verify accurately the proportionality between the order parameter to the square (S^2) and the elastic coefficient K_{33}. The accuracy is within 1%.

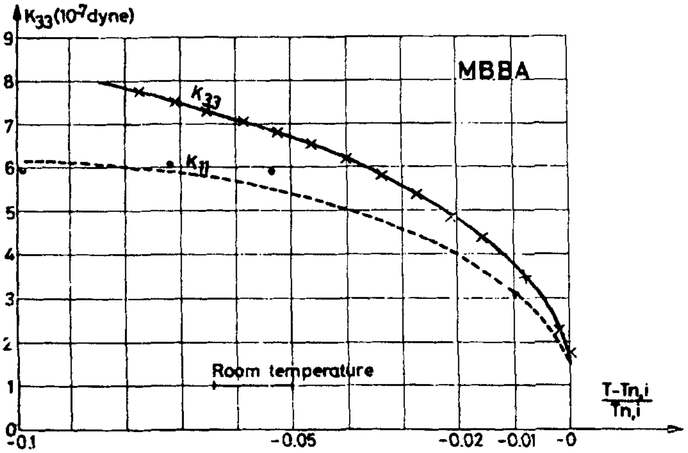

FIGURE 8 Elastic constants K_{33} and K_{11} versus reduced temperature.

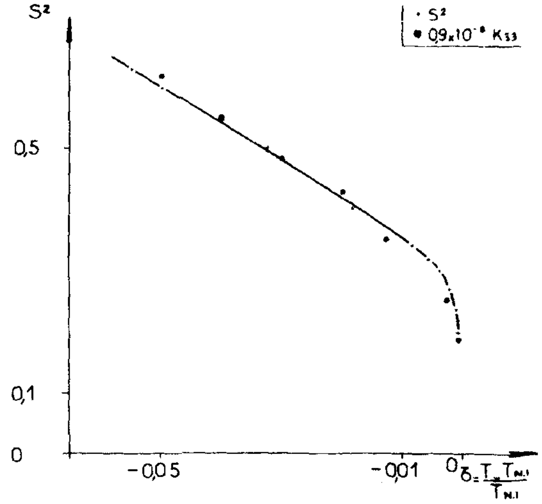

FIGURE 9 M.B.B.A. Comparison of reduced temperature dependence of the elastic constant K_{33} and the other parameter variation.

CONCLUSION

We have experimentally shown with a very good accuracy, that the order parameter in nematic liquid crystals is related to basic physical parameters when temperature changes within the mesophase. So in a general manner, the order parameter is a good index for physical behaviour of liquid crystals cells versus temperature within the mesophase and provides a clear understanding of microscopic properties and their relationships.

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