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COMPARED ACTION OF A ROTATING MAGNETIC FIELD ON SMECTIC A AND NEMATIC PHASES — APPLICATION TO THE STUDY OF THE $S_A \rightarrow$ NEMATIC TRANSITION

H. GASPAROUX, F. HARDOUIN, M. F. ACHARD and G. SIGAUD

Centre de Recherches Paul Pascal, University of Bordeaux I,
 Domaine Universitaire, 33405 Talence, France

Résumé. — Dans une première partie nous avons comparé le comportement d'une phase smectique et d'une phase nématique soumises à un champ magnétique tournant. L'analyse des deux types de comportement suggère deux possibilités d'application de cette technique à l'étude des transitions de phase.

Ensuite, nous avons décrit la détermination du coefficient de viscosité γ_1 dans le but d'analyser les conditions pour lesquelles cette quantité diverge près d'une transition. Trois composés sont étudiés et une discussion sur la nature de la transition Nématique-Smectique A est développée à partir de la comparaison entre des mesures calorimétriques et des mesures du coefficient de viscosité γ_1 .

Abstract. — In the first part we compare the behaviour of a Smectic A phase and a Nematic one submitted to a rotating magnetic field. The analysis of these two types of behaviour suggests two possibilities of application of this technique to the study of phase transitions.

Then we describe the determination of the γ_1 twist viscosity coefficient in order to analyse the conditions under which this quantity diverges near the transition. Three compounds are investigated and a discussion about the nature of the Nematic-Smectic A transition is developed from the comparison between calorimetric and twist viscosity coefficient measurements.

In order to estimate the medium magnetic anisotropy and some viscosity coefficients, Zvetkov [1] was first to analyse the behaviour of a nematic mesophase submitted to a rotating magnetic field. In 1971, we analysed this behaviour [2] and more recently we proved that it was possible to adapt such an experimental technique to the study of the smectic phase magnetic properties and to the analysis of the $S_A \rightarrow$ Nematic transition [3, 4].

1. Comparison between the behaviour of a S_A phase and a nematic one submitted to a rotating magnetic field.

— 1.1. NEMATIC BEHAVIOUR. — We already developed the theoretical study of a molecular motion induced by a rotating magnetic field in a nematic phase. We will only remind here that the analysis of the variation of the magnetic moment transmitted to the cupel depends on the pulsation ω of the rotating magnetic field H_0 and can provide an evaluation of the magnetic anisotropy.

At each rotation speed ω , a stationary state occurs and for a critical frequency ω_0 , defined as the maximum value of the transmitted moment, it can be written that :

$$\frac{M}{V} = \frac{1}{2} \Delta\chi H_0^2$$

V is the sample volume and M the magnetic moment.

We proved that the $\Delta\chi$ experimental value deduced from this method is always about 15 to 20 % below the real $\Delta\chi$ value. We explained the reasons for such an under-evaluation and Luckhurst recently confirmed such a result [5].

On the other hand, it must be pointed out that this technique is a good method for the determination of the twist viscosity coefficient γ_1 in a nematic phase [6]. When the pulsation ω of the magnetic field H_0 is below the critical value ω_0 , the magnetic torque moment operating on the volume V is given by the relation :

$$M = V\gamma_1 \omega .$$

By plotting M versus ω for different temperatures, it is possible to obtain the γ_1 thermal variation.

1.2 SMECTIC A PHASE BEHAVIOUR. — The behaviour of the S_A phase that we studied is not at all like the nematic phase one. We noticed, for example, that the S_A phases behave like a solid when they are submitted to a sufficiently intense magnetic field. The sample presents quasi-monocrystalline domains which perfectly follow the magnetic field rotation with an increasing phase difference due to the mechanical torsion torque of the quartz wire suspension.

The sample orientation is adjusted in the field so that the direction of the magnetic field may correspond with the one of the highest algebraic value of the susceptibi-

lity. If the magnet is turned through an angle α , the sample will turn through a smaller angle Ψ . If one revolves on the magnet, when $(\alpha - \Psi) = \Pi/4$, the sample quickly comes back to an equilibrium state. This method is usually called a « Krishnan's flip angle method ».

If one uses a reference method, one can directly determine the $\Delta\chi$ magnetic anisotropy of a material with a relative precision of about 0.1 % [7].

Owing to the fact that the S_A phase behaviour is a solid one, the γ_1 coefficient, defined in nematic phase, means nothing any longer here, since the molecules cannot turn round an axis perpendicular to their largest dimension.

The analysis of these two types of nematic and S_A phase behaviour suggests two possibilities of this technique for application to phase transition studies :
— In the smectic phases, the analysis of the evolution of the magnetic anisotropy, therefore the evolution of the orientational order parameter, according to temperature.

— In a nematic phase and, in particular, near a $N \rightarrow S_A$ transition, the determination of the γ_1 twist viscosity coefficient in order to analyse the conditions under which this quantity diverges near the transition.

We are now developing this second aspect, keeping for an other article the analysis of the magnetic anisotropy measurements in smectic phase in correlation with calorimetric determinations [8].

2. Divergence of the γ_1 viscosity coefficient near a $N \rightarrow S_A$ transition. — 2.1 PRINCIPLE OF THE METHOD. — The analysis of the experimental results can be summed up in the following way ; we assume that the thermal variation of the γ_1 experimental value may be described by the following expression :

$$\gamma_{1\text{exp}}(T) = \gamma_1^0(T) + B(T - T_c)^{-\nu}. \quad (1)$$

In this expression, $\gamma_1^0(T)$ corresponds to the part of $\gamma_1(T)$ which is not disturbed by the pretransitional effects. It may be simply the γ_1 experimental value measured at a temperature far enough from any phase transition. We have already proved that such a variation could be correctly expressed [9] by the relation ⁽¹⁾ :

$$\gamma_1^0(T) = A \cdot \Delta\chi(T) \cdot e^{E/RT}, \quad (2)$$

The thermal variation of the $\Delta\chi$ magnetic anisotropy has been determined in the nematic phase for every studied sample by Faraday's classical method.

The fit of the curves $\text{Log}(\gamma_1/\Delta\chi) = f(1/T)$ gives the value of both E and A parameters expressed in $\gamma_1^0(T)$.

(1) As several works proved it [3-17], we can consider other forms in order to describe the $\gamma_0(T)$ evolution and fit properly the experimental results. Besides, we can notice the expression recently suggested by Martins [19], which also leads to a fit in good agreement with experimental values [20].

Then we define the $\Delta\gamma_1$ enhancement of the twist viscosity coefficient as the difference between the terms $\gamma_{1\text{exp}}(T)$ and $\gamma_1^0(T)$ and we try to fit his enhancement with a law such as $\Delta\gamma_1 = k \Delta T^{-\nu}$.

2.2 CHOICE OF THE STUDIED SAMPLES. RESULTS. — The theoretical diagrams recently proposed [10, 11] prove that the nature of the $N \rightarrow S_A$ transition depends on the value of the ratio T_{NA}/T_{NI} .

(T_{NA} : $N \rightarrow S_A$ transition temperature, T_{NI} : $N \rightarrow$ Isotropic transition temperature.) In particular, if $T_{NA}/T_{NI} < 0.88$, these diagrams predict a second order transition with a transition enthalpy value equal to zero whereas when this ratio is larger than 0.88, the $N \rightarrow S_A$ transition enthalpy has a finite value. So, we choose to present here the results about three materials characterized by different values T_{NA}/T_{NI} listed in the following table :

Materials	T_{NA}/T_{NI}
p-Cyanobenzilidene-p'-Octyloxyaniline (CBOOA)	0.935
p-Butoxybenzilidene-p'-Octylaniline (BBOA)	0.955
Hexylazoxybenzene (HAB)	0.886

We can see that, according to the results of the theoretical diagrams, only the HAB is entitled to obtain a quasi second order $N \rightarrow S_A$ transition.

The results we have obtained by studying these three materials are collected on the figures 1 to 3.

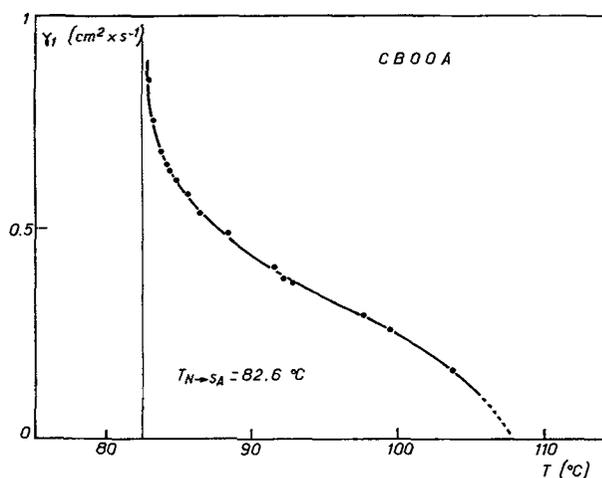


FIG. 1a. — CBOOA — Temperature dependence of the γ_1 viscosity coefficient.

The figures 1a, 2a, and 3a show the thermal variations of the coefficient γ_1 , obtained by using the method described in the first part.

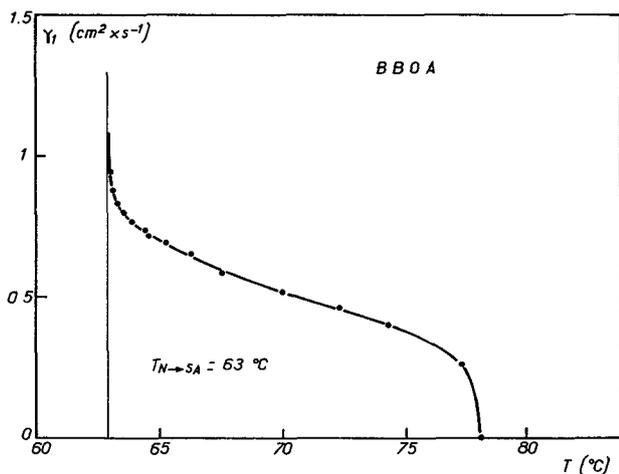


FIG. 2a. — BBOA — Temperature dependence of the γ_1 viscosity coefficient.

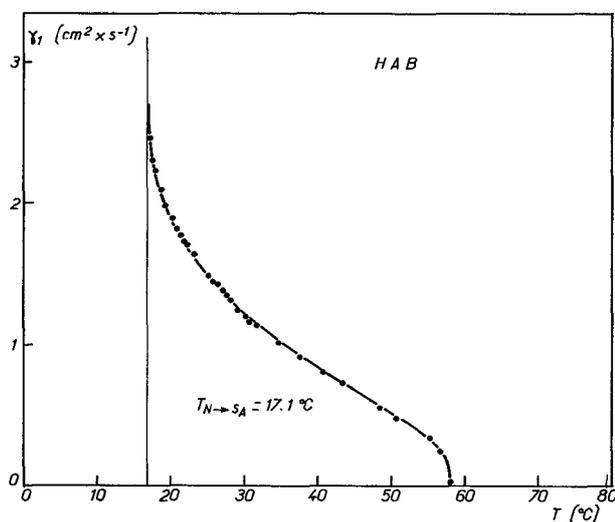


FIG. 3a. — HAB — Temperature dependence of the γ_1 viscosity coefficient.

On the figures 1b, 2b and 3b, we have the results about the thermal variation of the $\Delta\chi$ magnetic anisotropy measured in nematic phase by the Faraday's method. Whatever the material may be, we notice the usual increase of the order parameter when the temperature decreases.

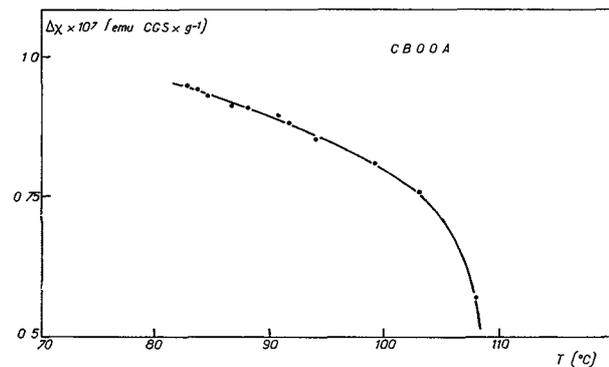


FIG. 1b. — CBOOA — Thermal variation of the $\Delta\chi$ magnetic anisotropy.

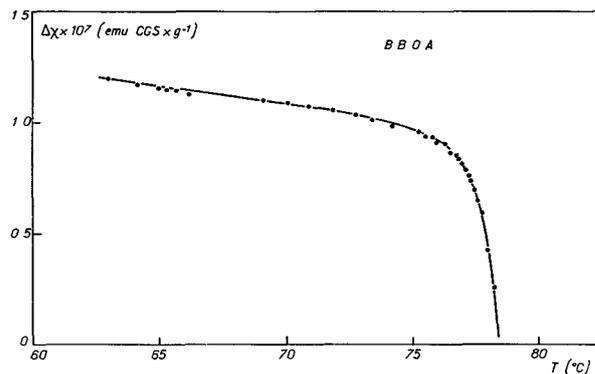


FIG. 2b. — BBOA — Thermal variation of the $\Delta\chi$ magnetic anisotropy.

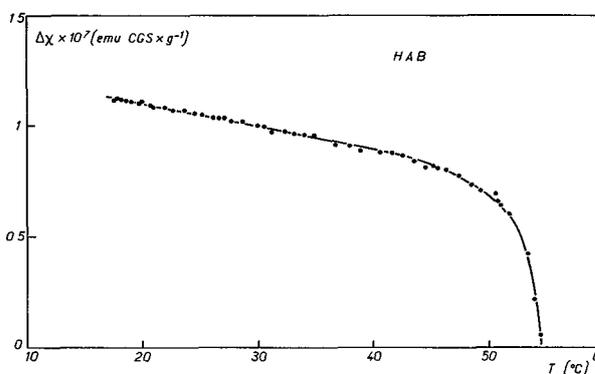


FIG. 3b. — HAB — Thermal variation of the $\Delta\chi$ magnetic anisotropy.

At last, the fits leading to the evaluation of the A and E values and of the critical ν exponent are summed up on the figures 1c, 2c and 3c; they show off quite different values of the critical ν coefficient characterizing the $N \rightarrow S_A$ transition.

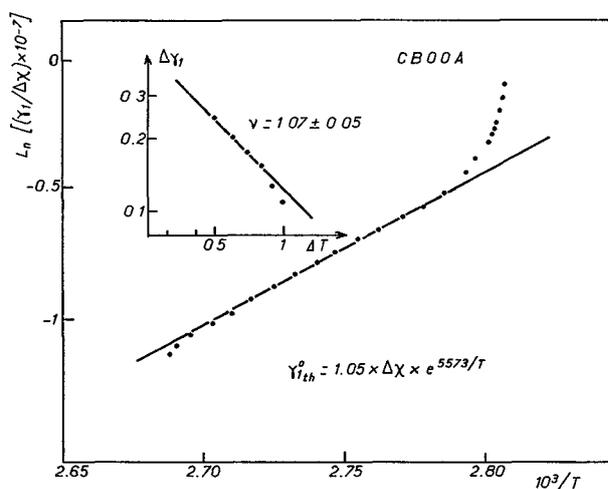


FIG. 1c. — CBOOA — Fit of γ_{1th}^0 and determination of the critical ν coefficient.

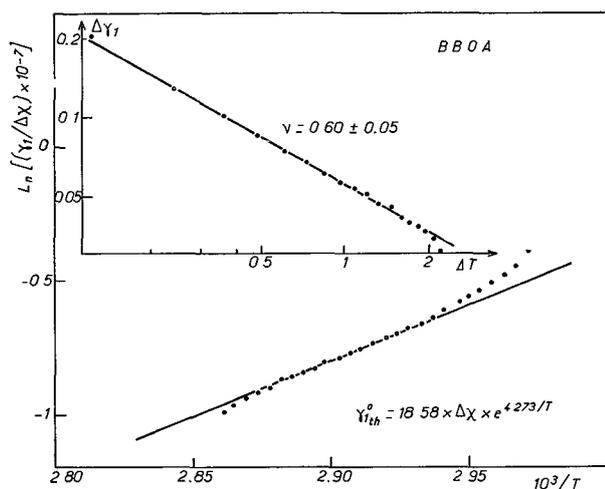


FIG. 2c. — BBOA — Fit of γ_{1th}^0 and determination of the critical ν coefficient.

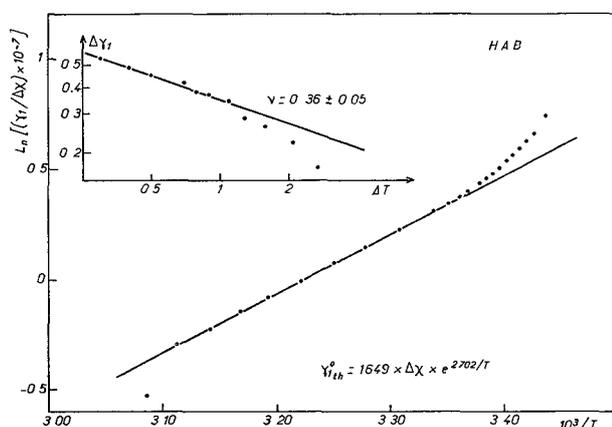


FIG. 3c. — HAB — Fit of γ_{1th}^0 and determination of the critical ν coefficient.

2.3 DISCUSSION. — We will wonder first how precisely the ν coefficient can be defined.

In the present form of our experimental device, it is impossible to obtain any result when ΔT is less than 0.2°C : the fast rotation of the magnet prevents a stable enough thermal regulation of the experimental device. Thereby, if the temperature field, available for ν evaluation, is reduced, it is sufficient however to prove certainly the γ_1 divergence.

We have to notice that the values of the A and E coefficients are graphically determined; by using the extreme straight lines $\text{Log } \gamma_1 / \Delta\chi = f(1/T)$ (obtained by taking into account a maximum error of 1% on the $\gamma_{1\text{exp}}$ and $\Delta\chi$ measurements), we can get two pairs of different enough A and E values. But, owing to the form and the theoretical expression chosen for γ_1^0 (eq. (2)),

these differences have but a small effect upon this term.

So finally, the uncertainty on the A and E values will have only a very little repercussion on the $\Delta\gamma_1$ values and, consequently, on the ν determination. Therefore, the uncertainty on the ν value (± 0.05) mainly comes from the error on the determination of the transition temperature ($\pm 1/20^\circ\text{C}$).

Of course, the values of the critical exponent ν which have been proposed depend on the form chosen by $\gamma_1^0(T)$. A confirmation of these values will involve the study of the temperature range such as

$$T - T_{NA} < 0.2^\circ\text{C}.$$

However, we must notice that only the coefficient corresponding to the HAB is in good agreement with F. Jähnig's and F. Brochard's theoretical prediction [12] ($\nu_{\text{theor}} = 0.33$) in the assumption of a λ type transition; this concordance confirms entirely the predictions of the theoretical diagrams.

In order to try and confirm this analysis, we have determined the $N \rightarrow S_A$ transition enthalpy corresponding to the CBOOA [13] and we have taken from the literature the values corresponding to the HAB [14] and the BBOA [15].

All these values are written down in the following table, as well as the ratio T_{NA}/T_{NI} and ν values:

Compounds	T_{NA}/T_{NI}	ν	ΔH_{NA} (cal.g ⁻¹)
CBOOA	0.935	1.07 ± 0.05	0.10
BBOA	0.955	0.60 ± 0.05	0.20
HAB	0.887	0.36 ± 0.05	0.01

If we refer not only to the theoretical diagrams, but also to the coefficient value in good agreement with F. Jähnig's and F. Brochard's theoretical prediction, we notice that the lowest enthalpy ΔH_{NA} corresponds to the $N \rightarrow S_A$ transition of the HAB, that is to say to the one which is the closest to a quasi second order transition.

In conclusion, we can say that the calorimetric measurements show that the $N \rightarrow S_A$ transitions are not always undoubtedly of the same type. When the ratio T_{NA}/T_{NI} is nearer and nearer the theoretical value 0.88, we notice that the ΔH_{NA} value approximates to zero, and, in that case, the ν critical exponent our analysis leads to seems in good agreement with F. Jähnig's and F. Brochard's theoretical prediction. The study of other products, joined with an improvement of the thermal regulation conditions will make possible measurements corresponding to $\Delta T < 0.2^\circ\text{C}$, and should allow us in the future to go further in this analysis and to compare these results with those obtained by other methods [16, 17, 18].

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Editorial Comment

The authors have found a remarkable anomaly of the friction constant γ_1 , in the nematic phase, due to short range smectic order. However, the assignment of a critical exponent, which is attempted here, appears extremely delicate at the present stage. For instance the unperturbed part γ_1^0 is assumed to be linearly dependent on the nematic order parameters. The corresponding eq. (2) gives a rather good fit to the data, but a theoretical argument (due to A. Farinha Martins) suggests that γ_1 should rather be proportional to S^2 at small S . Thus the separation assumed in eq. (1) and the resulting exponents are still, we think, open to some doubt.