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STUDY BY CALORIMETRIC AND MAGNETIC MEASUREMENTS OF PHASE TRANSITIONS IN LIQUID CRYSTALS

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Résumé. — Dans le but d'analyser les transitions de phases dans les cristaux liquides nous avons suivi l'évolution de deux paramètres physiques, la chaleur spécifique et l'anisotropie diamagnétique, au voisinage de diverses transitions de phase.

La chaleur spécifique $C_{\text{exp}}$ a été mesurée à l'aide d'un appareil adapté à l'étude de liquides ou de substances pulvérolentes.

L'anisotropie diamagnétique $\Delta \chi$ fut évaluée grâce à une méthode de Faraday classique ; dans le cas du Smectique A une méthode de détermination directe de l'anisotropie diamagnétique a en outre été utilisée.

Des transitions Nématic-Smectique A et Smectique A-Smectique C ont été étudiées à travers l'évolution des propriétés de quatre composés. Une discussion est faite autour de la nature de ces différentes transitions.

Abstract. — In order to analyse phase transitions in liquid crystals we measured the evolution of two physical parameters, the specific heat and the diamagnetic anisotropy.

The specific heat $C_{\text{exp}}$ was measured by using an apparatus usable for the study of liquids or powders.

The diamagnetic anisotropy $\Delta \chi$ was determined by Faraday’s classical method and a direct measurement method available only in the case of the smectic phases.

Nematic-Smectic A and Smectic A-Smectic C transitions were investigated through measurements of the evolution of the properties of four compounds.

A discussion is proposed of the nature of the different transitions.

1. Introduction. — The phenomenological [1] and microscopic theories [2, 3] established for the different phase-transitions in liquid crystals presuppose the existence of second order $N \to S_A$ and $S_A \to S_C$ transitions.

For the $N \to S_A$ transition, some recent works [4, 5, 6, 7, 8] enable us to appreciate the validity of these theories, but in the nematic phase, the study of the pretransitional effects cannot determine unambiguously the order of this transition.

The determination of the order of the phase transition is currently of great theoretical and experimental interest. We thus measured two physical parameters, the specific heat and the magnetic anisotropy, in order to describe these transitions by the evolution of these properties, near a phase transition.

2. Techniques. — 2.1 The Specific Heat $C_{\text{exp}}$. — We used two methods of measurement, both resorting to the use of an apparatus adapted to the study of liquids or powders [9]:

2.1.1 The adiabatic method. — A determined heat pulse $\Delta Q$ is applied to a sample thermally insulated from the external medium. We measure the ensuing increase of the temperature, $\Delta T$. This allows us to determine the absolute heat capacity $C_{\text{exp}} = \Delta Q/\Delta T$ which can be only identified with the true specific heat far from a transition.

2.1.2 A semi-adiabatic method. — A constant heating power is applied to the insulated sample. The variations in temperature are recorded versus time. In a stationary state, the recorded observed slope curve is in inverse ratio to the specific heat. Thanks to this method we can increase the number of experimental points near a specific heat discontinuity.

2.2 The Magnetic Anisotropy $\Delta \chi$. — $\Delta \chi$ is a macroscopic parameter in direct ratio to the orientational order parameter of the medium.

— In a nematic phase, one can deduce the magnetic anisotropy from a magnetic susceptibility measurement obtained by Faraday’s classical method [10, 11].

— In a smectic phase, two methods are available:
  - so called static measurement Faraday’s method,
  - the direct measurement method of $\Delta \chi$, realized thanks to a rotating magnetic field. This dynamic method is usually called the Krishnan’s flip-angle method [12].
3. Results and discuss. — 3.1 THE NEMATIC-SMECTIC A TRANSITION. — Recently para-cyanobenzilidene-p'-octyloxyaniline, CBOOA, has been one of the most studied materials. But if experimental results [13, 14, 15, 16] and some theoretical predictions are in favour of a second order N $\rightarrow$ S\textsubscript{A} transition, nevertheless some people do not agree with it [8, 17, 18, 19]. In order to complete this analysis, we studied CBOOA by the two properties previously defined.

Figure 1 shows the temperature dependence of $\chi$ and $\Delta\chi$ in the case of CBOOA. We find that, during the cooling from the liquid state, the order parameter increases when the temperature decreases especially when we pass from the nematic state to the smectic. The lack of an order parameter discontinuity, that we can detect experimentally, is in good agreement with the assumption that this may be a second order transition.

![Graph showing the temperature dependence of $\chi$ and $\Delta\chi$](image1)

The temperature dependence of the experimental specific heat is represented on figure 2 [18]. We notice that, together with the solid-smectic and nematic-isotropic transitions, important pre- and post-transitional effects appear. These hide the right value of the specific heat and distinguish these transitions from the first-order classical ones. An enlarged detail of the experimental curve near the N $\rightarrow$ S\textsubscript{A} transition is pointed out on figure 3. The specific heat-anomaly revealed by a small peak appears, characteristic of a first order transition. This is in good agreement with experimental results recently obtained [17, 20]. Besides, we can affirm that it is not an anomaly similar to a $\lambda$ transition on liquid helium because our measurement method allows us to estimate a specific heat divergence on a temperature range lower than 0.05 $^\circ$C. The integration of the specific heat anomaly gives us a value equal to 0.10 cal/g, slightly different from the value of the transitional enthalpy (0.06 cal/g) which P. E. Cladis obtained with an A. E. D. apparatus on an extremely pure sample of CBOOA [8]. These values are higher than those obtained by D. Djurek [20]. This can be explained by the fact that our investigation method over-estimates the transitional enthalpy because of the existence of pre- and post-transitional effects.

![Graph showing the thermal variation of the experimental specific heat $C_{exp}$](image2)

![Graph showing the thermal variation of $C_{exp}$ near the N $\rightarrow$ S\textsubscript{A} transition](image3)
Consequently we think that the assumption of a first order $N \rightarrow S_A$ transition, presenting a very small transition enthalpy, gives the best account of our results. This corroborates the latest theoretical predictions [21] based on the analogy between superconducting $\rightarrow$ normal metal and $N \rightarrow S_A$ transitions. In effect, the presence of an additional term in the expression of Landau's free energy suggests that all these transitions are of first order.

It is interesting to point out that we detect a small discontinuity of $\Delta \chi$ in the case of the p-butoxybenzilidene-p'-octylaniline (BBOA), which presents a $N \rightarrow S_A$ transition with a 0.20 cal/g latent heat [22] slightly higher than the one measured for the CBOOA. This corroborates that the transition is of first order. This compound has an orthogonal smectic B phase. The orientational order increases at the $S_A \rightarrow S_B$ transition. Besides, these results are in agreement with the $\Delta \chi$ direct measurement made in smectic phase on these uniaxial mediums (Fig. 4, 5).

3.2 THE SMECTIC A-SMECTIC C TRANSITION. — We studied the two following compounds: the heptyloxybenzilidene-p'-pentylaniline (705) and the heptyloxybenzilidene-p'-butylaniline (704) (Fig. 6, 7, 8, 9).

Their magnetic anisotropy, obtained by any previously mentioned methods, varies with no detectable discontinuity near the transition $S_A \rightarrow S_C$ realized under a magnetic field.
These results could presuppose (like in the TBBA case) that the $S_+ \rightarrow S_-$ transitions of both compounds are of second order [23, 24, 25]. Nevertheless, for the 705, the curve of the experimental specific heat ($C_{\text{exp}}$ versus to temperature: Fig. 10) discloses a small peak attributed to a latent heat estimated by integration at 0.12 cal/g. This result is in perfect agreement with previously made A.E.D. measurements [22]. So, by analogy with the $N \rightarrow S_A$ transition, we can conclude that the $S_A \rightarrow S_C$ transitions of the 704 and 705 compounds are of first order with a small transitional enthalpy. The specific heat discontinuity seems negligible but the proximity of the $S_C \rightarrow S_B$ transition may alter its evaluation.

The figures 6, 7, 8, 9, 10 call for some extra remarks:

- The results obtained from one hand by a Faraday's method, from the other hand by a $\Delta \chi$ direct measurement, present the same relative evolution versus to temperature. One can explain the differences observed in the absolute values simply because these two techniques are references methods; besides, differences of strength and above all of homogeneity of the magnetic field (Faraday's method involves a gradient) presuppose that the method of direct measurement leads to a best effective orientation of the molecules and therefore to better results.
- At the $S_C \rightarrow S_B$ transition of the 705 (Fig. 6, 7) the magnetic anisotropy increases suddenly; one can explain it by a molecular reorganisation in the planes, according to an hexagonal organisation with a strong coupling between the orientational and transitional orders. The order parameter-discontinuity, the specific heat anomaly (Fig. 7, 10) and the important transitional enthalpy found, irrefutably point out that this transition is of first order.
- On the other hand, no variation of the order parameter can be detected at the transition $S_B \rightarrow S_A$ of this same product (Fig. 6, 7). Besides, we must notice that the specific heat (Fig. 10) does not reveal any discontinuity and that the small anomaly of $C_{\text{exp}}$ can be attributed to a latent heat evaluated at 0.18 cal/g. This quasi continuous evolution at the $S_B \rightarrow S_A$ transition agrees with W. L. McMillan's previsions [26] about the orthogonal $S_B \rightarrow$ tilted $S_B$ (or $S_H$) transition. To identify the $S_A$ phase of the 705 with the $S_H$ phase would corroborate A. M. Levelut's and J. Doucet's (private communication) results achieved by X-Rays on 707 (a compound with the same number and the same kind of phases as the 705, that is to say I, N, $S_A$, $S_C$, $S_B$, $S_A$, $S_C$, $S_B$, and $K$).
- The different behaviour of the magnetic anisotropy, at the $S_C \rightarrow S_B$ transition of the 704 compound (Fig. 8, 9) expressed by an important diminution of the order parameter, can be explained by the passage to a tilted smectic B (smectic H) phase. In effect, we cannot organize, in a magnetic field, a biaxial medium ($S_H$) like a uniaxial one (orthogonal $S_B$).
In conclusion it is important to notice that the nature (slightly of first order or quasi-second order according to the vocabulary selected) of the $S_A \rightarrow S_C$ transition, that is to say the continuous evolution from an uniaxial medium to a biaxial one, allowed us to keep large monocristalline domains in the smectic C phase when the transition is realized under a magnetic field.

References