Classification

Physics Abstracts

61.30G — 64.70M — 77.40

New dielectric relaxation in a bilayered fluid smectic phase

L. Benguigui

Solid State Institute, Technion, Israel Institute of Technology, 32000 Haifa, Israel

and F. Hardouin

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

(Reçu le 21 octobre 1983, révisé le 7 décembre, accepté le 20 décembre 1983)

Résumé. — Nous présentons des mesures diélectriques effectuées sur le composé cyané « DB₈Cl » qui présente la séquence de phases smectiques fluides bicouches : Smectique A₂ → Smectique C₂ → Smectique ?. Nous observons en particulier une nouvelle relaxation perpendiculaire en phase S_γ, qui vraisemblablement traduit un ordre de dipôles. Un modèle simplifié rendant compte de ce résultat est proposé.

Abstract. — We present dielectric measurements of the « DB₈Cl » cyano compound which exhibits a Smectic A₂ → Smectic C₂ → Smectic ? sequence of bilayered fluid smectic phases. In particular a new perpendicular relaxation is observed in the S_γ which we interpret as indicative of a dipole ordering. A simplified model taking this result into account is proposed.

1. Introduction.

Recently a new smectic phase in the compound octyl-phenyl 2-chloro-4-(p-cyano-benzoyloxy) benzoate (« DB₈Cl » for short) [1] was discovered. Below the nematic state there first appear a smectic A₂ phase with a commensurate bilayer structure, followed, when the temperature is decreased by a smectic C₂, tilted phase in which the bilayer structure is kept. At lower temperatures the new smectic phase (smectic ?) exists over the interval 107 °C-85 °C.

No structural change between this phase and the S_{C₂} is observed on the X-ray patterns. Both phases exhibit a bilayer structure (as S_{A₂}) and the molecular order inside the layers remains liquid-like. The only noticeable difference between the S_γ and the S_{C₂} phases is that the 001 Bragg spots become more intense and more numerous in S_γ. It is possible that there is no qualitative modification between these two phases but before coming to this conclusion it is necessary to study their physical properties.

Let us note that similar polar systems exhibit S_A-S_A transitions [2] and that dipole ordering has been observed with particular dielectric properties in some of these S_A phases [3, 4]. This is why we have measured the dielectric properties of the « DB₈Cl » compound and in fact, our results give support of a dipole ordering characteristic of the S_γ phase.

2. Experimental results.

The real and imaginary parts of the dielectric constant $\epsilon^* = \epsilon' - j\epsilon''$ were measured from 5×10^3 Hz to 1 GHz by several methods : Bridge, Q meter and reflectometry, in the directions parallel ($\epsilon_{\parallel}$) and perpendicular ($\epsilon_{\perp}$) to the director. The sample was oriented by a magnetic field of 13 kG.

On figure 1, we present the thermal variations of $\epsilon_{\parallel}$ and $\epsilon_{\perp}$ (real part of the complex dielectric constant) at 5 kHz over the whole mesomorphic range. This frequency is below most of the frequencies of absorption domains and higher than frequencies of the conductivity mechanism ; thus, the measured values are not too far from the quasi static ones. $\epsilon_{\parallel}$ decreases as the temperature decreases and $\epsilon_{\perp}$ varies slowly around 3.7. The transitions are marked only by small anomalies. The relatively low values of $\epsilon_{\parallel}$ and $\epsilon_{\perp}$ are indicative of an antiferroelectric ordering.

In this respect DB_8Cl is quite analogous to the DB_6 compound which has only a S_{A2} phase [3, 4]. The results concerning the relaxations are more interesting.

One of the authors [5] has recently predicted that in the S_{A2} phase, due to the long range A.F. ordering, we should observe a second parallel relaxation with the amplitude proportional to $(T_{\text{NS}} - T)^2$ where T_{NS} is the temperature of the nematic-smectic A_2 transition. On figure 2, we

Fig. 1. — Thermal variations of the quasi static dielectric constants $\epsilon_{\parallel}$ and $\epsilon_{\perp}$.

Fig. 2. — Variations of $\epsilon_{2||}$ as function of the frequency showing the existence of a distortion at 110 °C.

show $\varepsilon_{2\parallel}$, the imaginary part of the dielectric constant, as a function of the frequency at 130 °C (S_{A_2}) and 110 °C (S_{C_2}). At 110 °C the diagram shows a distortion. If this distortion is assumed to be the result of the superposition of two absorption domains, this is in qualitative agreement with the predictions at low temperature.

However, the most striking feature concerns the dynamic permittivity when the electric field is perpendicular to the director. In figure 3 the variation of $\varepsilon_{2\perp}$ is plotted as a function of f at different temperatures. In the nematic, S_{A_2} and S_{C_2} phases, we observe one relaxation around 280 MHz. This is the usual relaxation associated with the rotation around the long molecular axis, and as expected it is almost independent of T . But in the S_7 phase, an unexpected second relaxation appears around 10-20 MHz. The thermal dependence of the corresponding relaxation frequency is weak, while the amplitude increases as T decreases. We interpret this last property as indicative of a dipole ordering in the S_7 phase. Nevertheless, the measurement by itself does not give any indication of what kind of ordering corresponds to this extra relaxation. We present a model based on energy arguments which permits us to explain the known structural properties of the S_7 phase.

3. Tentative model.

We can envision that in a perfect A.F. ordering of the S_{A_2} phase, the end dipoles of the molecules in one single-layer are in the same direction (say up) and in the following single-layer all the end dipoles are in the opposite direction (down). The two single-layers form the basic fluid bilayer from which we get 001 Bragg reflection at $d \simeq 2l$ [6]. At short range we can consider that in each monolayer the molecules are (on average) on a triangular lattice. In such an arrangement the dipolar interaction energy is minimized by the interpenetration of the end dipoles and this should be the qualitative explanation of the S_{A_2} structure. It is possible to show that when the molecules are tilted, the dipole-dipole interaction is increased. In other words the A.F. ordering of the end dipoles competes with the mechanism favouring the appearance of the S_C phase. When the temperature decreases, the competition becomes more severe and it may happen that the system prefers to adopt a new structure with a lower energy. This is a possible explanation for the S_7 formation.

Since our argument is only qualitative and based on energy considerations (neglecting the entropy) we shall present a calculation of the dipole-dipole energy of a row of point dipoles instead

Fig. 3. — Variations of $\varepsilon_{2\perp}$ versus the frequency. The S_7 phase is characterized by a new perpendicular relaxation.

of considering the two-dimensional array of end dipoles belonging to the two consecutive and interpenetrating single layers. The calculations have only an illustrative interest but the conclusions drawn from the linear model are qualitatively identical to those drawn from a complete two-dimensional calculation.

Let us consider a line of point dipoles μ equally spaced with distance a between them. In the situation analogous to the S_{A_2} phase, the dipoles are directed perpendicularly to the row (Fig. 4). The interaction energy of N dipoles is :

$$U_{A_2} = -\frac{N\mu^2}{2a^3} \left(1 - \frac{1}{2^3} + \frac{1}{3^3} - \frac{1}{4^3} + \dots \right)$$

$$U_{A_2} = -0.9 \frac{N\mu^2}{2a^3}. \quad (1)$$

In the case of the S_{C_2} phase, the dipoles make an angle α with the normal to the row (Fig. 4). The dipole-dipole energy is given by :

$$U_{C_2} = -\frac{N\mu^2}{2a^3} (1 - 3 \sin^2 \alpha) \left(1 - \frac{1}{2^3} + \frac{1}{3^3} \dots \right)$$

$$U_{C_2} = -0.9 \frac{N\mu^2}{2a^3} (1 - 3 \sin^2 \alpha) \quad (2)$$

U_{C_2} is larger than U_{A_2} : this shows the competition between the two orderings.

Since we observed a new relaxation in the $S_?$ when the field is perpendicular to the director, we have a new contribution to the molecular dipole moment in this direction. This contribution increases when T decreases. Thus our suggestion for the $S_?$ structure is the following : the tilt angle of two consecutive monolayers will not be equal to α as in the S_{C_2} phase, but slightly different : $(\alpha + \beta)$ in one monolayer and $(\alpha - \beta)$ in the next one (see Fig. 4). As α is the order parameter of

Fig. 4. — Proposed structure of the S_{A_2} , S_{C_2} and $S_?$ phases and row of dipoles corresponding to each phase.

the S_{C_2} phase, β can be seen as the order parameter of the S_7 one. In our linear model we alternatively have dipoles making angle $(\alpha + \beta)$ and $(\alpha - \beta)$ with the normal. The dipole-dipole interaction energy of the row of dipoles is now :

$$U_{S_7} = -0.9 \frac{N\mu^2}{2a^3} (1 - 3 \sin^2 \alpha) - 1.05 \frac{N\mu^2}{2a^3} \sin^2 \beta. \quad (3)$$

The energy in this structure is less than in the structure for which all the dipoles make the same angle with the normal. Therefore this mechanism may explain the formation of the S_7 . In the S_{A_2} and S_{C_2} , the end dipole contributes only to the parallel dipole moment (contribution to $\epsilon_{\parallel}$), but in our S_7 model it contributes also to $\epsilon_{\perp}$. In the linear approach, the extra dipole moment is equal to $\mu \sin \beta$.

The model can explain — a) The new relaxation perpendicular to the long molecular axis. — b) The fact that the layers of the S_7 are well defined since the permeation (passage of molecules from one layer to the next one) is hindered. Consequently the X-ray reflection orders on the layers are more intense and numerous than in the S_{A_2} or S_{C_2} phases. — c) The asymmetric bimolecular shape in S_7 conjectured from the X-ray analysis of the intensity profile of the diffuse spot at wide angles [1].

4. Conclusion.

The dielectric measurements of DB_8Cl show that the S_7 phase is really qualitatively different from the S_{C_2} phase : in S_7 a new relaxation appears around 10-20 MHz in the perpendicular configuration. We interpret it as the indication of a dipole ordering. Starting from simplified energetic arguments we describe a tentative model for the S_7 structure. More detailed calculations and experimental evidences are needed to put the model on a firm basis.

References

- [1] HARDOUIN, F., NGUYEN HUU TINH, LEVELUT, A. M., *J. Physique Lett.* **43** (1982) L-779.
- [2] HARDOUIN, F., LEVELUT, A. M., ACHARD, M. F., SIGAUD, G., *J. Chim. Phys.* **80** (1983) 53 and references therein.
- [3] BENGUIGUI, L., HARDOUIN, F., *J. Physique Lett.* **42** (1981) L-381.
- [4] DRUON, C., WACRENIER, J. M., HARDOUIN, F., NGUYEN HUU TINH, GASPAROUX, H., *J. Physique* **44** (1983) 1195.
- [5] BENGUIGUI, L., *J. Physique* **44** (1983) 273.
- [6] HARDOUIN, F., LEVELUT, A. M., BENATTAR, J. J., SIGAUD, G., *Solid State Commun.* **33** (1980) 337.