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Study of S_A Phase Structure Using Dielectric Relaxation†

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The results of a study of dielectric relaxation for several mesomorphous substances are presented. These compounds allow us to obtain information on the following phases: — the nematic phase — partially bilayer (S_{Ad}), bilayer (S_{A2}) and monolayer (S_{A1}) smectic A phases — the antiphase smectic A ($S_{\tilde{A}}$). The measurements were performed with the electric field parallel to the director. The absorption observed is due to the reorientation motion of the molecule round an axis perpendicular to its longitudinal axis. The activation energy W of this movement was measured for all phases. Results show clearly that for these compounds $W_{SAd} < W_N$, $W_{SA1} \sim W_N \sim W_{S\tilde{A}}$ and $W_{SA2} > W_N$. In each case an explanation has been suggested to interpret these changes in the activation energy. This points out the possibility of showing the existence of some S_A phases using dielectric relaxation.

INTRODUCTION

In previous papers, we have presented results obtained with compounds having nematic and partially bilayer smectic A (S_{Ad}) phases.[1] Recently, we have performed a study with a compound having tilted monolayer cybotactic groups in the supercooled range of the S_{Ad} phase.[2]

We have also obtained results for monolayer (S_{A1}) and bilayer (S_{A2}) smectic A phases and for an antiphase ($S_{\tilde{A}}$) formed by cyano-compounds.[3] For all these compounds a complete dielectric study has been performed. Moreover, using X-rays, the structure of the smectic A phases of compounds with cyano-end groups has been studied elsewhere[4] and information

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concerning the structure of DB6 (see below) and of a mixture of C5 stilbene in DB5 has been obtained.[5,6]

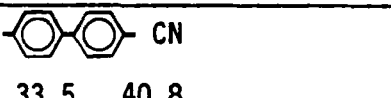
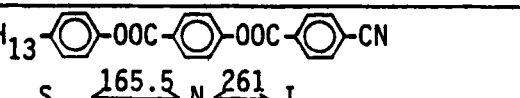
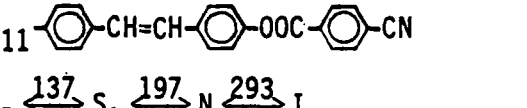
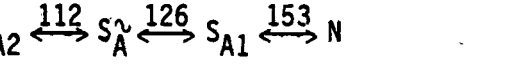
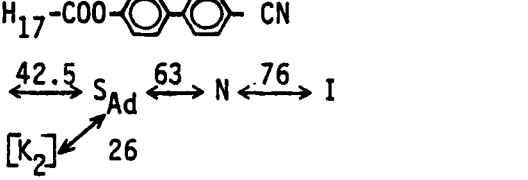
In this paper, we only consider the dielectric relaxation for the electric field parallel to the director. The results presented here were obtained with the four following compounds:

- 4-n-octyl-4′-cyanobiphenyl (8 CB)
- 4-n-hexylphenyl 4′-cyanobenzoyloxybenzoate (DB6)
- a mixture of DB6 (40%) in 4-cyanobenzoyloxy-4′-n-pentylstilbene (C5 stilbene)
- 4-nonanoyloxy-4′-cyanobiphenyl (8 COOCB).

The formulae and transition temperatures are listed in Table I.

TABLE I

Formulae and transition temperatures.

Compounds	Formulas and transition temperatures (in °C)
8 CB	
DB6	
Mixture : DB6(40%) in C5 stilbene	C5 Stilbene :  Transition temperatures of the mixture : 
8 COOCB	

- 8 CB was supplied by BDH Chemicals under reference K24.
- DB6 and C5 stilbene were synthesized at the Centre Paul Pascal.*
- 8 COOCB was synthesized at the Laboratoire Thomson CSF.**

EXPERIMENTAL

We measured the components of $\varepsilon^*(\varepsilon^* = \varepsilon' - j\varepsilon'')$ between 100 Hz and 1 GHz. In this frequency range, a cell constituted by a plane capacitor located at the end of a coaxial line is used.[7] The orientation in the nematic phase is obtained by placing the cell in the gap of an electromagnet. The alignment in smectic phases is obtained by means of a slow decrease in temperature of the sample submitted to a magnetic induction of 11 kG. The sample temperature is stable within ± 0.2°C.

For this measurement direction, it is to be remembered that the absorption obtained comes from the reorientation movement of the molecule round an axis perpendicular to its longitudinal axis.[8,9] Considering the plots of ε'' and ε' vs frequency, we notice that all diagrams obtained are of the same type. Plotting ε'' vs ε' (Cole and Cole diagram), we obtain, in all cases, a half circle centered on the abscissa axis. For example, Figures 1 and 2 show results obtained with DB6 and 8CB at two measurement temperatures. Consequently, the reorientation mechanism is approximately of the Debye type. Thus, it seems interesting to study the behavior of the critical frequency F_c vs temperature for each phase. The results obtained are shown in Figures 3, 4, 5 and 6 ($\log F_c$ vs $1/T$). We notice that these diagrams are made up of straight lines. This linear change in F_c vs $1/T$ follows an Arrhenuis equation:

$$F_c = F_o \cdot e^{-W/kT}$$

Thus, we can obtain the activation energy of the mechanism in each phase. Corresponding results are shown in Table II.

DISCUSSION

Considering these values we note that, in the different phases, the activation energies can be listed in the following order:

$$W_{SAd} < W_N$$

$$W_{SA1} \sim W_N \sim W_{S\tilde{A}}$$

$$W_{SA2} > W_N$$

Measurements performed with other compounds also showed that the activation energy in the nematic phase is higher than the energy obtained

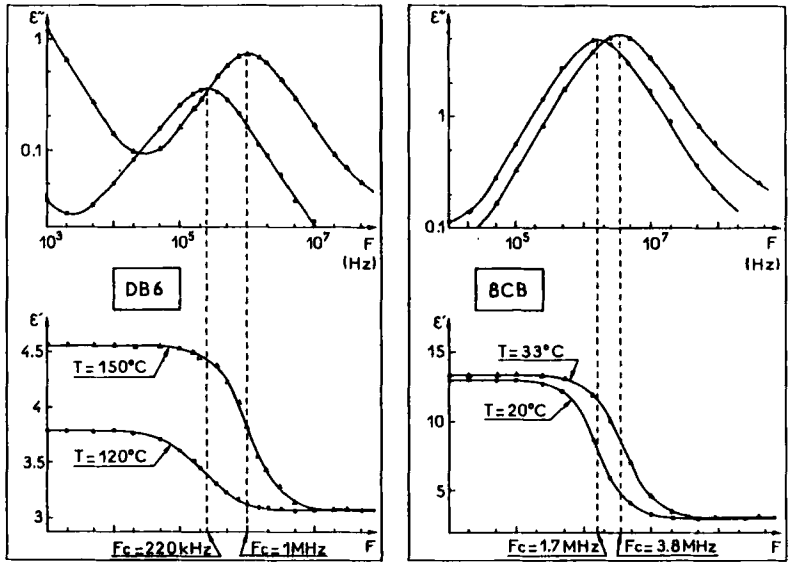


FIGURE 1 Trends in ε'' and ε' vs frequency for DB6 and 8CB at two measurement temperatures.

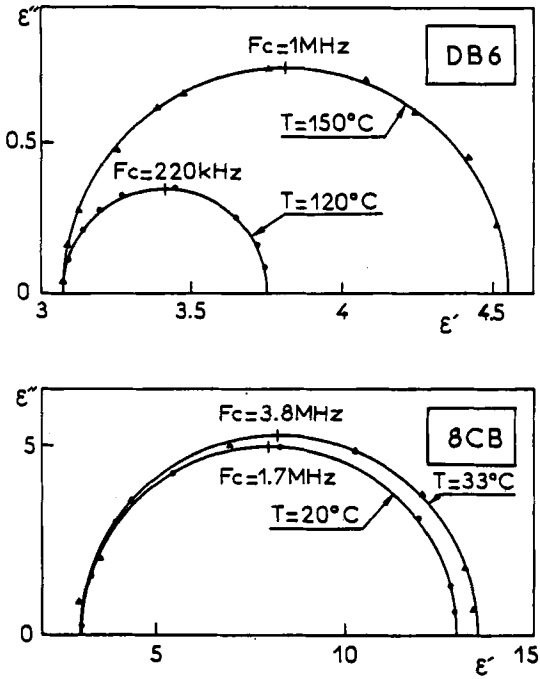


FIGURE 2 Trends in ε'' vs ε' for DB6 and 8CB at two measurement temperatures.

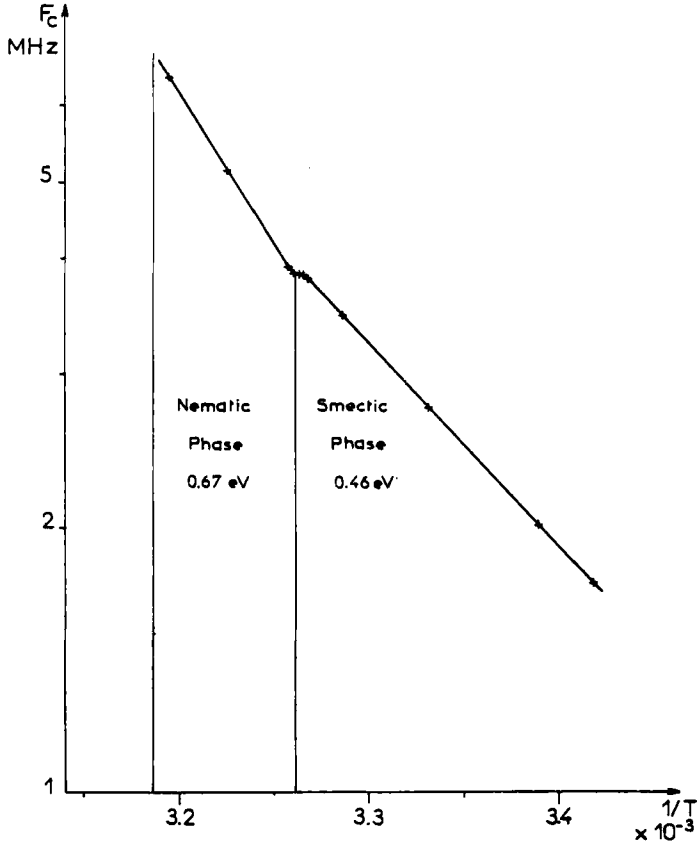


FIGURE 3 F_c vs $1/T$ for 8CB.

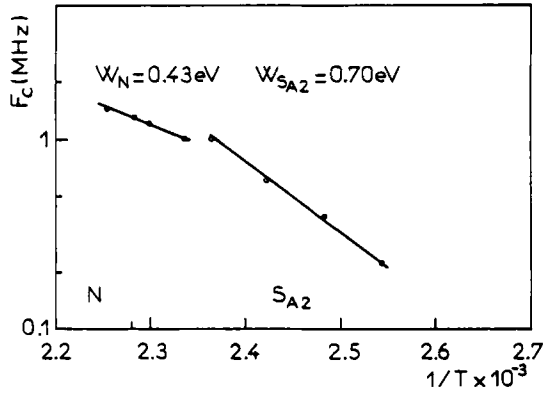


FIGURE 4 F_c vs $1/T$ for DB6.

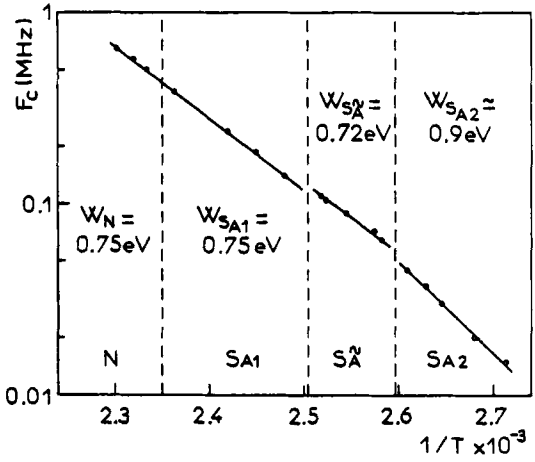


FIGURE 5 F_c vs $1/T$ for the mixture.

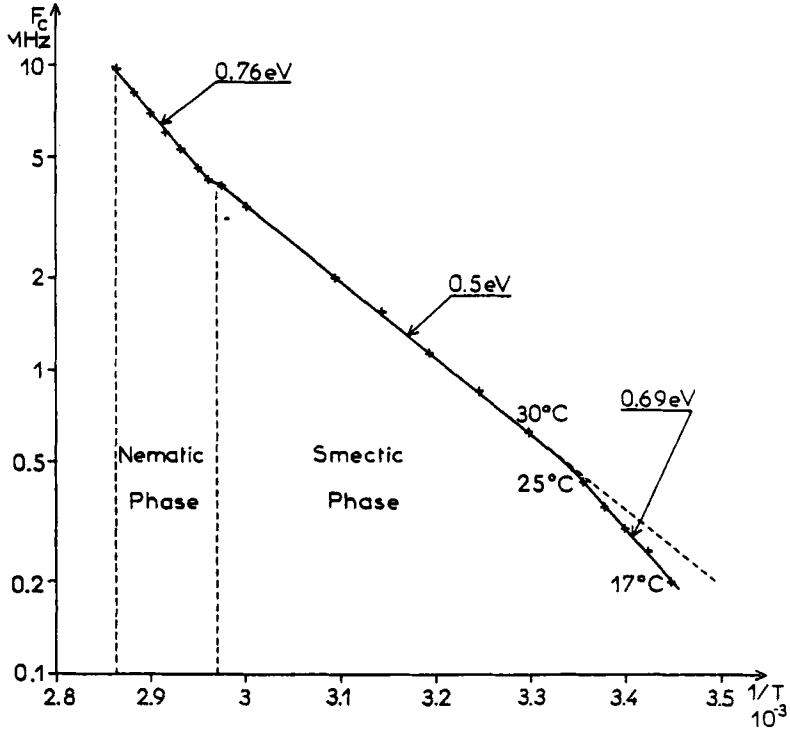


FIGURE 6 F_c vs $1/T$ for 8 COOCB.

TABLE II

Activation energy for each phase + monolayer tilted groups in S_{Ad} phase.

Phases Compounds	N	S_{Ad}	S_{A1}	S_A^-	S_{A2}
8 CB	0.67	0.46	–	–	–
DB6	0.43	–	–	–	0.70
Mixture	0.75	–	0.75	0.72	0.9
8 COOCB	0.76	0.50	0.69^+	–	–

in a partially bilayer smectic phase.[10,11] The activation energy is connected with the reorientation motion of the molecule round an axis perpendicular to the director, over the potential barrier "seen" by this molecule.

In the case of nematic and monolayer smectic phases, the potential shape is symmetrical. On the other hand, in the case of a partially bilayer smectic A phase, this potential becomes asymmetrical according to both preferential directions. This can be interpreted by the decrease in activation energy in the S_{Ad} phase.[12] For 8 COOCB, the activation energy obtained in the supercooled range of the S_{Ad} is higher than the energy obtained in the normal S_{Ad} phase. This result is consistent with the information obtained by X-ray measurements, i.e. the appearance of monolayer cybotactic groups in the S_{Ad} phase.[2]

For the S_{Ad} and the bilayer smectic A phase, an interpretation taking into account an antiferroelectric order in the layers has been proposed.[13] We have recently suggested that additional interactions appear for the compounds studied here, in the S_{A2} phase.[3] These can be linked to the polar groups having a strong component perpendicular to the longitudinal axis of the molecule. These interactions can hinder the reorientational motion of the molecule and can explain the increase in the activation energy in this phase.

In the case of the antiphase, the analysis is more difficult. Indeed a given molecule can be in different types of surrounding. Thus, the reorientation motion of the molecule is more or less easy.

In conclusion, this study points out the possibility of showing the existence of some S_A phases using dielectric relaxation.

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