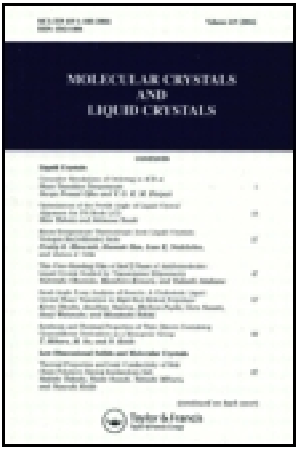

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

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To cite this article: A. Ferraz, A. C. Ribeiro & H. T. Nguyen (1999): Proton NMR Study of the Molecular Motions in Smectic-C* Ferri and Anti-Ferroelectric Mesophases, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 331:1, 67-74

To link to this article: http://dx.doi.org/10.1080/10587259908047501

Mol. Cryst. Liq. Cryst., 1999, Vol. 331, pp. 67-74
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Proton NMR Study of the Molecular Motions in Smectic-C*Ferri and Anti-Ferroelectric Mesophases

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We report the first study of molecular dynamics in $S^*_{C\gamma}$ (ferrielectric) and S^*_{CA} (anti-ferroelectric) mesophases of a liquid crystal, by means of proton NMR relaxation. The relaxation dispersion detected in both $S^*_{C\gamma}$ and S^*_{CA} mesophases is compared with the observed for the S_A and S^*_C phases of the same compound, which is similar to those observed in previous studies. However, to describe the relaxation behaviour detected in both $S^*_{C\gamma}$ and S^*_{CA} mesophases we had to include an additional relaxation mechanism. Considering the frequency range where it is observed, this mechanism may be related to the *antiphase azimuthal mode* previously detected by dielectric permittivity studies.

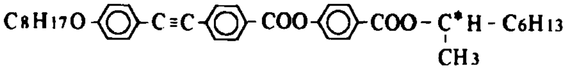
Keywords: Molecular Dynamics; NMR; Ferrielectric; Anti-ferroelectric

INTRODUCTION

The first observations of the ferri and anti-ferroelectric mesophases were reported in 1989[1] and, ever since, several studies specially concerning the structure of these phases have been published (e.g., [2]). Some other works concerning the molecular dynamics, mainly using dielectric relaxation as experimental technique, have also been published[3-8]. In this work we present the first study, to our knowledge, on Proton Nuclear Magnetic Resonance (NMR) relaxation in a liquid crystal exhibiting S_A, S^*_C, $S^*_{C\gamma}$ and S^*_{CA} mesophases. A large Larmor frequency range was covered, using conventional and fast-field cycling techniques, in order to identify the molecular movements that contribute for the relaxation rate in different frequency ranges.

EXPERIMENTAL

The compound used in this work[3]



presents the following mesophase sequence:

K 67.6°C S^*_{IA} 71.6°C S^*_{CA} 95.1°C $S^*_{C\gamma 1}$ 96°C $S^*_{C\gamma 2}$ 97°C S^*_C 104°C $S^*_{C\alpha}$ 105.5°C S_A 135.3°C I.

The relaxation dispersion data in the low frequency range was obtained in a fast-field cycling spectrometer[9] with a polarisation and detection field of 0.21 T and a switching time of 2-3 ms. In the S_A phase we measured $T_1(\omega)$ from 150 MHz up to 4 MHz. However, due to technical reasons, we were not able to collect T_1 data for frequencies smaller than 2 kHz for S^*_C and 20 kHz for $S^*_{C\gamma}$ and S^*_{CA} mesophases (the T_1 values are too short). The relaxation dispersion data in the high frequency range was obtained in conventional NMR pulsed spectrometers (BRUKER SXP 4-100 and MSL 300). The measurements were performed after a very slow cooling from the isotropic phase to the selected temperatures.

As an example, we present in Figure 1 some of the $T_1(\omega)$ data collected for one temperature in each mesophase.

For the frequencies higher than 1 MHz the behaviour of T_1 is very similar in all the mesophases. Therefore, the molecular motions usually dominant in the intermediate and high frequency ranges (molecular self-diffusion and local molecular rotations/reorientations, respectively) will probably be very similar for all the mesophases.

For the frequencies lower than 1 MHz we may easily distinguish three different shapes for the T_1 dispersion, corresponding to S_A, S^*_C and the third to both $S^*_{C\gamma}$ and S^*_{CA} mesophases, appearing the T_1 data of the S^*_C as an "intermediate" stage between the other two. For the S_A and S^*_C the behaviour resembles the observed in previous works[10-12]. We must remark that in the S^*_C phase the T_1 would probably become independent from the frequency for $\omega/2\pi \leq 1$ kHz, as in the S_A phase; this was detected for other compounds exhibiting these kinds of phases[10,11]. For the $S^*_{C\gamma}$ and S^*_{CA} mesophases we may see that the increasing of T_1 with the frequency is more pronounced than the detected for the other two phases in the low frequency range.

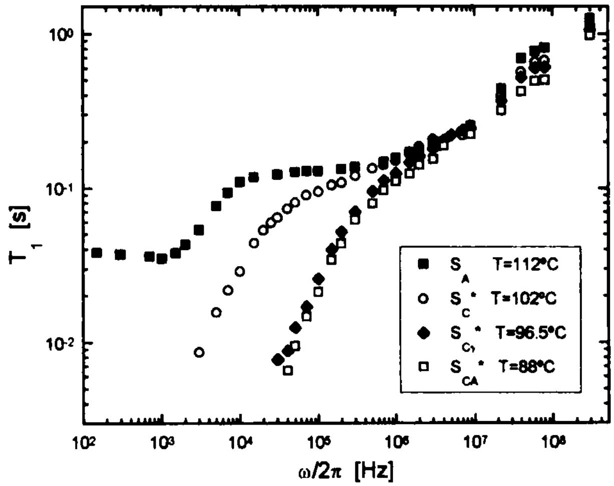


FIGURE 1 Experimental T_1 data for one temperature in each mesophase.

INTERPRETATION OF THE RELAXATION DATA

S_A and S^*_C mesophases

As in previous works[10-12] we considered the following relaxation mechanisms to explain the T_1^{-1} data:

a) *order director fluctuations* – described considering that they are only due to layer undulations[13];

b) *molecular translational self-diffusion* – first described by M. Vilfan and S. Zumer's theories for smectics[14];

c) *local molecular rotations/reorientations* – described by a model which accounts for the rotations along the short and the long molecular axis[15].

The analysis of the frequency dispersion was done for each temperature in both mesophases using a least-square method to fit the equation

$$T_1^{-1} = \left(T_1^{-1}\right)_{LU} + \left(T_1^{-1}\right)_{SD} + \left(T_1^{-1}\right)_{Rot} \qquad (1)$$

with the experimental data. The explicit expressions of each term can be found in the above mentioned references. A complete report on the obtained results, including the time scales of each movement, the cut-off frequencies of the *LU* model and the remaining model parameters, will be published elsewhere[16]. Nevertheless, we may say that for both mesophases, order director fluctuations, self-diffusion and rotations/reorientations, dominate the relaxation rate at low, medium and high frequency ranges, respectively.

$S^*_{C\gamma}$ and S^*_{CA} mesophases

The analysis of the T_1 data of these phases started considering the same relaxation mechanisms used in the S_A and S^*_C mesophases. However, it was not possible to get results with physical meaning from the fitting procedure.

Several studies on dielectric relaxation have been reported[3-8] for these kinds of mesophases, especially the S^*_{CA}. These works have been typically performed for a wide range of frequencies, from a few Hz to a few MHz. The dielectric spectra reported are strongly influenced by the experimental conditions, such as the type of alignment of the cells and their thickness.

In some of these works[5,7,8] the dielectric spectra reported for the S^*_{CA} phase exhibits two absorption peaks detected at frequencies near 1 kHz and 1 MHz. The assignment of these peaks to specific relaxation mechanisms is still the object of some discussion[8]. The characteristic frequency of the lower peak is too low to be easily detected by our NMR experiments and we will not consider it in our analysis. The higher frequency peak was attributed to both the soft mode[5] and to some process related to the antiferroelectric ordering[7,8]. This latter is described as the movement of the molecules against each other in their anti-tilt position, in anti-phase, i.e., with the azimuthal angle φ changing in opposite sense around the cones[8]. In principle, this movement is detectable by NMR. A model also based upon the variation of the azimuthal angle between the molecules in the neighbouring layers is described in ref. [3], but considering that the anti-tilt pairs are moving in phase around the tilt cones, i.e., with the angle φ changing in the same sense around the cones; the frequencies involved are much lower than those reported in reference [8].

From the analysis of the T_1 data of the S^*_C phase, and according to our previous NMR works[10-12], we are not able to distinguish the contribution of the soft mode from the one due to the smectic layer undulations. Taking into account the structural similarities (and differences) between $S^*_{C\gamma}$, S^*_{CA} and S^*_C mesophases, no reason has been found to justify why a contribution due to the soft mode in $S^*_{C\gamma}$ and S^*_{CA} phases (along with the contribution from layer undulations) would be clearly observed while it would not be in the S^*_C. Therefore, we have considered the ***anti-phase azimuthal angle fluctuations*** as described in reference [8] as a possible relaxation mechanism to explain the behaviour of $T_1^{-1}(\omega)$ that we detect in the low frequency range.

To our present knowledge, no theoretical model for the relaxation mechanism associated with this specific process is published. However, it is known that some contributions to the relaxation of the proton intermolecular interactions between the closest molecules have approximately the form of a weight summation of Lorentzians[13,17]. Thus, we have considered that this mechanism could be modelled, in a first approach, by Lorentzian type curves:

$$\left(T_1^{-1}\right)_{Anti} = \frac{9}{8}\left(\frac{\mu_0}{4\pi}\right)^2 \gamma^4 \hbar^2 \left[J^{(1)}_{Anti}(\omega) + J^{(2)}_{Anti}(2\omega)\right] \qquad (2)$$

with $$J^{(k)}_{Anti}(\omega) = \sum_{n=0}^{2} f_{kn} \frac{a_{Anti}\,\tau_{Anti}}{1+\omega^2\tau^2_{Anti}} \qquad (3).$$

τ_{Anti} is the correlation time characteristic of this movement.

The analysis of the frequency dispersion data has then been performed for each temperature by fitting the equation

$$T_1^{-1} = \left(T_1^{-1}\right)_{LU} + \left(T_1^{-1}\right)_{SD} + \left(T_1^{-1}\right)_{Rot} + \left(T_1^{-1}\right)_{Anti} \tag{4}$$

for both mesophases, with the experimental data, using a least-square method. The *LU*, *SD* and *Rot* contributions were described by the same models used in the analysis of S_A and S^*_C phases.

As an example, Figure 2 illustrates the best fit for one temperature in the S^*_{CA} mesophase. Similar quality fits were obtained for the remaining temperatures and for the $S^*_{C\gamma}$ phase. In Figure 2 we may see that the molecular rotations/reorientations are the dominant relaxation mechanism above 30 MHz. The self-diffusion dominates from near 20 kHz to 30 MHz. Below 20 kHz both smectic layer undulations and anti-phase azimuthal angle fluctuations are the most important relaxation mechanisms, with the latter presenting a larger contribution than the former.

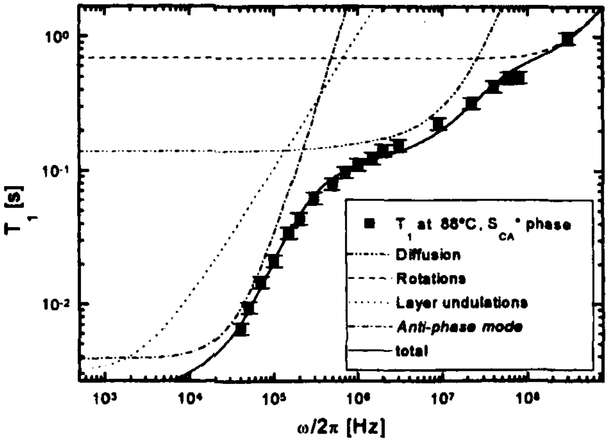


FIGURE 2 Model fit of equation (4) to the experimental T_1 data in the S^*_{CA} mesophase at T=88°C. The contributions of the four different relaxation mechanisms are also shown.

In Table 1 we present the values obtained for a_{Anti} and τ_{Anti}. A complete report on the remaining parameters will be published elsewhere[16]. Meanwhile, we may say that both high and low cut-off frequencies of the layer undulations mechanism present the same order of magnitude in all the four mesophases. The correlation times associated with both molecular self-diffusion and rotations/reorientations mechanisms, the diffusion constants and their dependence with the temperature are compatible with those found in previous works[10-12] and with those found for the S_A and S^*_C mesophases of this compound.

Mesophase	$S^*_{C\gamma}$	S^*_{CA}				
T [°C]	96.5	92	88	84	79	75
a_{Anti} [10^{54} m^{-6}]	47	70	58	27	9	5
τ_{Anti} [10^{-6} s]	2.6	2.9	3.4	3.6	4.2	5.0

TABLE 1 Model parameters obtained from the best fits of equation (4).

CONCLUSIONS

In conclusion we may say that the molecular dynamics in the $S^*_{C\gamma}$ and S^*_{CA} mesophases is rather different from the one in S^*_C mesophase in the low frequency range: an additional relaxation mechanism has to be considered in the analysis of the molecular dynamics in ferri and anti-ferroelectric mesophases. The frequency range where this additional relaxation mechanism is dominant is compatible with the characteristic frequencies presented for the *anti-phase azimuthal mode*[8]. This mode reflects the movement of the molecules against one another in their anti-tilt position, in anti-phase, i.e., with the azimuthal angle φ changing in opposite sense around the cones. From our study, this mechanism is well modelled by a Lorentzian type curve. Yet, further research should be done on this subject, especially in compounds exhibiting $S^*_{C\gamma}$ mesophases in larger domains of temperature.

Acknowledgements

We wish to express our gratitude to Prof. Noack for the use of NMR fast-field cycling facilities of the University of Stuttgart. We also thank Prof. Assis Farinha Martins and Dr. Gabriel Feio (CENIMAT – Faculdade de Ciências e Tecnologia da Universidade Nova de Lisboa) for the use of the MSL-300 spectrometer. We also acknowledge Program PRAXIS XXI (Project 3/3.1/MMA/1769/95) for financial support.

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