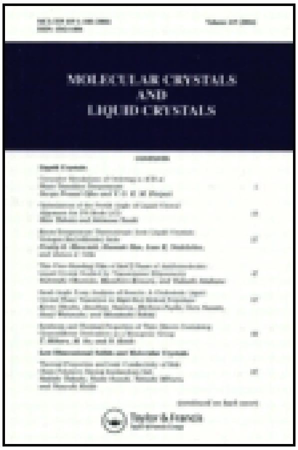

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Low Frequency Dielectric Relaxation Behaviour at the N-S_A and S_A-S_C Transitions of 8S5

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LOW FREQUENCY DIELECTRIC RELAXATION BEHAVIOUR AT THE N-S_A AND S_A-S_C TRANSITIONS OF $\overline{8}$S5

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Abstract It is shown that the dielectric relaxation time, connected with the reorientation about the short molecular axis, changes more or less continuously at the transitions: N-S_A and S_A-S_C of 4-n-pentylphenyl-4'-n-octyloxy-thiobenzoate ($\overline{8}$S5). Yet there is an evidence of pronounced steps in the intensity of the absorption at both transitions. The activation energy has about the same value in all liquid crystalline phases. It means that the S_A and S_C phases, having liquid like order within the layers, do not differ distinctly in molecular dynamics. However, the structure of both smectic phases has an impact on the dielectric increments.

INTRODUCTION

Dielectric properties of the nematic, S_A and S_C phases of $\overline{8}$S5 have been previously studied in the radio and microwave frequency ranges on the thick sample oriented by means of the magntetic field of 0.5 T[1]. There are a few papers devoted to dielectric relaxation properties of the S_C phases showing up in other homologous series[2-5]. It has been found that the low frequency absorption curves maxima are reduced[3,4] upon the transition to the layered structures. This effect is caused by the dipole-dipole correlations on one hand and some structural changes on the other. In one case the low frequency dielectric absorption shows also up perpendicular to the orienting magnetic field but it was most probably caused by some imperfections in the alignment[3]. In addition, it was found for alkoxyphenyl-alkoxybenzoates that the slopes of the Arrhenius plots are about the same in the N, S_{A1} and S_C phases[4].

It is surprising that the tilted S_C structure exhibits such a high reorientational mobility of molecules around their short axes, especially in comparison with the orthogonal S_A structure. This effect is probably partially caused by some distortions of the layer planes in the magnetic field which aligns the director and creates defects. So, the aligned S_C phase consits of "domains" in which the director is parallel to the field but the layer normals are evenly distributed on the cone with coning angle of 2Θ, where Θ is the tilt angle.

The aim of this paper is to study the N-S_A and S_A-S_C transitions by measuring - as suggested before[1] - the low frequency dielectric spectrum in much wider frequency range. To this end a wide band dielectric spectrometer[6], covering the frequency range between 1 Hz and 13 MHz, has been applied. The measurements done for $\bar{8}S5$ give answers to two questions:

1. How do the dielectric increment($\Delta\varepsilon = \varepsilon_{\parallel 0} - \varepsilon_{\parallel \infty} = 2\varepsilon''_{max}$) of the low frequency dielectric relaxation and the $\tau_{\parallel}$ relaxation time vary at the phase transitions as well as within the liquid crystalline phases?
2. Is the low frequency relaxation seen for the S_C phase in the direction perpendicular to the orienting magnetic field?

EXPERIMENTAL

Two components of the complex electric permittivity, $\varepsilon^*_k = \varepsilon'_k - i\varepsilon''_k$ for k=$\parallel$ and $\perp$, have been measured in the frequency range from 1Hz up to 13 MHz on the thin samples (d = 25 µm) of $\bar{8}S5$ aligned by means of the magnetic field of 1.2 T. The dielectric spectrometer used has been described elsewhere[6]. Transition temperatures for the substance studied are the following: Cr.-30°C- S_C-54°C-S_A-63 °C-N-85°C-I[1]. The orientation of the sample, obtained by slow cooling of the nematic phase in the magetic field, was optically controlled. Accurate measurements of ε' and ε'' have been done for both principal directions in the N and the orthogonal S_A phase, and also for the S_C phase parallel to the director ($\vec{n}$) and perpendicular to it.

RESULTS AND DISCUSSION

Figure 1. presents the low frequency dielectric spectrum taken for the S_C phase at different temperatures. The same kind of measurements have been done for the N and S_C phases.

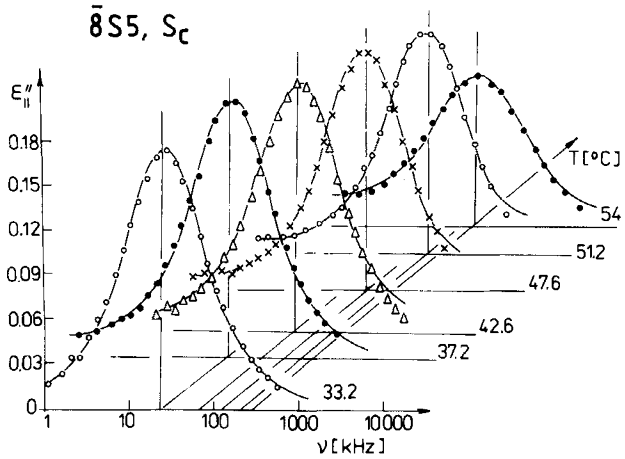

FIGURE 1. Low frequency dielectric spectrum obtained for the S_C phase of $\bar{8}$S5. Solid lines are Lorentzian curve fits.

In Figure 2. one can see how the intensity of the absorption curve vary at the N-S_A and S_A-S_C transitions. At the first transition the ε''_{max} jumps from 0.35 to about 0.1 whereas at the second it increases stepwisely from 0.1 to 0.2. These results allow us to draw the following conclusions:

1. A pronounced decrease of the ε''_{max} at the N - S_A transition, i.e. between the two uniaxial phases, is caused by the interlayer dipole-dipole correlations[7,8] what has been shown previously[1] by analysing the behaviour of the $\varepsilon_{\parallel}$ component extrapolated to low frequencies ($\varepsilon_{\parallel o}$). In this paper it is experimentally proved.

2. An increase of the dielectric absorption at the S_A-S_C transition is probably due to the reduction of dipole-dipole correlations coming presumably from the defects in S_C structure created by the strong orienting magnetic field.

3. The absorption peaks are pure Debye-type spectra characterised by a single dielectric relaxation time ($\tau'_{\parallel}$). It means that one has to do here with only one molecular process connected with the reorientation of molecules about their short axes (180°- jumps).

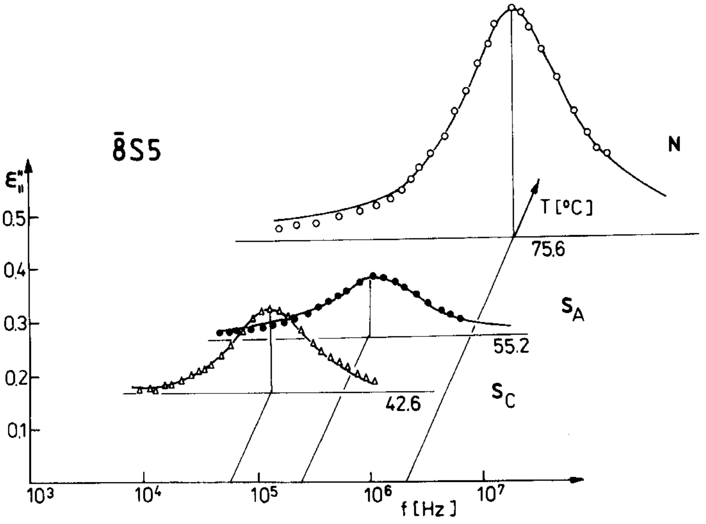

FIGURE 2. A Comparison of the low frequency dielectric spectra obtained for the N, S_A and S_C phases.

In addition it was found that there is no low frequency relaxation for planar textures of both S_A and S_C phases. Assuming that the electric permittivity tensor ($\hat{\varepsilon}$) is diagonal in the director frame ($x,y,z \parallel \vec{n}$) one can get that in the laboratory frame ($X,Y,Z \parallel \vec{B}_0$) the following expressions for the principal components: $\varepsilon_{\perp}=\frac{1}{2}(\varepsilon_{xx}+\varepsilon_{yy})$ and $\varepsilon_{\parallel}=\varepsilon_{zz}$. It means that due to the homogenous distribution of the director on the conical surface with angular field 2Θ, the ε_{xx} and ε_{yy} components become mixed. The S_C phase under investigations is then uniaxial from the dielectric standpoint. In the case of highly ordered tilted smectics (e.g. S_I*) one can obtain dielectrically biaxial phase, the layers of which are either parallel or penpendicular to the measuring electric field[9].

Due to the dipole-dipole correlations present in both smectic phases it is difficult to calcualte the Θ tilt angle from the ratio of the respective dielectric increments. It has been done before for one of the alkoxybenzoates[3] and the authors obtained a resonable value for Θ. Using their method of computing one obtains for $\overline{8}S5$ $\Theta = (47 \pm 2)^o$ which is definitely too high value. However, it shows that the dipole-dipole correlations reduce the $\varepsilon_{\parallel}$ componet as well as ε''_{max} very strongly.

On the other hand molecular dynamics is not much disturbed upon going from the N to the S_C phase via the S_A one. It is seen very clearly in Fig. 3 showing an Arrhenius plot spanned over all three liquid crystalline phases.

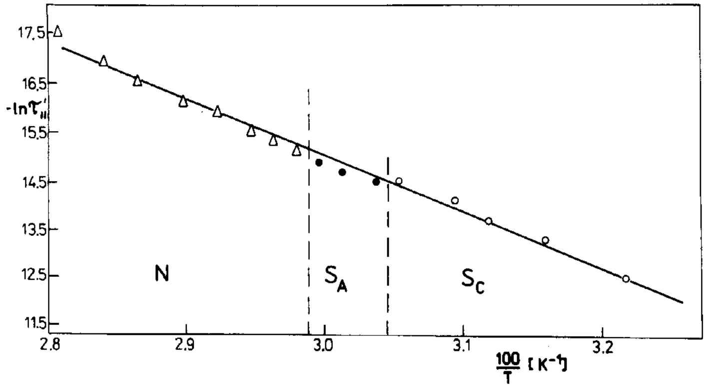

FIGURE 3. Arrhenius plot of $\tau_{\parallel}$ for the nematic, S_A and S_C phases of $\overline{8}S5$. Solid line is a least square fit to the experimental points.

The values of the activation energies are about the same for the all liquid crystalline phases and the average value amounts to (95 ± 4) kJ/mole. One can also notice that there are practically no steps of $\tau_{\parallel}$ at both transitions. A conclusion can be then drawn that the molecular dynamics is - in the case of $\overline{8}S5$ - insensitive to the phase transitions and the dipole-dipole correlations do not influence the value of activation energy.

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