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B. Gestblom[a]; M. Makrenek[b]; W. Haase[c]; S. Wróbel[d]
[a] Department of Physics, University of Uppsala, Uppsala, Sweden [b] Department of Physics, Holy Cross University of Technology, Kielce, Poland [c] Institut für Physikalische Chemie, Darmstadt, Germany [d] Institute of Physics of the Jagellonian University, Kraków, Reymonta 4, Poland

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Hindered reorientation of chiral molecules around their long axes in the S_C^* phase

by B. GESTBLOM, M. MAKRENEK†, W. HAASE‡ and S. WRÓBEL*§
Department of Physics, University of Uppsala, Box 530, S-75121, Uppsala, Sweden
† Department of Physics, Holy Cross University of Technology, 25-342 Kielce, Poland
‡ Institut für Physikalische Chemie, TH Darmstadt, Petersenstr. 20, D-6100 Darmstadt, Germany
§ Institute of Physics of the Jagellonian University, 30-059 Kraków, Reymonta 4, Poland

In this work,the high frequency dielectric relaxation process has been studied for the N*, S_A^* and S_C^* phases of the mixture ZLI 3654. To this end, time domain spectroscopy (TDS) was used to cover the frequency range from 10^7 to 10^{10} Hz. The dielectric parameters obtained show that the high frequency spectrum is mostly influenced by the reorientation of molecules around their long axes. In addition, the latter process seems to be strongly hindered in the S_C^* phase, because the necessary relaxation time is of the order of 1 ns, whereas for the N* and S_A^* phases, the relaxation time is remarkably shorter and equal to 0.3 and 0.4 ns, respectively.

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1. Introduction

According to the theory of the soft mode and Goldstone mode dynamics derived for the S_C^* phase [1, 3], there are at least four contributions to the dielectric increment:

(i) the Goldstone mode, corresponding to a damped Larmor precession of the molecular long axes around the layer normal;
(ii) the soft mode describing the 'in phase' fluctuations of the tilt angle and also the polarization;
(iii) the stiff mode originating from out of phase fluctuations of the tilt and polarization. This mode splits up into two branches on going from the S_A^* to the S_C^* phase.

The Goldstone mode and soft mode relaxation processes for the mixture ZLI 3654 were studied by us previously [4, 5] by using a classical dielectric spectrometer in the frequency range from 5 Hz to 13 MHz. We should mention that a new collective mode was also observed [5], which is now described in the literature as a domain mode [6, 7].

In previous papers devoted to the mixture ZLI 3654, it was also reported that the $\varepsilon_{\perp\infty}^S$ for the soft mode is distinctly higher than the refractive index squared ($n_\perp^2$). According to the Kronig–Kramers relations, there should be then some high frequency relaxation processes above 10 MHz. Therefore, we have performed dielectric measurements in the frequency range from 10 MHz to 10 GHz by using a TDS

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*Author for correspondence.

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spectrometer [8]. Up to now, there have been a few attempts [9–11 (a, b)] to study high frequency relaxation processes in FLCs by means of a steady state method [9, 10, 11 (b)] and recently by the TDS reflection technique [11 (a)]. In this paper, a whole dielectric spectrum of the ferroelectric and paraelectric phases is presented, and it seems to be qualitatively consistent with the Blinc and Zeks theory [1] and its recent extension by Carlsson *et al.* [12].

2. Experimental

The mixture ZLI 3654 is a multi-component system exhibiting a room temperature ferroelectric S_C^* phase. Its phase sequence is the following: C – 30°C S_C^* 62°C S_A^* 76°C N* 86°C I. The material was a gift from Dr T. Geelhaar (E. Merck, Darmstadt).

To measure the complex electric permittivity $\varepsilon^*(\omega)$, the TDS transmission system was used [8], allowing for measurement of the dielectric spectrum in the frequency range from 10 MHz to 10 GHz. The amount of sample used was 1 g. As the system consists of coaxial waveguides, there was no way to align the sample studied using a regular sample holder. However, in this frequency range, only the fast relaxation processes connected with reorientation around the long axes of the molecules contributes to the dielectric spectrum. The measurement cell was filled with the material in the isotropic phase.

The dielectric data were processed by using the Cole–Cole function:

$$\varepsilon^* = \varepsilon_\infty + \frac{\varepsilon_0 - \varepsilon_\infty}{1 + (\mathrm{i}\omega\tau_\mathrm{M})^{1-\alpha_\mathrm{M}}}, \qquad (1)$$

where ε_0 is the static electric permittivity for the high frequency molecular process, τ_M is the relaxation time connected with reorientation of molecules around their long axes, α_M is a parameter accounting for the distribution of the relaxation times, ε_∞ is the high frequency limit of the dielectric permittivity and ω is the angular frequency from the Fourier analysis of the pulse. We should notice that equation (1) is the first term in a complex formula [4] used by us before to describe the dielectric spectra of the S_C^* phase, which shall be taken into account in the discussion below.

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3. High frequency dielectric spectra of the mixture ZLI 3654

The dielectric spectra were recorded for all liquid crystalline phases (N*, S_A^*, S_C^*) of the mixture ZLI 3654. The spectra obtained are presented in figures 1 and 2. As we can see, there is a broad dielectric spectrum in the frequency range from 10^7 Hz to 10^{10} Hz. This high frequency dielectric spectrum is noticeably shifted to lower frequencies when going from the S_A^* to the S_C^* phase; also the dielectric increment is slightly suppressed and the distribution parameter (α_M) is on average bigger in this phase. In figure 3, we can see that the dielectric permittivities obtained in the S_C^* phase at frequencies from $7{\cdot}08 \times 10^7$ Hz to 10 GHz decrease, whereas in the N* and the S_A^* phases, at the lowest frequencies, they increase with decreasing temperature. This shows that the high frequency dielectric spectrum of the S_C^* phase is to a certain extent different from that acquired for the N* and the S_A^* phases as well.

The dielectric parameters obtained by fitting formula (1) to the experimental data are gathered in the table. As we can see the ε_0 values (column 4) obtained here by studying the high frequency dielectric spectrum, agree fairly well with the $\varepsilon_{\perp\infty}^\mathrm{s}$ values (column 6) found in previous studies [5] of the low frequency relaxations by another method. In addition, the spectrum obtained consists of at least two components,

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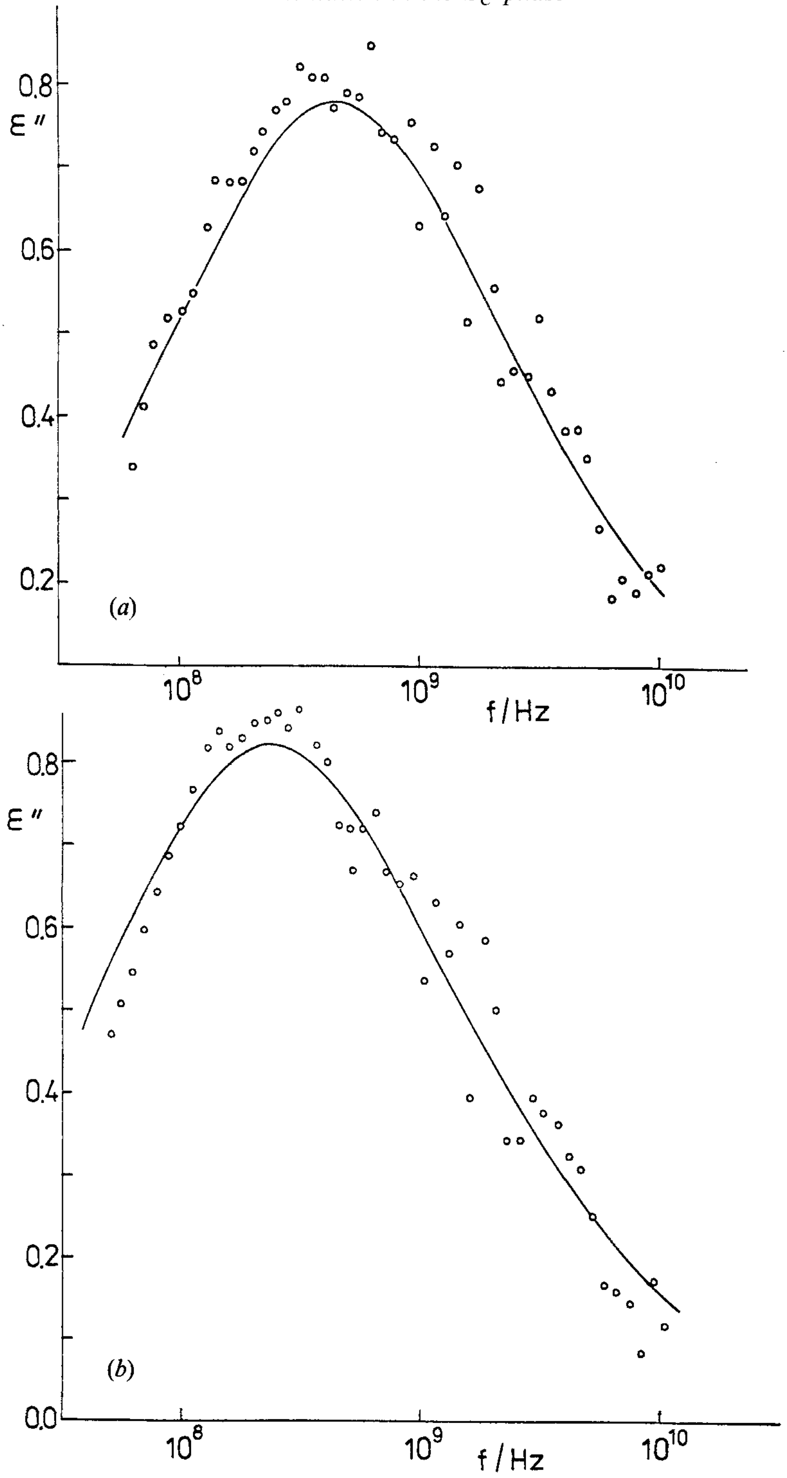

Figure 1. (*a*) Dielectric spectrum obtained for the mixture ZLI 3654 by the TDS technique for the nematic phase. $T = 76{\cdot}7°\mathrm{C}$, $\varepsilon_0 = 4{\cdot}801$, $\varepsilon_\infty = 2{\cdot}444$, $\tau = 3{\cdot}485 \times 10^{-10}\,\mathrm{s}$, $\alpha = 0{\cdot}255$. (*b*) Dielectric spectrum obtained for the mixture ZLI 3654 by the TDS method for the S_C^* phase. $T = 55{\cdot}2°\mathrm{C}$ (S_C^*), $\varepsilon_0 = 5{\cdot}017$, $\varepsilon_\infty = 2{\cdot}379$, $\tau = 6{\cdot}603 \times 10^{-10}\,\mathrm{s}$, $\alpha = 0{\cdot}293$. Open circles are experimental points. Solid lines are least squares fits of equation (1) to the experimental points.

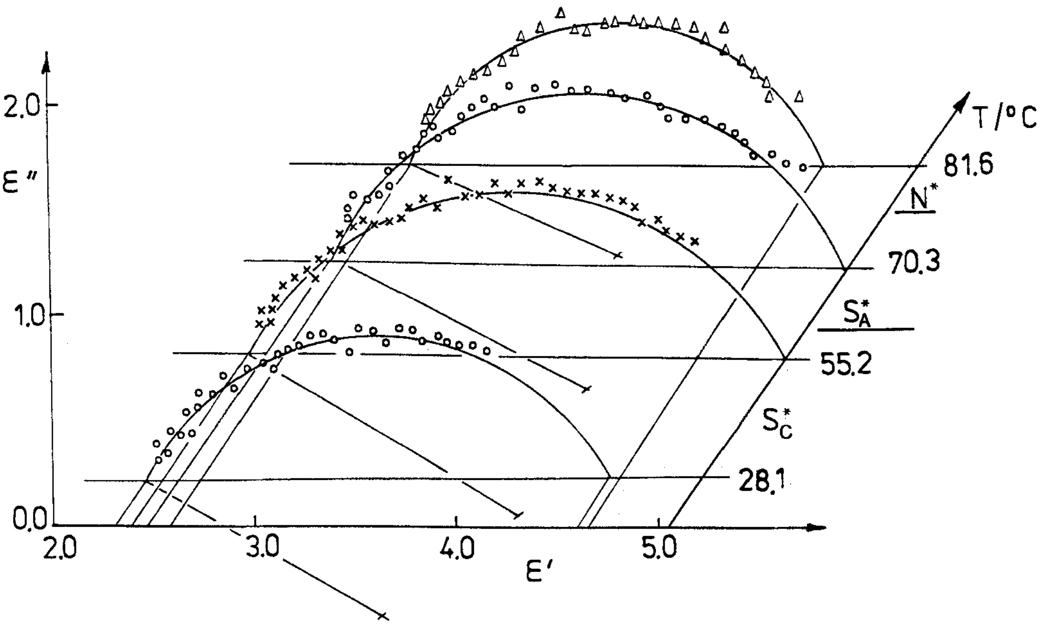

Figure 2. Cole–Cole diagrams acquired for different phases of the mixture ZLI 3654. Solid lines are least squares fits of equation (1) to the experimental points.

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which are merged and it is difficult to split them in a unique way. However, there has been an attempt [11] to break down such a spectrum into a group of four single relaxation processes.

Figure 4 shows the critical (or relaxation) frequencies versus temperature obtained from the low frequency dielectric measurements [4, 5] for the Goldstone mode, the soft

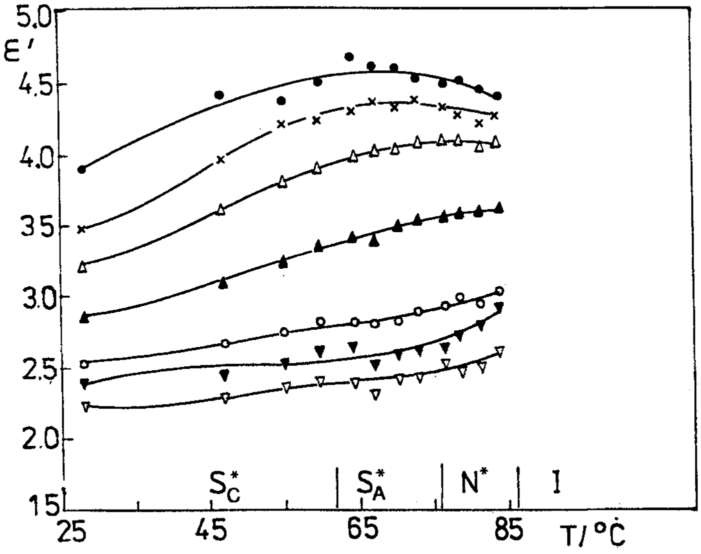

Figure 3. Temperature dependences of the electric permittivities measured at different frequencies in the GHz range for the liquid crystalline phases of the mixture ZLI 3654. Solid lines are simply guides for the eye. ●, 7·080 × 10^7 Hz; ×, 1·000 × 10^8 Hz; △, 1·995 × 10^8 Hz; ▲, 5·012 × 10^8 Hz; ○, 0·585 × 10^9 Hz; ▼, 5·012 × 10^9 Hz; ▽, 1·000 × 10^{10} Hz.

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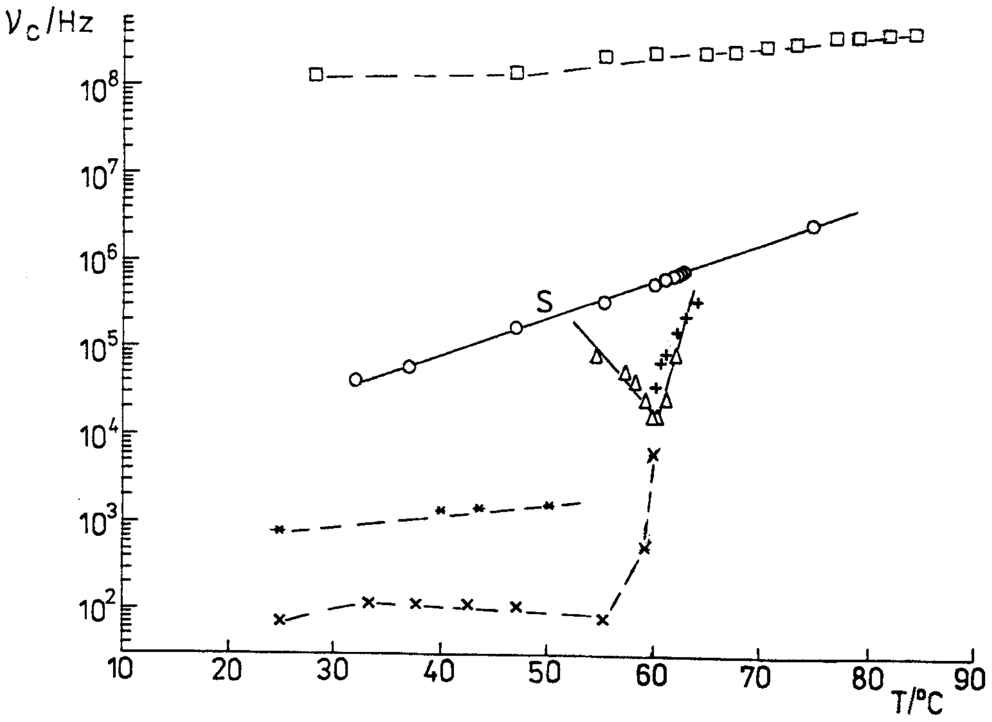

Figure 4. Critical frequencies for different dielectric modes obtained for the S_A^* and S_C^* phases of the ZLI mixture. The points obtained in this work (squares) represent critical frequencies for the high frequency molecular relaxation (molecular mode L). The data acquired for the Goldstone mode (crosses), soft mode (plusses) and molecular mode S (open circles) were taken from [4]. The points representing the domain mode (stars) and soft mode (triangles)—both studied under a bias field of 10 V/25 μm—were obtained in [5].

mode and the low frequency molecular mode (molecular mode S, which is seen for homeotropic alignment only). This Figure also incorporates the critical frequencies —obtained in this study by the TDS technique—for the high frequency relaxation process, which is mostly connected with the biased reorientation of molecules around their molecular long axes (molecular mode L).

4. Discussion

As shown, the high frequency relaxation process studied in this paper for the N*, S_A^* and S_C^* phases is in all cases a broad spectrum, which spans the frequency range from 10^7 to 10^{10} Hz (see figures 1(*a*) and (*b*) and figure 2). The dielectric parameters obtained for this mode by fitting equation (1) to the experimental points are gathered in the table. As we can see, the τ_M relaxation time becomes remarkably longer for the S_C^* phase, where $\tau_M \approx 1$ ns. However, on the logarithmic scale (see figure 4) we can hardly see any difference between the S_A^* and S_C^* phases as far as the critical frequency for the high frequency process is concerned. The α_M parameter becomes bigger and the dielectric permittivities decrease slightly in this phase with decreasing temperature. This may mean that the reorientation around the long axis is more hindered in the S_C^* phase, but not frozen out. We can then make an assumption that there are at least two fast molecular processes in the S_C^* phase, but due to their overlapping nature, we cannot isolate the relevant relaxation times and the dielectric increments as well. Additionally, we are dealing here with two kinds of polar molecules [4].

Dielectric parameters of the high frequency relaxation process studied by the TDS method.

	$T/°\mathrm{C}$	$\tau_{\mathrm{M}}/\mathrm{ns}$	α_{M}	ε_0	ε_∞	$\varepsilon^{\mathrm{S}}_{\perp\infty}$ †	$\nu^{\mathrm{S}}_{\mathrm{c}}/\mathrm{MHz}$	Theoretical values [12]
S_C^*	28·1	1·191	0·306	4·614	2·324	5·71	133·6	
	47·0	1·003	0·319	5·236	2·345	5·32	158·7	$\nu_c^{PS} = 1030\,\mathrm{MHz}$
	55·2	0·660	0·293	5·017	2·379	5·16	241·1	$\nu_c^{PG} = 630\,\mathrm{MHz}$
	59·9	0·588	0·272	4·991	2·474	5·06	270·0	
S_A^*	64·5	0·569	0·260	5·081	2·510	4·97	279·7	
	67·3	0·541	0·311	5·184	2·335	4·91	294·2	
	70·3	0·457	0·288	5·032	2·407	4·85	348·3	
	73·1	0·413	0·279	4·956	2·417	4·79	385·4	
N*	76·7	0·348	01255	4·801	2·444	4·72	457·3	
	78·8	0·346	0·264	4·779	2·517	4·68	460·0	
	81·6	0·325	0·233	4·631	2·590	4·62	489·7	
	84·1	0·315	0·211	4·550	2·720	4·57	505·3	

† These values were interpolated by means of linear regression applied to the data reported in [5].

The theoretical values were obtained from the data presented in [12] and they correspond to a temperature 6° below T_c.

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It is worth noting that the same kind of spectrum was obtained for a single component system [11], and the authors analysed the data assuming that there are four Debye-type processes involved. Two of them are being slowed down in the S_C^* phase, whereas the other two are as fast as in the S_A^* phase. The former two are of intermolecular origin, whereas the latter two have some intramolecular implications. Recently, the same group [18] analysed the data obtained for diluted mixtures of the same substance and introduced the idea of two mechanisms influencing the spectra, namely, (i) the intermolecular reorientation of the molecule as a whole, and (ii) a fast intramolecular motion of two moieties around a single bond. This would be rather consistent with the Boulder model [21], assuming that conformational and rotational orientations of molecules are responsible for ferroelectricity in the S_C^* phases.

On the other hand Kremer *et al.* [15, 16] have suggested that for a ferroelectric liquid crystal polymer, the reorientation of the mesogenic group around its molecular long axis does not change at all at the S_A^*–S_C^* transition. The authors obtained continuous temperature dependences of both the relaxation time and the dielectric strength. However, their spectrum is also broadened. A moderated discussion of this problem is presented in [14].

On the contrary, the high frequency relaxation spectrum—studied for one of the alkoxythiobenzoate FLCs [11 (b)]—seems to be influenced by the S_A^*–S_C^* phase transition. However, the substance shows a monotropic S_C^* phase with a tendency to form a glassy state upon cooling. Due to this, the increase in viscosity (and relaxation times) may be greater than for enantiotripoc systems.

It is worth mentioning here that the dielectric studies performed for non-chiral compounds [13 (a, b), 17] are complex even for the nematic, and S_A phases. For instance, in the case of 4-octyl-4′-cyanobiphenyl [13 (a)] for both phases a broad spectrum centred at *c.* 50 MHz is obtained, and the authors analysed this in terms of three Debye-type processes connected with inter- and intra-molecular motions. In the case of 4-nonanoyloxy-4′-cyanobiphenyl [13 (b)] (8COOCB), the dielectric spectrum is even broader and centred at *c.* 500 MHz in the S_A phase. The analysis of the

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spectrum leads to six Debye-type processes coming form intra- and inter-molecular motions, including libratory motions. One of the modes with a critical frequency in the gigahertz range corresponds to the reorientation of the nonanoyloxy chain around the mean axis of the molecule. As is seen, the high frequency dielectric spectra of such model compounds appear to be complicated even in the nematic and smectic A phases.

Our studies of the non-chiral thioester series [17], by using the TDS technique, show that the high frequency dielectric spectrum is also complex in the nematic, S_A and S_C phases, and no pronounced changes in the spectrum are revealed at the N–S_A or the S_A–S_C transitions. There is, of course, a distribution of the relaxation times caused by libratory motions of the molecules and by some intramolecular motions as well.

According to the theory by Blinc and Zeks [1] as well as its extension by Carlsson, Zeks, Filipic and Levstic [12], there should be a splitting of the high frequency dielectric relaxation spectrum at the transition S_A^*–S_C^* into two independent processes: PG and PS polarization modes. The latter theory predicts that the splitting on the frequency scale should be equal to $\Delta\nu \approx 400$ MHz inside the S_C^* phase. Taking into account that the relaxation frequency obtained in this paper is of the order of 10^8 Hz, we can conclude that there is no way to obtain experimentally resolved relaxation peaks. It is well known that relaxation frequencies must differ by at least one order of magnitude to resolve them uniquely. It is possible that two modes analysed theoretically by Carlsson *et al.* [12] contribute to the dielectric spectrum on its high frequency side, as their relaxation frequencies are higher than the average relaxation frequency obtained from our experiment (see the table). We should add that some theorists also have doubts [22] about whether or not the splitting should occur.

As far as the high frequency relaxation is concerned, we should stress that at the moment there is no clear experimental evidence for pronounced differences between the spectra observed for chiral and non-chiral compounds on the one hand, and between the high temperature orthogonal S_A^* phase and the tilted S_C^* phase on the other.

There follow below a few questions which arise when we compare the high frequency dielectric spectrum with theories:

(i) Are the PG and PS modes collective or molecular processes? Are they not librational oscillations?

(ii) As is seen in the table, both critical frequencies predicted by the theory are higher than the average critical frequency obtained from the experimental spectra. Maybe, in addition to two orientational modes, connected with biased rotation around the long axis and/or intramolecular reorientation, there are two libratory modes observed for non-chiral polar systems in the far infra-red region. All together therefore there should be four relaxation processes—as suggested in [11]—which merge into a broad spectrum

(iii) According to the microscopic model [19, 20], incorporating a single particle potential for rotation of a molecule around its long axis, the dipolar order parameter (originating from chirality) appears to be much smaller than the quadrupole one, except in the vicinity of T_c. However, the authors were analysing the experimental data for spontaneous polarization only. It would be interesting to apply this model to an analysis of the high frequency dielectric data.

To sum up, we may say the following: our experimental data confirm qualitatively the theoretical predication of a complex high frequency dielectric spectrum for the S_C^* phase. However, we cannot break down the spectrum observed in a unique way to search for a quantitative matching. At the moment the data are not adequate to solve this problem. More research must be done—both theoretically and experimentally —on different chiral systems to understand better the molecular origin of ferroelectricity.

5. Conclusions

(i) The high frequency dielectric spectra obtained for all the liquid crystalline phases of the mixture ZLI 3654 show that to a certain extent there may be stronger hindrance of molecular reorientation around the long axis in the S_C^* phase than in the S_A^* and N* phases.

(ii) Due to a distribution of the relaxation times, we cannot reach a conclusion about splitting of the high frequency mode into two modes on going from the S_A^* to the S_C^* phase.

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