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Dielectric characterization of samples showing the $SmCP_A/B_7$ transition

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Dielectric measurements on samples consisting of banana-shaped molecules with a polymorphism $I/SmCP_A/B_7$ have been performed for the first time. The dielectric increment for the reorientation of the molecules about the long axis, and the corresponding relaxation time, surprisingly decrease at the $SmCP_A/B_7$ transition. This effect is discussed in terms of the undulated structure which partially destroys the ferroelectric short range order. Decreasing temperature gives an even stronger hindrance for this reorientation and could explain controversial results obtained in the B_7 phases of different samples. At lower temperatures a further mesophase was detected. This was additionally observed by calorimetric and atomic force microscopy methods.

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1. Introduction

Recently Pelzl *et al.* reported the first bent-shaped samples which show the polymorphism $SmCP_A/B_7$ [1]. This interesting phase sequence now allows the possibility to compare for the first time the dynamical behavior in these two phases. These 'banana'-shaped molecules form a new system of liquid crystalline mesophases in which the lateral order of the molecules and the order of neighbouring layers gives rise to unique physical behaviour [2–6]. All these interesting effects result from the hindered reorientation of the molecules about their long axes [6].

The molecules in the SmCP (polar smectic C, or B_2) phase are tilted within the layers as in a classical SmC phase. Due to a reduction in the symmetry of such phases, a polar axis can exist [4] which results in ferroelectric ordering within a layer. The behaviour of the bulk depends on the orientation of the neighbouring layers to each other (synclinic or anticlinic) and on the direction of the vectors of the spontaneous polarization (ferroelectric, antiferroelectric). Among the four different possible modifications [3, 4] the antiferroelectric $SmCP_A$ phase is often observed because in this case the spontaneous polarizations of neighbouring layers compensate each other and in this way minimize the free energy of the system.

On cooling from the isotropic phase, the B_7 phase appears under a polarization microscope similar to wire or screw-like germs [7] which can also be seen in atomic force microscopy (AFM) [8]. The structure of the B_7 phase is not yet completely clear, because no oriented samples necessary for X-ray investigations have been obtained. Diele *et al.* have found numerous reflections at small angles indicating a complicated structure [9]. The wide angle reflection responsible for the lateral distances is broad, corresponding to a fluctuation of the molecular long axes. Dielectric measurements give a confused picture: Salfetnikova *et al.* have found that the relaxation time of the molecules for the reorientation about their long axes increases strongly at the transition from the isotropic into the B_7 phase and is of the order of $\tau=0.05$ ms [10]. In the 'original' B_7 sample, for which it was very difficult to separate a relaxation range, at much higher temperature a time constant of $\tau>1$ ms was detected [8]. In both cases an increase of the dielectric constant at the I/B_7 transition was observed, pointing to a positive dipole correlation. Recently Coleman *et al.* [11] have shown that the B_7 phase is a modification of the $SmCP_A$ phases because at the phase transition into the B_7 the reflections of the $SmCP_A$ phase remains essentially unchanged and new reflections appear in the small and wide angle regions. Therefore they proposed a structure in which the layers are undulated. The undulation is a result of the frustration caused by the polarization of the layers. This conclusion is based mainly on microscopic, electro-optic and small angle X-ray measurements. Not all of the results discussed here are completely consistent with each other. Therefore one has to call into question whether all these B_7 phases investigated in different samples are in fact the same. For this reason dynamical investigations were

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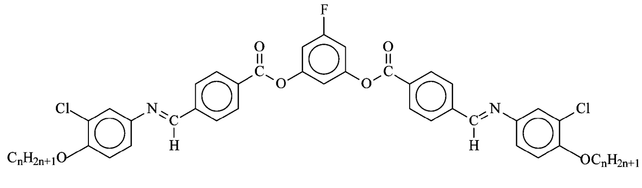
performed in order to study the changes of the different relaxation processes at the SmCP$_A$/B$_7$ transition and within the B$_7$ phase and relate the results to known behaviour and structured models.

2. Experimental

The two banana-shaped molecules characterized here are [1]:



Sample **1** $n=6$ Cr 334 (from the first heating run) B$_7$ 387 SmCP$_A$ 411 I (T/K)

Sample **2** $n=10$ (no crystallization [1]) B$_7$ 390 SmCP$_A$ 410 I (T/K)

For sample **1**, not discussed in [1], the phase transition temperatures were estimated by DSC (Pyris 1, Perkin-Elmer). Based on texture investigations the same phase sequence was assumed for both compounds.

Dielectric measurements were made during slow cooling using the Solartron-Schlumberger Impedance Analyzer Si 1260 and a Chelsea Interface. A brass cell coated with gold ($d=0.1$ mm) was used as capacitor. The samples could not be oriented. Experimental details are given elsewhere [10]. The complex dielectric function $\varepsilon^*=\varepsilon'-j\varepsilon''$ of sample **1** at three different temperatures plus the fits to equation (1) (see below) are shown in figure 1. In particular at low frequencies and at high temperatures only the contribution of the conductivity to ε'' and that of the electrical double layer to ε' dominate the spectrum. At frequencies of about 10 kHz the real part of the measured dielectric function ε' approaches the 'static' dielectric constant ε_1, figure 1 (*a*). At frequencies higher than 4 MHz the beginning of an absorption range is seen. The relaxation frequency for the related reorientation of the molecules about the long axes is out of our experimental range.

A complete change of the dielectric behaviour is observed in the SmCP$_A$ phase as demonstrated in figure 1 (*b*) at 392 K. Now two broad relaxation ranges are seen in the dielectric spectrum. The low frequency mechanism has to be separated from the strong influence of the double layer at very low frequencies and the second relaxation regime at high frequencies, figure 1 (*b*). By further cooling, a third absorption range appears which reduces the dielectric constant from about 5 to 3, figure 1 (*c*). The experimental data could

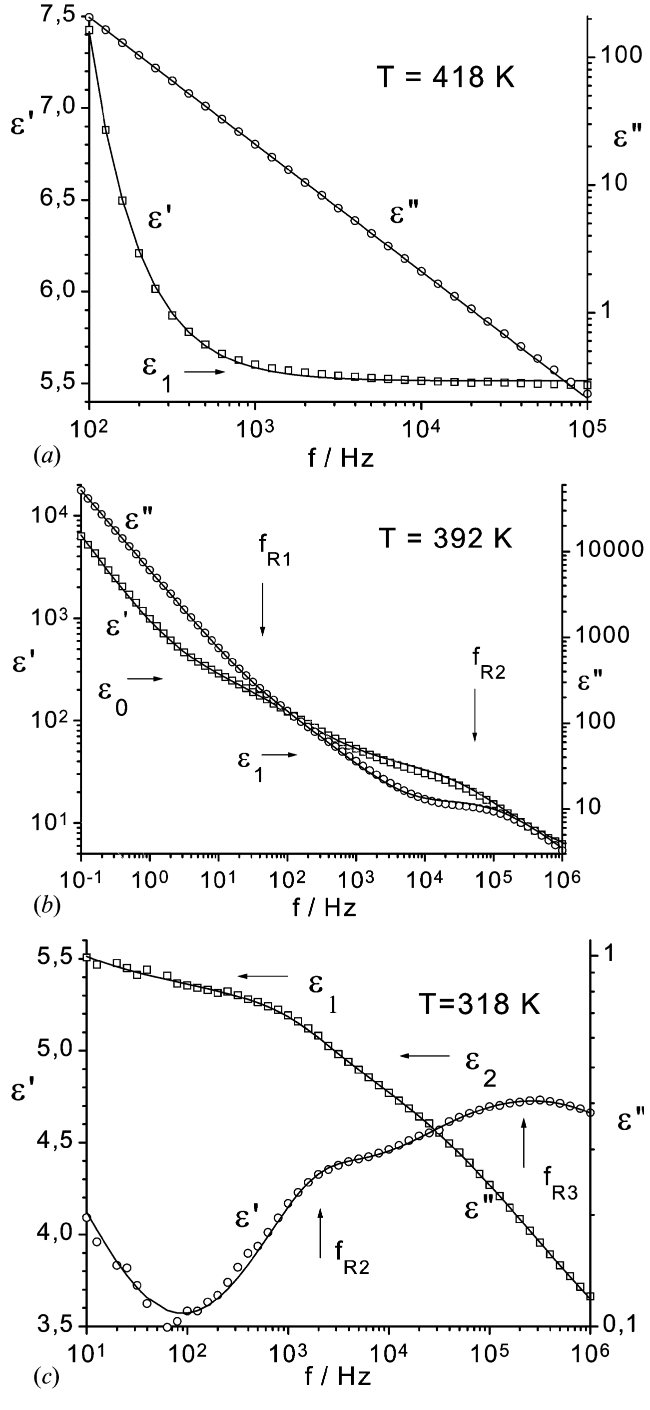


Figure 1. Experimental points and fitted data of the complex dielectric function of sample **1** measured in the (*a*) isotropic (standard deviation of ε_I: less than 0,1%); (*b*) SmCP$_A$ (standard deviation ε_0: 10%, increasing with decreasing temperature, ε_I: 5%, ε_2: 5%, increasing with increasing temperature, f_{R1}: 50%, f_{R2}: 10%); (*c*) B$_7$ phase (standard deviation, limiting values of the dielectric constants ε_i and calculated relaxation frequencies f_{Ri} are indicated by arrows).

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be well fitted to two Cole-Cole mechanisms

$$\varepsilon^* = \varepsilon_2 + \frac{\varepsilon_0 - \varepsilon_1}{1 + (j\omega\tau_1)^{1-\alpha_1}} + \frac{\varepsilon_1 - \varepsilon_2}{1 + (j\omega\tau_2)^{1-\alpha_2}} - \frac{jA}{f^M} + \frac{B}{f^N} \quad (1)$$

the limiting values of the dielectric constants with the corresponding relaxation times τ_i, where ε_i are $\omega = 2\pi f$ (f=frequency), α_i=Cole-Cole distribution parameters; the conductivity term A and M, B and N (further fit parameters responsible for the slope of conductivity and capacity of the double layer) were calculated. Up to frequencies of 10 kHz the data in the isotropic phase could be described by the first and the last two terms as demonstrated in figure 1 (*a*). In all cases the exponent M of the conductivity parameter was found to be between 0.99 and 1.00. Up to 310 K the experimental points could be well fitted by two Cole–Cole mechanisms if the fit was finished after the second relaxation maximum, see figure 1 (*b*). In order to separate the third relaxation range from the second, only the high frequency part of the low frequency relaxation was considered and fitted as 'conductivity' and 'double layer', as shown in figure 1 (*c*). In this way the more simple formula (1) could be used. This technique was chosen in order to avoid too many running parameters and to reduce the errors resulting from the separation of the less intensive second and third relaxation ranges from the dominant first process. A test shows that the dielectric constant ε_1 used as open parameter in both fits agrees well.

The second sample was measured and analysed in the same way. This sample was investigated in order to exclude accidental errors.

3. Results and discussion

The limits of the dielectric constants ε_i and the relaxation times τ_i of sample **1** are given in figures 2 and 3. In the isotropic state only one relaxation regime was found; in the SmCP$_A$ and B$_7$ phases two relaxation regimes were found. For a better understanding of the low frequency limit of the dielectric constant in the isotropic phase, ε_1 values are indicated by filled circles. This enables us to use the symbol ε_0 for the low frequency limit of the new relaxation spectrum appearing at $T<408$ K (open squares) in the SmCP$_A$ phase. The estimation of the static dielectric constant ε_0 becomes difficult with decreasing temperature because of the overlapping of the spectrum with the effects due to the double layer and conductivity. Therefore the fit was stopped at $T<348$ K. The time constants τ_1 of some ms (figure 3) and the increments $\Delta_1 = \varepsilon_0 - \varepsilon_1$ of about 200 in the SmCP$_A$ phase (see figure 4) are too high to interpret the low frequency mechanism as a molecular process. Therefore we regard this first mechanism as the

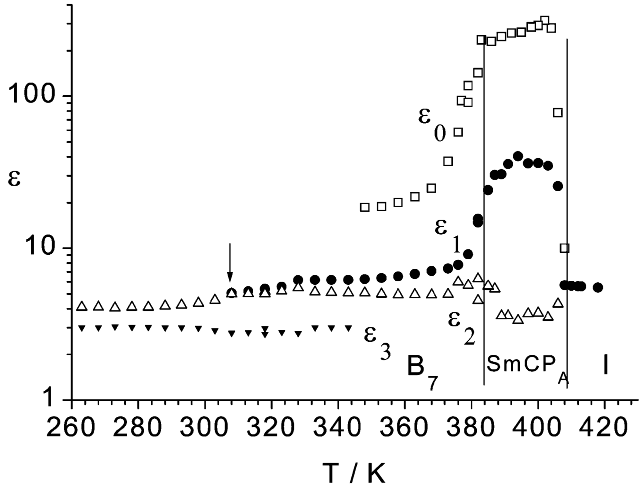

Figure 2. Limits of the dielectric constants for sample **1**.

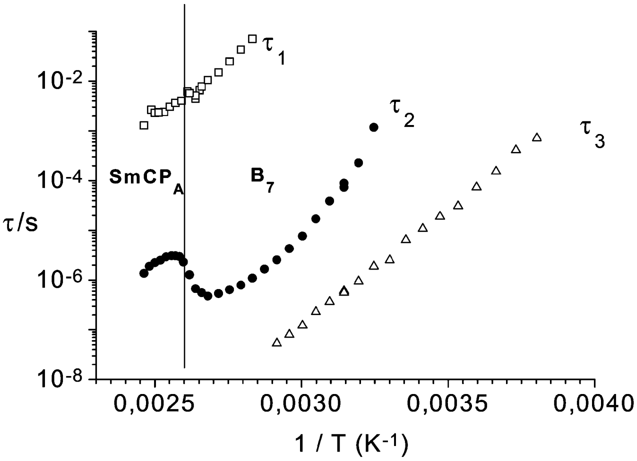

Figure 3. Relaxation time versus the reciprocal temperature for sample **1**.

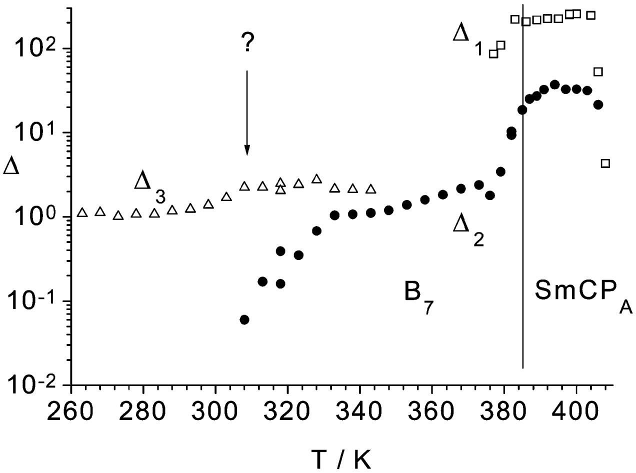

Figure 4. Dielectric increments on the logarithmic scale for sample **1**.

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collective dynamics of the ferroelectric basic units [12]. It has to be pointed out that only the dielectric increment Δ_1 changes at the $SmCP_A/B_7$ transition whereas the corresponding time constants τ_1 seem to be unchanged.

The second mechanism is commonly related to the reorientation of the molecules about their molecular long axes. Recently it was shown on an oriented sample that this process develops from a molecular mechanism in the isotropic state to a strong cooperative motion in the $SmCP_A$ phase [6, 13]. An unexpected result is seen as the sample passes the $SmCP_A/B_7$ transition (figure 4). Both, the dielectric increment $\Delta_2=\varepsilon_2-\varepsilon_1$ and the relaxation time τ_2 of the second mechanism decrease. That means this motion becomes faster on cooling and passing the transition into the B_7 phase! This quite unexpected behaviour is also the reason why a partial overlapping with the third mechanism, probably the reorientation of the terminal chlorophenylene groups, is seen [10]. Further cooling results in the expected increase of τ_2, indicating the even stronger hindrance for this motion.

An interesting effect becomes more clear by plotting the dielectric increment versus temperature, see figure 5. The intensity of the motion 2 decreases continuously and reaches zero at about 308 K; the corresponding relaxation time τ_2 did not show a slowing down. On the other hand the dielectric increment of the third mechanism $\Delta_3=\varepsilon_3-\varepsilon_2$, and the corresponding relaxation time τ_3, are essentially uninfluenced by this process. That means that the benzene units with chlorine substitution can rotate below 308 K.

In general, sample **2** exhibits the same dielectric behaviour as **1**, as shown in figures 6 and 7. In this case also, the dielectric increment of the second mechanism decreases with falling temperature and becomes zero at about 300 K (arrow in figure 6, line in figure 7). Below this temperature only the very broad third mechanism is seen.

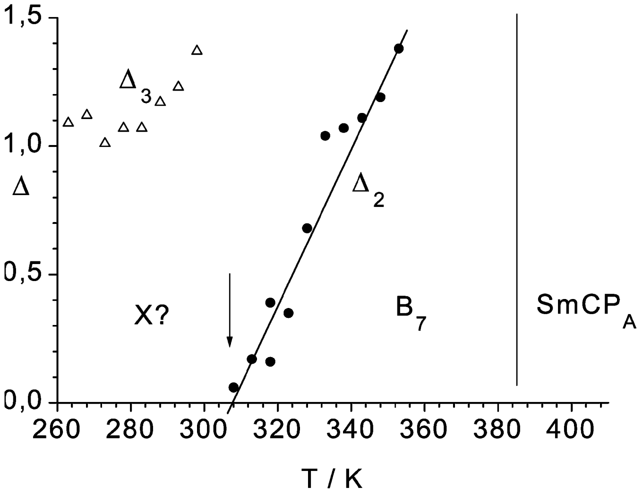

Figure 5. Dielectric increment of the second and the third mechanisms of sample **1** (cut of figure 4, in linear scale).

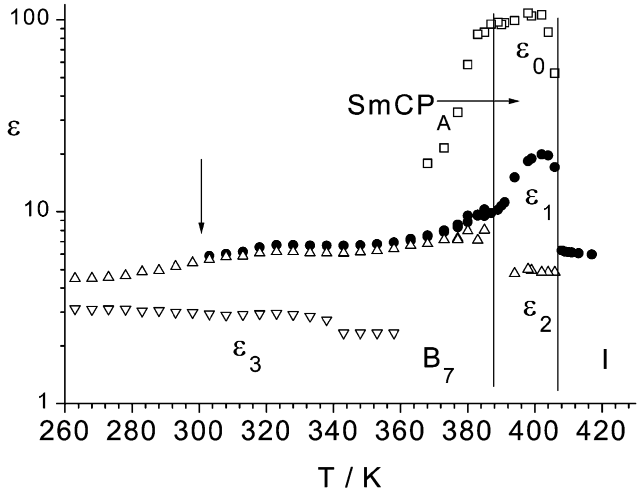

Figure 6. Limiting values of the dielectric function of sample **2**.

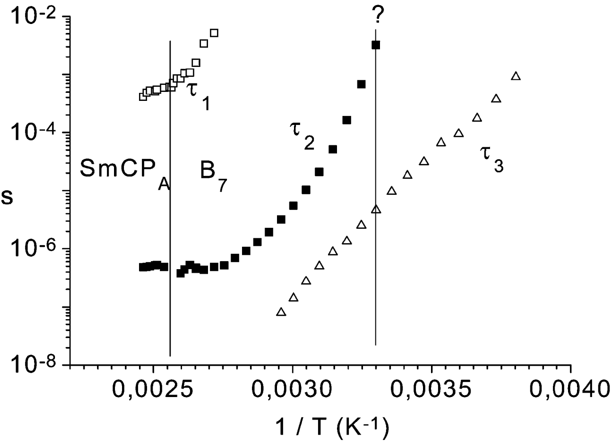

Figure 7. Relaxation times of sample **2**.

For a comparison of the dynamics in the $SmCP_A$ phase, previously published results [8, 14] can be used. There is a good agreement of the relaxation times τ_1 and τ_2 in the $SmCP_A$ phase of a similar sample with almost the same $I/SmCP_A$ transition temperature. Therefore we assume that the first and second processes in our sample are related to the same mechanisms as discussed before, namely the collective motion and reorientation about the long axis. In the former measurements, an increase of the relaxation time and of the dielectric increment for the reorientation about the long axis at the $I/SmCP_A$

(named in [8] B2) transition was detected. This effect was interpreted as a result of a stepwise transition from a more statistical orientation of the molecules to a ferroelectric packing within a layer, which results in an increase of the lateral dipole correlation. The samples investigated here additionally show the SmCP$_A$/B$_7$ transition, where both the relaxation times τ_2 and the increments Δ_2, are reduced. With respect to the interpretation at the I/SmCP$_A$ transition discussed above, such a behaviour can indicate a decrease of the cooperativity at this phase transition. This plausible explanation results in a problem: why is the intensity of the second process, the reorientation about the long axes, again reduced between 330 and 300 K in both samples?

For the second sample, no crystallization was observed, thus one has to discuss the possible formation of a new solid-like 'banana phase' where the reorientation about the long axes is even more hindered due to an increase of the rotation potential, as discussed in [6] and [12]. This hypothesis can also explain the very small enthalpy effect in this temperature range seen on cooling and shown in figure 8 for sample **1**. Clear evidence for the appearance of a new phase is obtained from AFM measurements at 295 K, see figure 9. For this investigation, sample **1** was prepared on glass by heating to the clearing temperature $T_{\mathrm{SmCPA/I}}$. The sample was subsequently cooled 5 K below $T_{\mathrm{SmCPA/I}}$ at a rate of 0.2 K min^{-1} and further to room temperature with a cooling rate of 20 K min^{-1}. One day after preparation, the AFM measurements were performed with the scanning force microscope, TopoMetrix TMX 2010, in the non-contact mode (163 kHz) under ambient conditions. The observed surface is modulated by focal conic domains which are surrounded by irregular ring-shaped structures. These non crystalline focal-conic domains [15–17] with a diameter of about 1.5 µm and a depth of about 200 nm are also observed after 80 days.

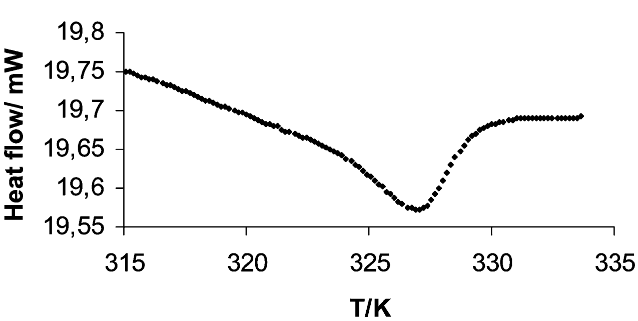

Figure 8. A part of the DSC trace of sample **1** under high magnification.

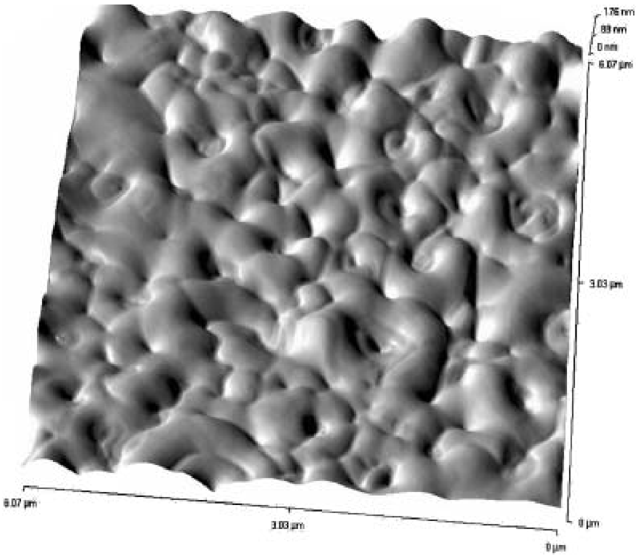

Figure 9. AFM image of sample **1**, obtained at 295 K. The focal-conic and non-crystalline texture demonstrates that at low temperatures a further liquid crystalline phase exists.

4. Conclusions

The decrease of the absorption intensity and relaxation time for the reorientation about the long molecular axis at the SmCP$_A$/B$_7$ transition is the main result of this investigation. This effect can partially explain contradiction in behaviour seen between 'different' B$_7$ phases: at the SmCP$_A$/B$_7$ transition the undulated structure of the B$_7$ modification proposed in [11] disturbs the dipole correlation. This results in a decrease of the relaxation time and of the dielectric increment with respect to those in the SmCP$_A$ phase. At lower temperatures the hindrance of the reorientation about the long axis again becomes stronger. This effect is caused by an increasing potential for the reorientation about the molecular long axis and may also result at lower temperatures in an even closer packing. Whether the change from the undulated B$_7$ phase [11] to the 'classical' [7] is a continuous process driven by the even stronger hindrance of the reorientation about the long axis of the molecules, or is a stepwise process, cannot be determined at present.

Further cooling of the samples investigated results at about 330 K in a decrease of the absorption intensity due to a slow phase transition. At about 300 K the reorientation about the long axis can no longer be detected. The low temperature phase shows a more 'solid-like' character. Similar effects have been found in other samples [8, 10].

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