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Observation of a possible random ferroelectric liquid crystal phase

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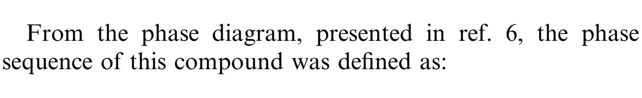
A random ferroelectric tilted smectic phase has been observed and investigated for the first time. In this phase, the molecular director in smectic layers is tilted with respect to the smectic layer normal but the tilt directions in different smectic layers are randomly oriented. This structure is confirmed by electrooptics, effective birefringence measurements and dielectric spectroscopy.

We report the observation of a disordered SmC* phase. The non-chiral analogue of this phase was suggested and investigated first by de Vries in 1974[1] (called A_3). The smectic C_3 phase on heating would yield an SmA phase (called A_3), and this changeover at the C_3–A_3 transition temperature is likely to occur without an alteration in the smectic layer spacing and without a change in the molecular tilt angle. Prior to this in 1972, Diele *et al.*[2] had reported an SmA phase, with the same layer spacing as a non-chiral SmC. In a smectic A_3 phase, the molecules are tilted with respect to the smectic layer normal, similar to those in an SmC* phase but the tilt directions in different smectic layers are randomly oriented,[3] or an uncoupling of the tilt directions from layer to layer occurs. The existence of such a random phase had been explained in terms of a diffuse-cone model.[4,5] Due to the absence of chirality, and consequently the absence of local spontaneous polarization, the A_3 phase being actually a tilted smectic phase (or in other words smectic C), cannot be distinguished from the orthogonal SmA phase.

In fact, the smectic A_3 phase could have been a non-chiral analogue of a disordered antiferroelectric phase.[6,7] The existence of a disordered antiferroelectric phase is also predicted by the axial nearest next neighbour interactions (ANNNI) model,[8] where the competitive disordering effect of the thermal fluctuations is greater than the interactions due to the correlation between the smectic layers. In such a phase, the molecular tilt directions in smectic layers are rather arbitrary, with the consequence that the macroscopic polarization is zero. The application of an external electric field changes this random distribution of the molecular tilts and thus induces macroscopic polarization. In fact, the name "disordered antiferroelectricity" is misleading in this context, since antiferroelectricity implies antiferroelectric order and a threshold in switching to the ferroelectric state. Hence, the classification as a "random smectic C-like"[7] or a random ferroelectric phase—SmC_R* (where the directors are tilted but are randomly stacked in the neighboring layers) is more appropriate for the reasons stated.

The sample under investigation was MC513, which is the second compound of a three-component mixture investigated in ref. 6. The molecular structure of this compound is as follows:



From the phase diagram, presented in ref. 6, the phase sequence of this compound was defined as:

$$\mathrm{Cr{-}35\,^\circ C{-}SmC_A{-}73\,^\circ C{-}SmC^*{-}81.7\,^\circ C{-}SmA{-}84.5\,^\circ C{-}Is}$$

The electrooptic and dielectric measurements have been made on 8 μm cells, glass plates of which were coated with ITO and covered with PVA as an alignment agent. Dielectric spectroscopy has been carried out in the frequency range from 1 Hz to 1 MHz using a Schlumberger-1255 frequency response analyzer connected to a Chelsea dielectric interface. Fig. 1 shows the temperature dependence of the dielectric spectra shown from the high temperature side of the sample. The temperature increment between the two neighboring curves is 0.2 °C. It is clear that there are three different liquid crystalline phases in this sample. The spectra with high dielectric loss corresponds to a common ferroelectric SmC* phase. On cooling, this phase transforms to an antiferroelectric SmC_A* phase, with a correspondingly low dielectric loss and its weak temperature dependence. On the high-temperature side of the SmC* phase, where the SmA phase is expected[6] to appear, the dielectric spectrum in the first instance appears similar to that of the SmA phase, with a relaxation process corresponding to the soft mode. This phase was assigned to SmA in Ref. 6. Nevertheless in a conventional SmA phase, the soft mode relaxation process follows the Curie–Weiss law and in the conventional SmC* phase the Goldstone mode is dominant. In our sample at intermediate temperature (about 82.5 °C), the Goldstone relaxation process coexists with a higher frequency relaxation process which is also dominant at the same temperature. This implies the existence of a first-order phase transition, which contradicts the usual SmC*–SmA transition. DSC investigations of the component[9] of the A_3 phase[1,3] reveal an unusually high enthalpy change for the A_3–C phase transition ($0.146\ \mathrm{kcal\ mol^{-1}}$), which is an appropriate value for the first-order phase transition. Therefore we conclude that in our case we have a chiral analogue of the smectic A_3 phase, called a random ferroelectric phase SmC_R*.

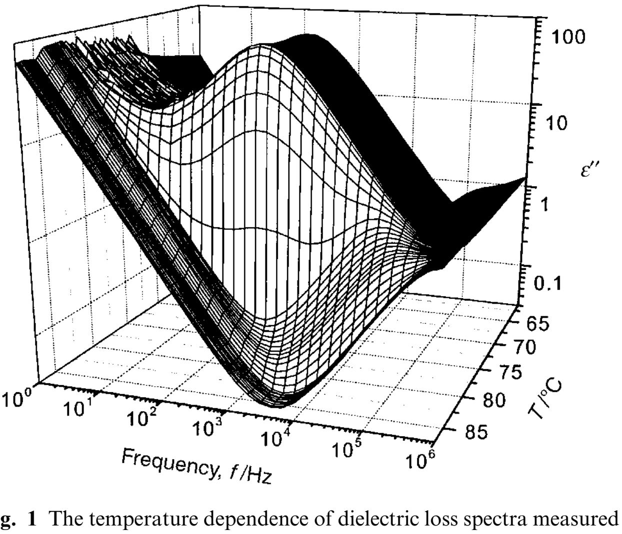


Fig. 1 The temperature dependence of dielectric loss spectra measured on an 8 μm cell during cooling, the temperature step being 0.2 °C.

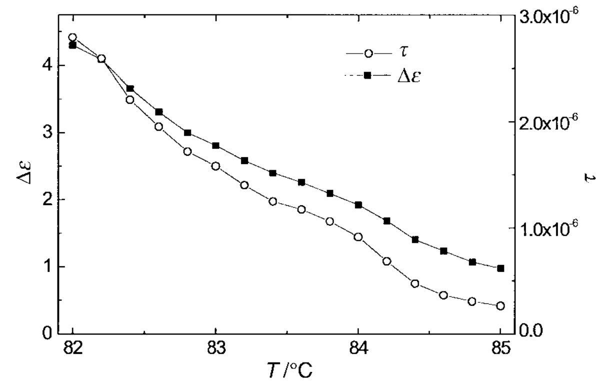


Fig. 2 Temperature dependence of the dielectric amplitude ($\Delta\varepsilon$) and relaxation frequency (τ) of the relaxation process in SmC$_R$*.

Fig. 2 shows the temperature dependencies of the dielectric parameters of a high-frequency relaxation process in the SmA phase (SmC$_R$*). It is clear that both the dielectric amplitude ($\Delta\varepsilon$) and the relaxation time (τ) cannot be described by the Curie–Weiss law.[10] This also supports our assumption that the phase under discussion is not a conventional SmA phase.

Another feature of this phase is the observation of an unusual dependence of the dielectric spectra on bias voltage. Fig. 3 shows the dependence of the dielectric parameters (a—dielectric amplitude, b—relaxation frequency) on bias voltage, found from the fitting of the dielectric spectra, measured at 83.4 °C. In addition to the main high-frequency process ($f \approx 100$ kHz), two additional relaxation processes gradually appear with an increase in bias voltage. The middle frequency relaxation process is likely to correspond to the ferroelectric Goldstone mode since its relaxation frequency is the same as the relaxation frequency of the Goldstone mode in the SmC* phase. The origin of this relaxation process will be discussed later. The measurements of an apparent tilt angle (switching angle) provided the most interesting results. Fig. 4 shows the dependence of the apparent tilt angle on applied voltage for different temperatures corresponding to this high temperature phase.

On applying the external electric field when the field is lower than a threshold, the electrooptic response and the sample texture are found to be similar to those exhibited by the electroclinic effect in SmA. In other words, the electrically induced apparent tilt (switching) angle increases almost linearly with electric field. However, at some threshold voltage, the apparent tilt angle jumps to a saturated value ($\approx 27°$). The threshold voltage decreases rapidly with temperature, while the saturation angle stays almost the same. It is known that in a smectic liquid crystal with a direct, SmC*–Is, phase transition, the smectic tilt angle is almost independent of temperature. Such a behavior in our sample provides an indication that a saturation value of the apparent tilt (switching) angle corresponds to the thermodynamic molecular tilt angle in the smectic layers.

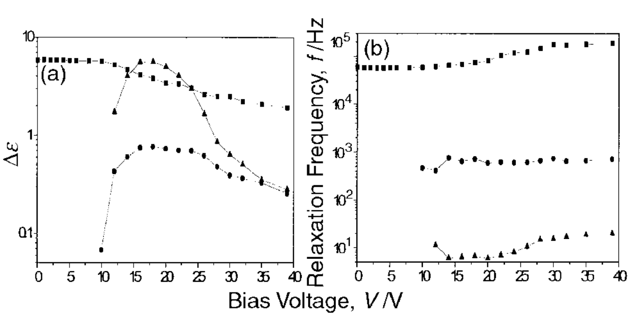


Fig. 3 The dependence of dielectric parameters (a, dielectric amplitude; b, relaxation frequency) on bias voltage.

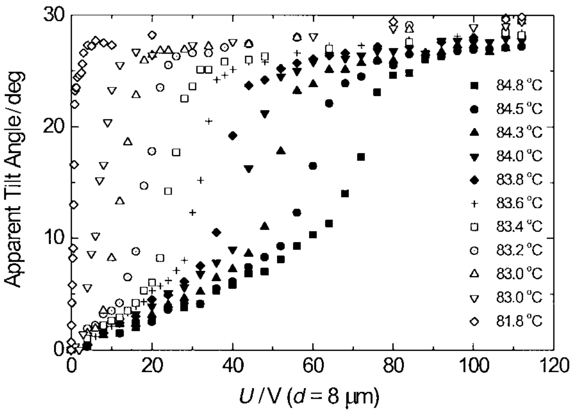


Fig. 4 The dependence of apparent tilt angle on the applied voltage for different temperatures corresponding to the SmC$_R$* phase.

It may also be pointed out that the dependencies presented in Fig. 4 appear to be very similar to those observed by Bahr and Heppke[11] in 1989. The experimental results were explained on the basis of an electric field-induced SmA–SmC transition[11] and modeled[12] by taking the higher power (up to 5) of tilt angle in the Landau free energy expansion. On the contrary, the zero-apparent tilt angle without electric field can be a result of the averaging of tilt directions by the azimuthal angle φ. To find whether our results can be interpreted by the explanation given by Bahr and Heppke,[12] we made the measurement of the effective birefringence *versus* applied voltage.

The dependence of the effective birefringence of a liquid crystal cell on the angle between the molecular director and the plane of the electrodes is given by the following relation:

$$\Delta n(\vartheta)=\frac{n_0 n_e}{\sqrt{n_e^2 \sin^2(\vartheta)+n_0^2 \cos^2(\vartheta)}}-n_0 \qquad (1)$$

For a field-induced SmA–SmC* phase transition[11,12] of the type proposed by Bahr and Heppke, all liquid crystalline molecules would have been in the plane of the electrodes ($\vartheta = 0$) and therefore the effective birefringence of the sample must be independent of the applied electric field. On the contrary, if we were to suppose that all directions in a random SmC* phase are equi-probable, then an average value of the birefringence would be lower than for a completely unwound structure, for which all molecules would lie in the plane of the electrodes. The higher is the smectic tilt angle, the larger would be the difference between the two values. In our case the smectic tilt angle is about 27°. The averaging of Δn for this angle gives a 30% difference between the disordered and the unwound structures.

Fig. 5 shows the dependence of the apparent tilt angle and the effective birefringence for an 8 μm cell measured at a temperature of 84.8 °C. Both curves show similar dependencies on electric field. The effective birefringence in the absence of applied voltage is 0.167 and the saturated value is 0.193. The difference between these two values is 13%, which is in fact lower than the calculated value for a random structure (30%). This discrepancy can be explained by the surface interactions. In our case, for the planar surface conditions the molecular director has a tendency to be parallel to the plane of the surfaces and to induce some planar order in an originally disordered volume structure. In fact, the birefringence measurements on a 16 μm cell give a difference of 18% between values of the effective birefringence in the absence of electric field and the saturated value at high electric field. These results rule out a Bahr–Heppke type of electric field-induced phase transition[11] and support our assumption that the phase under discussion is random SmC$_R$*.

It may also be mentioned that a disordered antiferroelectric phase has historically been associated with so-called V-shaped

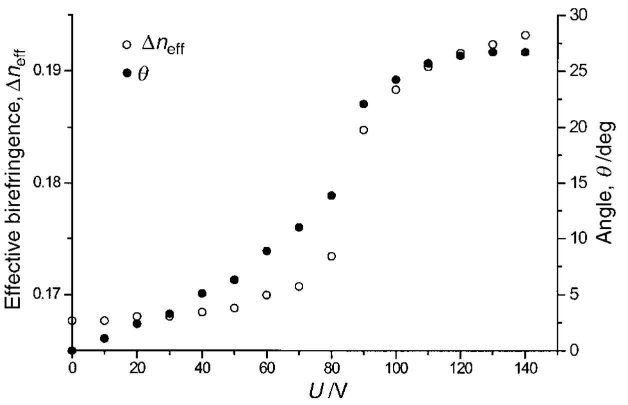


Fig. 5 The dependence of the apparent tilt angle and the effective birefringence for an 8 μm cell measured at 84.8 °C.

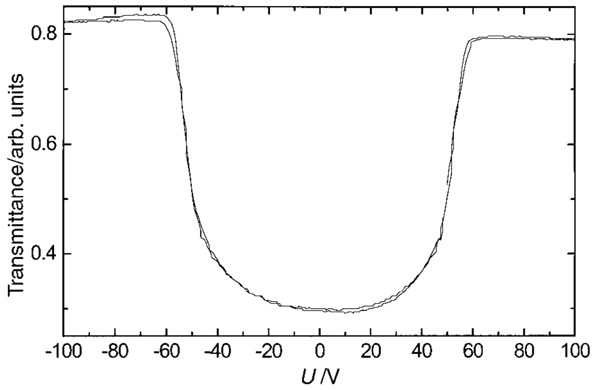


Fig. 6 U-Shaped electrooptic response of an 8 μm cell at $T = 84.4$ °C, $f = 50$ Hz.

switching,[6,7] which may not be the underlying cause of V-shaped switching as has recently been pointed out by Rudquist *et al.*[13] and Seomun *et al.*[14] Fukuda *et al.*[6,7] did not investigate the material in detail in the range of temperatures investigated by us. Nevertheless in $\mathrm{SmC_R}$*, since the induced switching angle is linearly dependent on the applied electric field (Fig. 3), the transmittance therefore follows the quadratic dependence on the switching angle. In this case, the shape of electrooptic curves should be U-shaped as is observed in Fig. 6 and not V-shaped. The observation of U-shaped switching validates the assumption of the $\mathrm{SmC_R}$* phase. An important feature of U-shaped switching is that the electrooptic response is found to be hysteresis free up to a frequency of 100 Hz. In addition, the initial state (in the absence of electric field) possesses a very large optical extinction. These two properties are desirable features for display applications.

In summary, on the basis of the experimental results presented, we identify the liquid crystalline phase under investigation to be a disordered (random) tilted smectic phase, $\mathrm{SmC_R}$*. The molecules in a smectic layer are tilted, but the tilting directions (**C**-director) from layer to layer are randomly distributed. A smectic layer does possess the local spontaneous polarization. The azimuthal distribution of the **C** directors of the various layers is schematically illustrated in Fig. 7. In the absence of an electric field, the local spontaneous polarization vectors in different smectic layers are randomly distributed as shown in Fig. 7a. An application of the external electric field causes a deformation in the disordered distribution of the local polarization of smectic layers and induces some order (macroscopic polarization, apparent tilt) as shown in Fig. 7b. The induction of macroscopic polarization causes an appearance of the Goldstone relaxation mode seen in the dielectric spectra (Fig. 2). A further increase in the electric field causes the local spontaneous polarization vectors in all smectic layers to be pointed in the same direction (direction of electric field) as shown in the Fig. 7c.

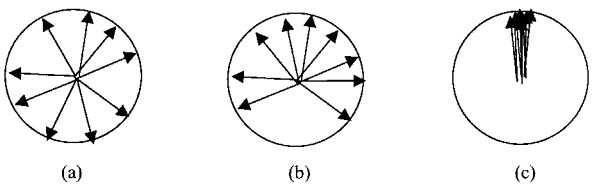

(a) (b) (c)

Fig. 7 Schematic presentation of the deformation of a disordered structure under an applied electric field. The arrows are local spontaneous polarization vectors and the electric field is directed upward.

According to the ANNNI model,[8] the higher the temperature of the LC, the higher is the energy or in this case electric field required to unwind the disordered structure. This is found in qualitative agreement with our experimental results (see Fig. 4). One of the questions is still open: "Should the shape of the voltage dependence of the switching angle be of Langevin-type or be similar to those observed in Fig. 4, 5?". A further theoretical and experimental study would clarify this question.

Acknowledgements

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