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Behavior of frustrated phase in ferroelectric and antiferroelectric liquid crystalline mixtures

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Binary mixtures of two successive homologues from a series of 4-(4′-alkoxy-biphenyl-4-yloxymethyl)-benzoic acid 2-octanol esters exhibit a polar phase that differs from both ferroelectric (FE) and antiferroelectric (AF) phases, which exist in the pure compounds. When the concentration of the FE component is increased, this phase gradually changes its polar character from AF-like to FE-like, which is confirmed by the study of dielectric properties. Sample boundaries as well as the dc electric field introduce the FE phase, which remains stable after the field is switched off. Dielectric study confirms that this phase is composed of FE and AF clusters. The clusters arise due to frustration of FE and AF molecular order, which occurs as a result of the lowering of interlayer interactions.

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I. INTRODUCTION

In mixtures composed of liquid-crystalline materials with both ferroelectric (FE) and antiferroelectric (AF) phases, frustrated (nonconventional AF-like) phases may appear. It has been concluded that in these phases, a frustration between AF and FE dipolar order takes place as a result of lowered interlayer interactions [1–4]. The properties of these phases depend on the mixture composition and are easily influenced by electric bias field and surface interactions. In thin sample cells, these phases exhibit a thresholdless (V-shaped) switching [1–7].

Two types of structural models have been suggested for such a frustrated phase: In Refs. [1,5–7] a *random model* is considered to explain the behavior of the frustrated phase in three- or two-component mixtures of fluorinated compounds. This model supposes that the director tilting is uniform in a smectic layer, but its azimuthal angle varies randomly from layer to layer. Under an applied electric-field Langevin-type director-reorientation is considered, which is compatible with the thresholdless switching. However, this model is still considered, and recent experimental data suggest that the V-shaped switching might be related to the smectic FE order [8].

In Refs. [2,4], a *cluster model* is proposed for the AF-like, frustrated phase observed in binary mixtures of compounds of the same homologue series exhibiting exclusively the FE phase, or both the FE and AF phases. In this model, clusters of FE and AF ordering of a diameter lower than the wavelength of visible light are considered to compose the phase. It is supposed that the concentration of FE and AF regions depends on the mixture composition. It may explain the observed gradual evolution of polar properties of the frustrated phase from AF- to Fe-like under a concentration increase of the homologue with the FE phase only. The concentration of clusters may also be influenced by the surface interactions or the electric-field treatment. Sufficiently strong surface interactions might change the properties of the phase from smectic-C_A^*, Sm-C_A^* order to smectic-C^*, Sm-C^* order. This might explain why the V-shaped switching is sometimes observed in thin cells of AF-bulk materials. In this contribution, we will study the frustrated phase in more detail with the aim of establishing the cluster nature of this phase. We will use the same system as we did in [2,4]. This system is promising for the study of the frustration phenomenon, because the molecular structures of the nearest homologues are very similar but only one of them exhibits the AF phase.

II. EXPERIMENTAL RESULTS

The mixtures studied are composed of homologues belonging to a series of 4-(4′-alkoxy-biphenyl-4-yloxymethyl)-benzoic acid 2-octanol esters [9] exhibiting a strong discrimination of polar properties when the length of the nonchiral terminal chain is changed. For compounds with 13 carbon atoms in alkoxyl chain (C13) and longer homologues, only FE phases (Sm-C^* and hexatic smectic-I^*, Sm-I^*) have been detected. For compounds C12 and shorter, AF properties dominate and the FE Sm-C^* phase, existing just above the AF Sm-C_A^* phase, is very narrow (~1 K). The phase diagram of the mixture of C12 and C13 compounds is shown in Fig. 1. The phase-transition temperatures have

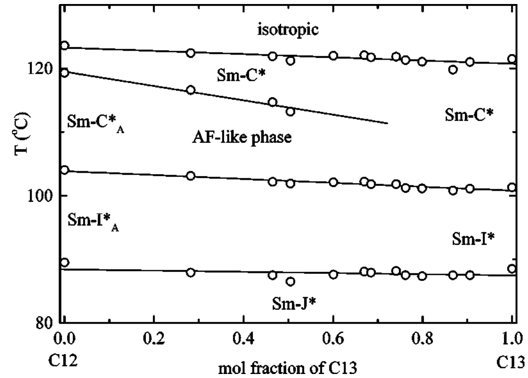

FIG. 1. Phase diagram of a mixture of C12 and C13 homologues determined from DSC and texture studies.

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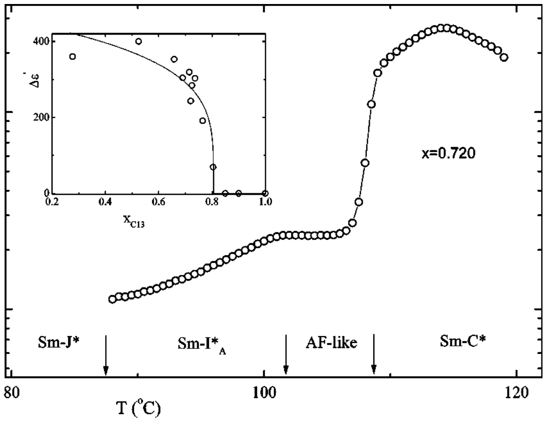

FIG. 2. Temperature dependence of permittivity measured on heating at a frequency of 120 Hz for a mixture with $x = 0.72$ mole fractions of C13. The jump in the permittivity value reveals the transition between the Sm-C^* and AF-like phases. The inset shows concentration dependence of the permittivity jump at the Sm-C^*–AF-like phase transition. All data correspond to the sample thickness 23 μm.

been determined from texture observations under a polarizing microscope and confirmed by differential scanning calorimetry (DSC) study. The phase transition from the Sm-C^* to the AF-like (frustrated) phase becomes still less visible (the DSC peak is gradually decreasing) when increasing the concentration of C13. For concentrations of C13 higher than about 0.5 mole fraction, this phase transition could be observed in neither microscope observation nor DSC measurement. The lowest transition enthalpy detected was 0.02 J/g (12.1 J/mole).

The cells for measurements under an electric field consisted of glass plates coated with indium tin oxide (ITO), transparent electrodes, and parallel rubbed polyimid layer. Dielectric measurements were carried out with cells of various thicknesses filled by a capillary action in the isotropic phase. A good sample showing planar alignment was obtained by slow cooling of the sample from the isotropic phase. Frequency dispersion of the complex permittivity $\varepsilon^*(\omega) = \varepsilon' - i\varepsilon''$ was measured in the range 20 Hz–1 MHz using a Solartron 1260 impedance analyzer. The strength of the dielectric relaxation mode $\Delta\varepsilon$ and its relaxation frequency f_r were obtained from the fitting of the complex permittivity to the Cole-Cole equation

$$\varepsilon^* - \varepsilon_\infty = \frac{\Delta\varepsilon}{1 + (if/f_r)^{(1-\alpha)}} - i\frac{\sigma}{2\pi\varepsilon_0 f}.$$

In fitting, the conductivity-contribution σ was subtracted.

In all mixtures studied, the value of low-frequency permittivity in the FE Sm-C^* phase is the same when measured on samples of the same thickness. The temperature dependence of dielectric permittivity has been measured at heating runs, because on cooling runs supercooling takes place at the FE-AF-like phase transition. At this phase transition, a significant jump of permittivity is observed at the AF-like–FE phase transition (see Fig. 2). This jump is biggest for pure C12, in which the low-temperature phase is a classical AF Sm-C_A^* phase. When increasing the concentration of C13, the permittivity in the low-temperature AF-like phase is increasing and the jump of permittivity detected at the phase transition becomes lower (see inset in Fig. 2). Note that in dielectric properties the phase transition is visible up to the concentration $x = 0.8$ mole fraction of C13, while in DSC no transition peak is visible above $x = 0.5$ (as for the 23-μm-thick sample).

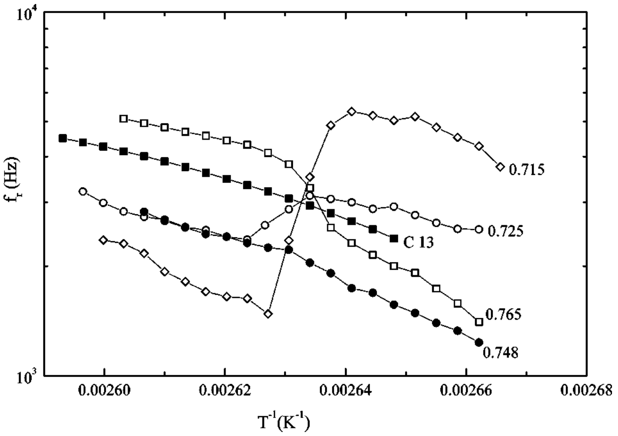

FIG. 3. Characteristic frequency of the dielectric relaxation versus the reciprocal temperature for mixtures of indicated compositions. The FE phase is on the left and the AF-like phase is on the right side. The kinks correspond to the phase transitions. The sample thickness is 23 μm.

The evolution of the character of the AF-like phase and the phase transition with the sample composition is also seen in Fig. 3, which shows the relaxation frequency determined from the Cole-Cole formula depending on the reciprocal temperature for various mixtures (Arrhenius graphs). The kinks on curves correspond to the phase transitions. Pure C13 exhibits only the FE phase.

The influence of sample surfaces on the properties of the AF-like phase and on the observed phase transition is studied by comparing the results of dielectric spectroscopy study on samples of different thicknesses. In Figs. 4(a) and 4(b), there are dielectric strength $\Delta\varepsilon$ and relaxation frequency f_r, respectively, of the relaxation mode obtained for mixture with $x = 0.72$ mole fraction of C13 with dependence on temperature. In the whole temperature region both $\Delta\varepsilon$ and f_r are sample thickness dependent. The dependence found in the high-temperature Sm-C^* phase is typical for the FE phase [10,11], namely, $\Delta\varepsilon$ is increasing and f_r is decreasing with increasing sample thickness. An anomaly in the temperature dependence of both dielectric characteristics in the temperature range 115–117 °C can be attributed to the phase transition between the FE and AF-like phases (Fig. 4); the higher the sample thickness, the stronger the anomaly. For thin enough samples, the anomaly is lost, showing that the phase transition disappeared. A critical thickness for the disappearance of phase transition depends on the mixture composition, e.g., for 0.72 or 0.83 mole fractions of C13 being 5 μm or 75 μm, respectively.

As has been reported in Ref. [2], an applied electric field significantly influences the dielectric properties of the AF-like phase. When the mixtures are cooled through the phase transition under a sufficiently high dc field, no jump in permittivity is observed in the measurement done at subsequent heating runs, and the low-temperature phase keeps the high value of permittivity, the same as in the FE phase [2]. This

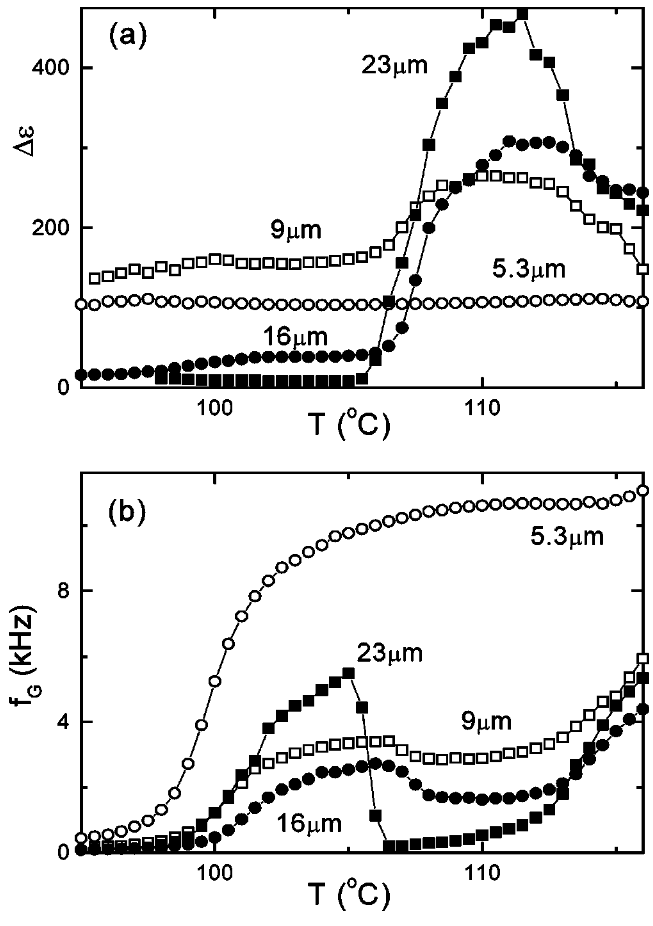

FIG. 4. Temperature dependence of (a) dielectric strength and (b) relaxation frequency of a mixture with $x = 0.72$ mole fractions of C13 for samples of indicated thickness.

state becomes stable until the sample is annealed in the isotropic phase. We have also quantitatively studied the effect of the ac electric field on the AF-like phase by increasing the time of the electric-field treatment. The field has been applied for a definite time in the AF-like phase at a definite temperature, and after the field has been switched off the dielectric dispersion has been measured. After each measurement the sample was heated to the isotropic phase. The results are shown in Fig. 5, where the characteristic frequency and dielectric strength of the relaxation process are shown versus the time of the field treatment. After each point the sample was heated to the isotropic phase.

III. DISCUSSION AND CONCLUSIONS

The dielectric properties of the low-temperature phase in studied mixtures suggest that this phase cannot be a classical AF phase. When the concentration of the FE component C13 is increased, this phase gradually changes its polar character from AF-like to FE-like. This is manifested in the gradual increase of permittivity in that phase (measured on a 25-μm-thick cell) up to the concentration $x = 0.8$ mole fraction of C13 (see Fig. 2). Above this concentration, the high-temperature FE phase and low-temperature AF-like phases are not distinguishable in dielectric properties. The critical concentration, at which the phase transition is lost, depends strongly on the cell thickness; the thinner the sample, the lower the critical concentration. The evolution of the AF-like phase to the FE one when increasing the concentration of C13 is also demonstrated in the behavior of relaxation frequencies (Fig. 3).

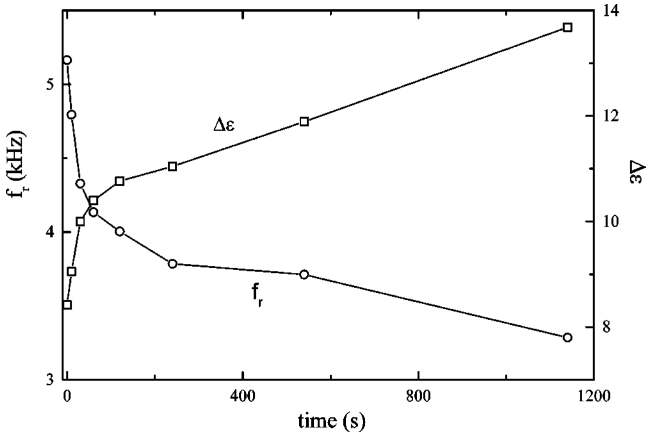

FIG. 5. Relaxation frequency and dielectric strength for a mixture with $x = 0.732$ mole fractions of C13 at the temperature 104 °C versus a time of ac electric-field ($0.087\, V_{\mathrm{rms}}/\mu\mathrm{m}$) treatment. Each point was measured after the sample was heated to the isotropic phase. The sample thickness is 23 μm.

FE properties of the AF-like phase are enhanced when decreasing the sample thickness, which is manifested in an increase of $\Delta\varepsilon$ [see Fig. 4(a)]. This fact indicates that the sample boundaries generally prefer the FE molecular order. Homogeneous polar surface-anchoring seems to be a reason for this effect. Let us point out that in the high-temperature FE phase the thickness dependence of $\Delta\varepsilon$ is just opposite, $\Delta\varepsilon$ increases with increasing sample thickness [see Fig. 4(a)]. The thickness dependence study shows that the origin of the dielectric relaxation in the FE- and AF-like phases might be different, as explained below.

It is known that a continuous evolution from one phase to the other one can observe in a system in which both phases have the same symmetry, and a first-order line separating both phases in the temperature-concentration phase diagram terminates at a critical end point. This cannot be the case with the FE-AF phase transition, as both phases have different symmetry. The other possibility of a pseudocontinuous evolution involves the occurrence of intermediate ferroelectric phases, but no traces of these phases were detected in detailed studies of this system in the vicinity of the FE-AF phase transition [2].

The described properties of the AF-like phase are compatible with the *cluster model*, which we have considered in Refs. [2,4]. A similar model was also applied for a binary solid solution of ferroelectrics and antiferroelectrics [12]. We suppose that in the AF-like phase clusters of FE and AF molecular order are formed, the phase separation being on a scale shorter than the wavelength of the visible light. The relative concentration of the AF and FE regions is basically controlled by mixture composition. Besides, as mentioned above, the FE phase is preferred near the sample surfaces due to FE anchoring. Let us point out that, in solid mixtures, the phase exhibiting a dipolar disorder in the form of the coexistence of AF and FE clusters has been called a dipolar glass [12].

The dielectric relaxation detected in the FE Sm-C^* phase can be attributed to the Goldstone mode. The thickness dependence of its relaxation frequency and dielectric strength (see Fig. 4) is typical for the Goldstone mode, as also found in other materials [10]. The mode detected by the dielectric spectroscopy in the AF-like phase in samples thick enough is quite different (see Fig. 4). There are two possible mechanisms that can significantly contribute to the permittivity in this phase. One is a reorientation of director (changing the azimuthal angle) inside the FE clusters, and the other is a vibration of FE cluster boundaries (a phenomenon similar to domain-wall vibration in solid ferroelectrics). As the experiment shows only one relaxation in the AF-like phase, both modes seem to be merged. We are not able to assess which of these processes is dominating, but one can expect that for both these modes the relaxation frequency will decrease and the dielectric strength increase with increased FE cluster dimension. The results presented in Fig. 5 are in accordance with the above discussion when taking into account a reasonable presumption that the FE clusters grow gradually under an applied electric field. This experiment thus confirms the cluster nature of the AF-like phase.

The formation of clusters in the AF-like phase can be understood as a consequence of *frustration* between AF and FE molecular arrangements in mixed materials [2–4]. From phenomenological theory [13] it follows that the onset of FE and/or AF phases is driven by the interactions between the neighboring layers, described by a free-energy term $A_1(\vec{\xi}_j \cdot \vec{\xi}_{j+1})$, where $\vec{\xi}_j$ and $\vec{\xi}_{j+1}$ are directors in the neighboring layers. For $A_1 > 0$ this term prefers the antiparallel (AF) order, for $A_1 < 0$ the parallel (FE) order [13]. Keeping in mind that both homologues studied are nearly identical, this energy term for both homologues cannot strongly differ in the same temperature region. This can be satisfied only when A_1 is not far from zero. Consequently, in their mixtures $A_1 \approx 0$, which means that azimuthal tilt angle correlations between the neighboring smectic layers are very weak. The lowering of these correlations is probably the origin of frustration between FE and AF phases in the studied mixtures.

For the system studied in this contribution, the random model of director orientation in the next layers can be excluded. The reason is the memory effect observed in the AF-like phase in samples treated by the field, which has been found here as well as in Ref. [2]. If the random model were true, the molecules should return to the random orientation just after the field was switched off following the Langevin-type reorientation [1,3,5–7]. On the other hand, to build up the FE-AF clusters when the field is switched off, the energy barrier to form the cluster boundaries must be overcome. The high barrier is an origin of the observed memory.

The frustrated behavior has also been found for a series with a modified chiral tail, which exhibits the odd-even effect in polar properties upon the tail elongation [14]. The frustrated phase takes place in binary mixtures of consecutive homologues showing only FE or both FE and AF phases.

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