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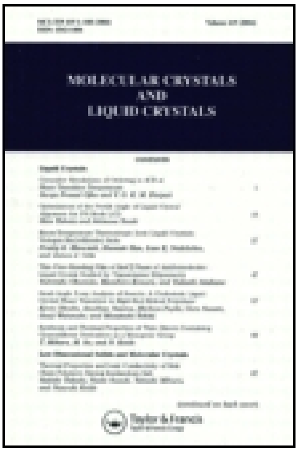

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Ferrielectric Chiral Smectic Liquid Crystalline Phase

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Ferrielectric Chiral Smectic Liquid Crystalline Phase

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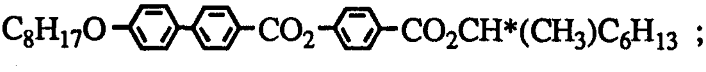
We summarize the experimental results observed in the ferrielectric smectic liquid crystalline phase of MHPOBC by such as DSC, dielectric, X-ray, conoscope, rotatory power and electro-optic measurements. By using the newly obtained information for the pitch in this phase, we propose a novel structure of the ferrielectric phase; the repeating unit consists of three layers, so that the molecules have ferroelectric and antiferroelectric interactions with the ratio of 1:2.

Keywords: ferrielectricity, antiferroelectricity, ferroelectricity, chiral smectics

1. INTRODUCTION

Since the antiferroelectric liquid crystalline phase was discovered,[1] much attention has been payed from both the basic and the application points of view. Two intermediate phases have also been found in MHPOBC,



SmC_α^* between the paraelectric SmA and the ferroelectric SmC* phases and SmC_γ^* between the SmC* and the antiferroelectric SmC_A* phases.[2,3] The SmC_α^* phase seems to be a helical biaxial SmA by means of circular dichloroism measurements.[4] For the SmC_γ^* phase, some ferrielectric structures have been proposed. The purpose of this paper is to show the final model of the ferrielectric structure. After summarizing the experimental results so far obtained, we will present a pitch measurement and propose a reliable model structure, in which the molecules have ferroelectric and antiferroelectric interactions with the ratio of 1:2.

2. SUMMARY OF THE PREVIOUS EXPERIMENTAL RESULTS

2.1 DSC

Four small but distinct DSC peaks were observed between five phases[2,3,5]; SmA, SmC_α^*, SmC*, SmC_γ^*, and SmC_A^*. Therefore, all these phases are thermally stable. The intermediate phases, SmC^*_α and SmC^*_γ, disappear in the substances with low optical purity such as 90% ee. It is not easy to determine the order of the transition by DSC. At least, the transitions SmC^*–SmC^*_γ and SmC^*_γ–SmC^*_A seem to be the first order from their structural points of view.

2.2 Dielectric Constant

The temperature dependence of the dielectric constant also certifies the existence of the five phases.[6–8] The dielectric constant is very small in SmC^*_A because there is no spontaneous polarization, while it is very large in SmC^* because of the Goldstone mode. The SmC^*_γ phase has an intermediate dielectric constant, suggesting the existence of an intermediate spontaneous polarization in this phase.

2.3 Layer Structure

According to the X-ray measurements,[9] the layer spacing shows more or less smooth temperature dependence through the transition points. The layer structure in SmC^*, SmC^*_γ and SmC^*_A are chevron type. The chevron angle (layer tilt angle) also shows smooth temperature dependence although small discontinuities were observed.[9]

2.4 Conoscope

The conoscopic figure in SmC^*_γ changes very characteristically under an electric field.[10] In the absence of the field, a uniaxial figure is observed. Under a high field, the biaxial figure same as the one in SmC^* is observed; the axis of smallest refractive index is perpendicular to the field. Under medium field strength, the center of the conoscopic figure shifts toward the direction perpendicular to the field, and the optic plane of the biaxial figure is parallel to the field. This behavior of the conoscopic figure in the metastable state gives a hint to discuss the unwound SmC^*_γ structure; the structure has a spontaneous polarization and the axis of the smallest refractive index is parallel to the field.

2.5 Electro-optic Measurements

By applying a triangular voltage wave, four transmittance states can be observed in SmC^*_γ under crossed polarizers.[11] The two of them observed under a high field are the ferroelectric states. The other two intermediate states are unwound SmC^*_γ states. Since the transmittance changes are associated with switching current peaks, the orientation change of the spontaneous polarization also takes place in the field-induced transitions.

2.6 Rotatory Power and Circular Dichroism

The absolute signal intensities of the rotatory power[2] and the circular dichroism[4] in SmC^*_γ are larger than those in SmC^* and SmC^*_A, suggesting the larger helical pitch in SmC^*_γ. The signs of these signals change at the transition point between SmC^* and SmC^*_γ, pointing out the helix handedness change at the transition point.

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3. PREVIOUSLY PROPOSED MODELS

According to the experimental results mentioned above, it is safely concluded that the SmC_γ^* phase is the one with an intermediate spontaneous polarization and an intermediate apparent tilt angle compared with those in SmC*. Therefore, the SmC_γ^* phase is a helical ferrielectric phase. So far, four model structures have been proposed as shown in Figure 1. The models (a) and (b) are essentially the same; the ferrielectric phase has a structure composed of ferroelectric and antiferroelectric regions. In (a), the antiferroelectric region grows and makes their boundaries of ferroelectric nature. In (b), the antiferroelectric structures are excited in the ferroelectric structure.[11] The model (c) is similar to the antiferroelectric structure except for the existence of two tilt angles; θ_1 and θ_2 appear alternately so that a finite spontaneous polarization and an apparent tilt angle can exist.[12] A crucial experiment for this model will be the observation of the X-ray diffraction peak due to the double layers. This experiment has not been successful yet. The model (d) is a structure with incomplete cancellation of the dipoles.[10,12] In other words, the tilt directions in the successive layers are not exactly the opposite. This model structure also gives rise to a finite spontaneous polarization and an apparent tilt angle. According to the conoscope measurements, however, this model is ruled out.[10]

4. PITCH MEASUREMENT AND FINAL MODEL STRUCTURE

Figure 2 shows temperature dependence of the wavelength of the selective reflection band. The wavelengths in the SmC* and the SmC_A^* phases were measured directly by the transmittance measurements, and those in the SmC_γ^* phase were determined by comparing the circular dichroism signal intensities in SmC_A^* and SmC_γ^*.[4] The sign of the wavelength distinguishes the handedness of the helix. As clearly seen in Figure 2, the handedness of the helix changes at the SmC*–SmC_γ^* phase transition point as already mentioned in 2.6. The model structure of SmC_γ^* composed

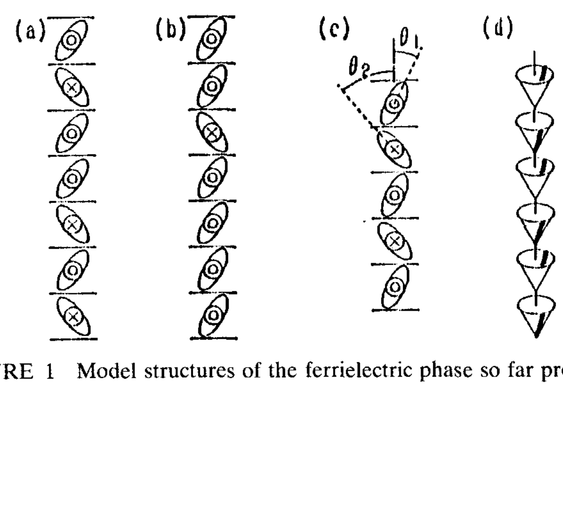

FIGURE 1 Model structures of the ferrielectric phase so far proposed.

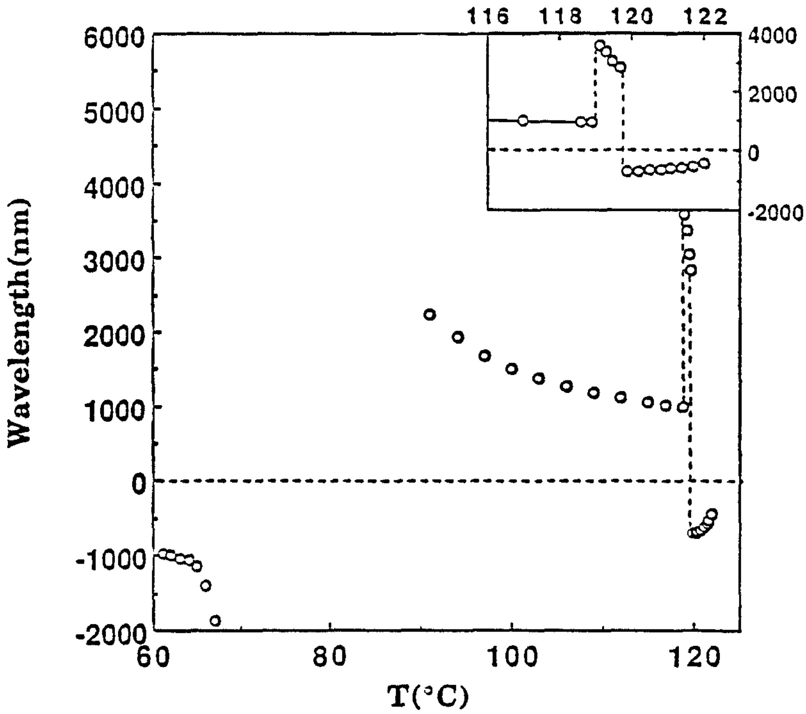

FIGURE 2 The temperature dependence of the wavelength of the selective reflection band. The sign distinguishes the handedness of the helix. In (S)-MHPOBC, the handedness is right in SmC* and left in SmC_γ^* and SmC_A^*.

of the ferroelectric and the antiferroelectric regions requires the conservation of the twisting power,

$$\frac{1}{\lambda_0(SmC_\gamma^*)} = \frac{F}{\lambda_0(SmC^*)} + \frac{1-F}{\lambda_0(SmC_A^*)}, \tag{1}$$

where λ_0 stands for the wavelength of the selective reflection band in each phase, and F is the fraction of the ferroelectric region. Using λ_0's in each phase, we can determine F to be 0.3. Therefore, the ratio of the ferroelectric and the antiferroelectric regions is concluded to be 3:7.

Since the ferrielectric SmC_γ^* phase is a thermally stable phase, the structure must have a periodic regular structure with a rather short interaction length. As for a conclusive local model structure, we can suggest one as shown in Figure 3. Twisting the structure around the layer normal easily gives the helical structure to be formed in the unperturbed state. The repeating unit of the structure consists of three layers, in two of which the molecules tilt to the same direction and the rest to the opposite. Thus, any successive three layers, as shown in Figure 3, can be regarded as a unit cell. It was confirmed that the periodic structure corresponding to the single layer was observable by an X-ray diffraction. There will be a Bragg peak corresponding to the three layers (a unit cell), since one of the layer spacings

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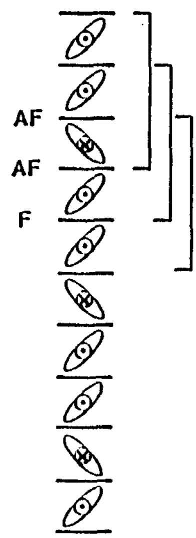

FIGURE 3 The conclusive model structure of the ferrielectric phase. The repeating unit is three layers.

is not necessarily the same as that of the others. However, we have not confirmed the periodicity of the unit cell because of the small angle of the X-ray diffraction.

Let us consider the ferroelectric and the antiferroelectric interactions of the model structure. As shown in Figure 3 by F (ferroelectric) and AF (antiferroelectric), the repeating unit has one ferroelectric and two antiferroelectric boundaries. Thus, the ratio of the ferroelectric and the antiferroelectric interactions is 1:2, which is very close to 3:7 obtained by the pitch measurement. It is also clear that the model structure has a finite average tilt angle and consequently a finite spontaneous polarization. Moreover, it is easily understood that the model structure depicted in Figure 3 accounts for every experimental result. In conclusion, we can obtain a very realistic model structure of the ferrielectric SmC_{γ}^{*} phase. The quantitative comparison between the model and experimental results will be reported elsewhere.

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