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OBSERVATION AND INVESTIGATION OF THE FERRIELECTRIC
SUBPHASE WITH \( q_T > \frac{1}{2} \)

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Abstract. The high-temperature ferrielectric phase with \( q_T > \frac{1}{2} \) has been found to exist in an antiferroelectric liquid crystal. This phase has been identified using dielectric spectroscopy and conoscopy.

INTRODUCTION

The appearance of different subphases in the sequence AFLC - FiLC - FLC can be understood to be a result of the competition between the antiferro- and ferroelectric interactions in adjacent smectic layers which stabilize the SmCA and the SmC* phases. This competition produces various ferrielectric subphases with a different arrangement of antiferroelectric (A) and ferroelectric (F) ordering between adjacent smectic layers. These phases can be characterised by the parameter \( q_T = \frac{m}{n} \) denoting the fraction of ferroelectric ordering which appears in the antiferroelectric structure where \( n \) indicates the number of smectic layers and \( m \) is the number of ferroelectric orders in the pitch of the periodic structure. The existence of several subphases with \( 0 < q_T \leq \frac{1}{2} \) had earlier been reported but the possibility of the existence of the phase with \( q_T \geq \frac{1}{2} \) is still under discussion. The sample under investigation reveals some unusual properties which can be explained by the existence of a ferrielectric phase with \( q_T > \frac{1}{2} \).

EXPERIMENTAL

We provide investigations of a AFLC sample under bias voltage for a cells of thicknesses 8-100 \( \mu \)m. The AFLC sample used in experiments was AS-573 (Hull, UK) possessing the following structure and phase transition sequence:

\[
\text{H}_{25}C_{12}O - \begin{array}{c} F \end{array} \text{COO} - \begin{array}{c} F \end{array} \text{COO} - \begin{array}{c} F \end{array} \text{CH}_3_
\]

\[\text{C}_6\text{H}_{13}\]
Sample cells for dielectric measurements consisted of ITO coated glass plates with the low resistance of 30 Ω. For planar alignment the conducting inner surfaces were spin-coated with PVA alignment layer and rubbed parallel. Dielectric measurements were made using Schlumberger 1255 frequency analyzer with Chelsea dielectric interface.

For conoscopic measurements we used homeotropically aligned cells of 160 μm thickness. Aluminium foil stripes were used as electrodes and spacers with approximately 1 mm gap between them. Homeotropic alignment was produced using carboxylatochromium complexes (chromolane) as aligning agent without rubbing.

RESULTS AND DISCUSSION

Dielectric Spectroscopy

We studied dielectric response of AFLC sample in cells with following cell thicknesses: 8, 20, 50 and 100 μm. Fig. 1 presents the dependence of the dielectric loss spectra versus temperature under the absence of direct bias voltage for 8 μm and 50 μm cells. A comparison of these two plots reveals a remarkable dependence of a part of the spectra on the sample thickness. For a cell with larger of the two thicknesses, we find that in the temperature range from 83 to 85°C between SmCy and SmC*, the dielectric spectra look similar to the spectra of an Antiferroelectric phase SmCA and belong to a high temperature antiferroelectric phase with \( q = 1/2 \) (AF). The experimental dielectric spectra are found to be practically independent of the cell thickness for cells thicker than 20 μm. We therefore conclude that in thin cells (with thickness of the order of 8 μm or less) some of the antiferro- and ferroelectric subphases are suppressed by the surface interactions.

The dielectric spectra are fitted to Havriliak-Negami equation for \( n \) relaxation processes:

\[
\epsilon^*(\omega) = \epsilon_\infty + \sum_{j=1}^{n} \frac{\Delta \epsilon_j}{1 + (i \omega \tau_j)^\alpha}
\]

where \( \epsilon^*(\omega) \) is the frequency dependent complex permittivity, \( \epsilon_\infty \) is the high-frequency permittivity, \( j \) is a variable denoting the number of the relaxation processes up to \( n \), \( \tau_j \) is
the relaxation time of j-th relaxation process, \( \alpha \) and \( \beta \) are the fitting parameters and \( \Delta \varepsilon_j \) is the dielectric relaxation strength for the j-th process.

FIGURE 1. Dielectric loss spectra versus temperature for AS-573, (a) \( d=8 \mu m \), (b) \( d=50 \mu m \).

Figure 2 present the temperature dependence of the dielectric parameters of AS-573 which were found from the dielectric spectra.

FIGURE 2 Dependence of the relaxation frequency (open labels) and dielectric strength (closed labels) on temperature for ferrielectric (circles) and ferroelectric (squares) relaxation modes (\( d=50 \mu m \)).
In the SmC* and SmCγ phases there exist only one collective relaxation process: ferroelectric and ferrielectric Goldstone mode respectively. In the temperature range from 85 to 90 °C these two processes however do exist together. This range lies between AF phase (\(q_T = 1/2\)) and SmC* (\(q_T = 1\)) phases and according to the temperature Devils' Staircase one could expect the existence of the ferrielectric phase with \(1/2 < q_T < 1\). The most probable explanation of these facts is to assume the existence of some ferrielectric mesophase with \(q_T = m/n = 3/5\) or \(5/7\).

In the literature so far, no ferrielectric phase with \(1/2 < q_T < 1\) have yet been reported either in individual substances or in binary mixtures. According to Fukuda et al., the Ising model is a good for the describing the temperature induced Devil's staircase for the structures where the ferroelectric ordering (\(Q\) appears as defects in the antiferroelectric structure \(AAAA\). In the phases with \(q_T > 1/2\), \(A\) ordering appears as defects in the \(FFFF\) orderings. For such a structure, what is important for its stable existence is the repulsive forces between the \(A\) orderings,..., it is not clear whether \(A\) orderings repel one another. Therefore this mesophase with \(q_T > 1/2\) could be considerably disturbed. Therefore the coexistence of two Goldstone relaxation processes at the same temperature could be explained by the existence of the mixture of two different subphases (ferrielectric and ferroelectric) which is also supported by conoscopic pictures.

Conoscopic investigation.

Fig.3 presents the conoscopic pictures for three different temperatures and applied voltages for homeotropic orientation. In SmC* phase (\(T = 91^\circ\text{C}\)) with increasing of voltage, the centre of the image is shifting perpendicular to the direction of applied field. Then the structure is getting biaxial with the optical plane perpendicular to the direction of applied field. Such behaviour is typical for ferroelectric SmC* phase. In SmCγ phase (Fig.3, \(T = 82^\circ\text{C}\)) the dependence of conoscopic image with voltage is similar to SmC* phase with only one difference: the optical plane is parallel to the direction of applied field. For the temperature range from 83°C to 85°C and less the 78°C conoscopic pictures are typically antiferroelectric and are not presented here.
The unusual behaviour was found in the temperature range from 85°C to 90°C where there are two different Goldstone relaxation processes: ferro- and ferrielectric. The application of sufficiently small voltage makes the image very blurred although on closer examination one could find the existence of four centres: one pair as in ferroelectric phase and another as in ferrielectric phase. Such an existence is impossible to obtain in the uniform structure. The further increase of applied voltage makes the conoscopic image clearly ferroelectric. It is also shown that at this range of bias voltage there exist only ferroelectric Goldstone mode while the ferrielectric mode is suppressed. Therefore we conclude that in this temperature range there exist two phases SmC* and some ferrielectric phase (FiLC) with $1/2 < q_T < 1$. 

FIGURE 3: Conoscopic pictures for different temperatures and voltage.
CONCLUSION.

As has already been shown the AFLC sample under investigation in some temperature range (85-900°C) reveals several unusual properties which could be explained by the coexistence of two different subphases: SmC* and FiLC - ferrielectric phase with $q_T$ parameter higher than 1/2. This is supported by dielectric and conoscopic results of investigation. This ferrielectric phase is not stable and could be easily affected by temperature and bias voltage changes which is in agreement with the considerations presented in Ref.1. It is still unclear - whether the ferrielectric phase (with $1/2 < q_T < 1$) is unstable or could it have a stable existence in some other AFLC samples?

REFERENCES