OPTIC, ELECTROOPTIC AND DIELECTRIC PROPERTIES OF NOVEL ANTIFERROELECTRIC LIQUID CRYSTAL COMPOUNDS

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The optic, electrooptic and dielectric spectroscopy characterisation of novel four-ring thiophene-based chiral esters comprising suitably 5,5'-disubstituted 2,2'-bithiophene (antiferroelectrics) is reported. The two compounds exhibit interesting hysterises in their phase sequences, and we show that even whole phases (e.g. their relatively wide ferri-phases) may be suppressed by the surface interactions in thin cells.

INTRODUCTION

Due to continual development of the tristate switching phenomenon, there is a strong demand for liquid crystalline compounds which exhibit the SmC_γ^* and SmC_A^* phases[1-3]. The latter participate in tristate switching which is deemed as the switching from the antiferroelectric state to one of

two field-induced ferroelectric states (corresponding to positive and negative electric fields, respectively) via a very sharp electric field threshold.

A structural survey of such compounds reveals that the majority possess a calamitic molecular architecture comprising the 1-methylheptyl moiety as a terminal group. However, due to many of the preconceptions associated with liquid crystallinity and molecular geometry there are very few compounds reported in the literature which both show strong deviation from the classical molecular architecture and SmC*, SmC$_\gamma$* and SmC$_A$* phases [4,5].

In 1998, Matharu *et al.*[6], reported the synthesis and textural investigation of a novel partially non-linear compound (**A4**, R=C$_{12}$H$_{25}$) comprising suitably di-substituted bithiophene as the molecular core. Despite its bent or non-linear molecular architecture, **A4** exhibits the SmC* and SmC$_A$* phase types as well as a moderately wide SmC$_\gamma$* phase.

We now report further extensive studies: electro-optical response, pitch and dielectric spectroscopy on **A4** and the newly synthesised **CG50** (R=C$_{10}$H$_{21}$) in order to confirm initially the textural study reported by Matharu *et al.*[6], and more importantly to gain an insight to the molecular processes involved with such rather unusual structures.

SYNTHESIS

The synthetic pathway for the preparation of **A4** and **CG50** is summarised in figure 1. The synthetic procedure for **CG50** is analogous to the one for A4, which has been reported previously [6].

Bithiophene (**1**) was prepared using the nickel-catalysed cross-coupling methodology reported by Tamao *et al.*[7], whereby, the Grignard reagent of 2-bromothiophene was coupled with 2-bromothiophene to afford (**1**) in high yield (85%). Friedel-Crafts acylation of (**1**) with the appropriate alkanoyl chloride, catalysed by titanium(IV) tetrachloride, gave the intermediate acyl-compounds which were reduced immediately (Huang-Minlon) to the alkyl-compounds (**2a** and **2b**). Lithiation (1.6M BuLi, -78°C) of compounds (**2a** and **2b**) followed by solid carbon dioxide quench, furnished the desired thiophene-based carboxylic acids (**3a** and **3b**). DCC esterification[8] of compounds (**3a** and **3b**) with (*S*)-

1-methylheptyl 4'-hydroxybiphenyl-4-carboxylate (**4**)[9] produced the required chiral bithiophene esters (**A4** and **CG 50**).

(**1**)

(**2a**, n=10; **2b**, n=12)

(**3a**, n=10; **3b**, n=12)

(**CG 50**, n= $C_{10}H_{25}$; **A4**, n=$C_{12}H_{25}$)
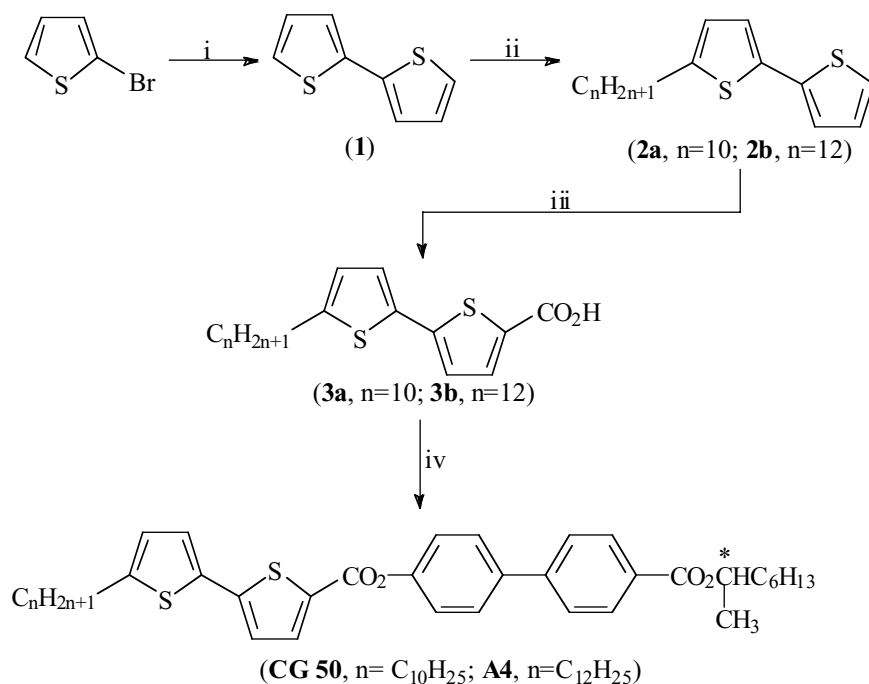
i. $[(C_6H_5)_2PCH_2CH_2CH_2(C_6H_5)]NiCl_2$, ether
ii.   a. $TiCl_4$, $C_nH_{2n}COCl$, CH_2Cl_2; b. $NH_2NH_2.H_2O$, KOH, diethylene glycol
iii.   a. 1.6 M BuLi, -78°C, N_2; b. CO_2, H^+
iv.   (**4**),Dicyclohexylcarbodiimide (DCC), dimethylaminopyridine, CH_2Cl_2

FIGURE 1: The reaction scheme for the two compounds A4 and CG-50.

PHASE SEQUENCE

The phase sequence for the two materials are (as measured by DSC on heating):

CG-50: SmX* • 86.7 • SmI$_A$* • 96.9 • (SmC$_A$* • - • SmC$_\gamma$* • - • SmC*) • 131.0 • SmA* • 144.2 • iso /(°C)

A4:   SmX* • 83.6 • SmI$_A$* • 92.0 • (SmC$_A$* • - • SmC$_\gamma$* • - • SmC*) • 132.9 • SmA* • 138.9 • iso /(°C)

where the transitions written within brackets have been detected by means of optical microscopy and by measurements reported below.

ELECTROOPTIC MEASUREMENTS

We have studied the spontaneous polarisation P_S and molecular tilt θ as a function of temperature, shown for CG-50 in figure 2. Both show a plateau in the temperature range of the SmC_γ^* phase (in this 10 μm cell approx. 110 to 120 °C), the origin of which is not yet clear. The existence of the SmC^*, SmC_γ^* and SmC_A^* phases was evidenced by the electrooptical and current response as well as by the voltage dependence of P_S in these phases. As can be seen from figure 3(a), P_S in the SmC_γ^* phase saturates with the applied field first at the value of approximately 1/3 of the value of P_S at high fields. In the SmC_A^* phase, P_S exhibits a clear threshold behaviour with a threshold of more than 10 V/μm. The switching in the SmI_A^* phase has a more complex character, which is shown by the electrooptic and current response depicted in figure 3(b). More than three switching states can be seen in the electrooptic reponse which relate to changes in the current response. Below the SmI_A^* phase there is another higher order smectic phase which exhibits a linear electrooptic response. We belive that this phase might be an orthogonal phase, but additional studies are necessary to prove it.
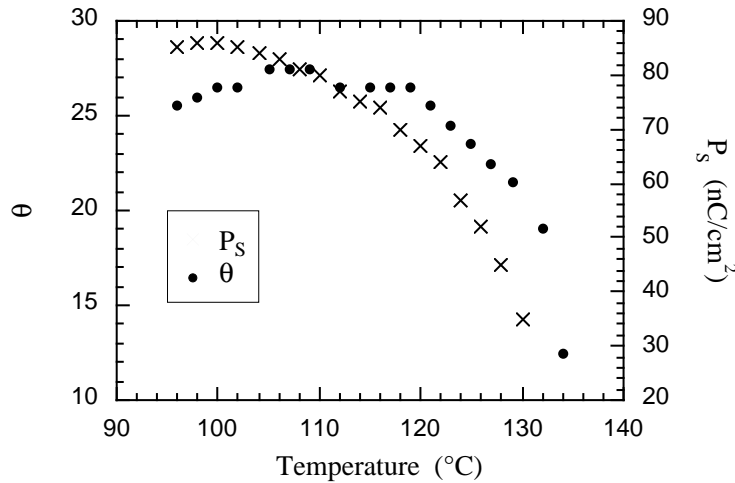

FIGURE 2: Spontaneous polarisation P_S and molecular tilt angle θ as a function of temperature for the material CG-50.
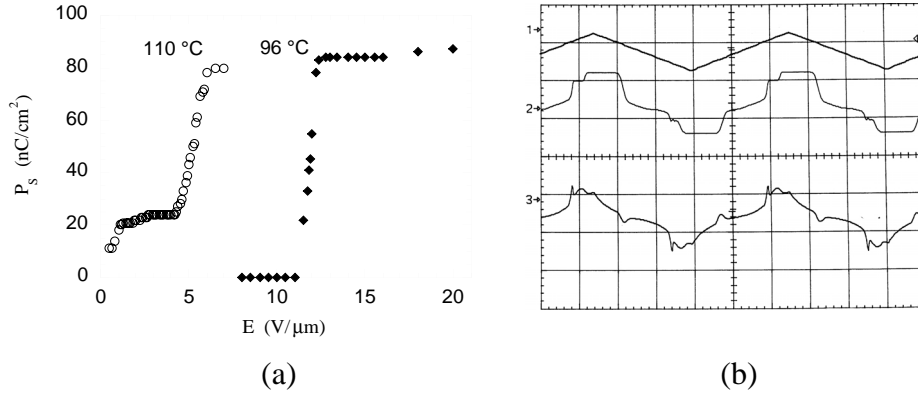
(a)   (b)

FIGURE 3: (a) Spontaneous polarisation P_S as a function of the applied field for the material CG-50 in the SmC_γ^* (110 °C) and SmC_A^* (96 °C) phase. (b) Electrooptic (curve 2) and current (curve 3) respons as a function of the applied field (curve 1) in the SmI_A^* phase of CG-50 (arb. units).

PITCH MEASUREMENTS

In order to measure the pitch, we analysed the selective reflection from free-standing films of the two materials. Free-standing films (or freely suspended films) are highly interesting for investigations of various liquid crystal phases since they provide possibilities to escape from boundary effects, which at least for thin conventional samples may affect the behaviour of the pitch, as well as the phase sequence itself [10,11].

In this study, we also have to ensure that the film is sufficiently thick to give selective reflection, which in practice means that the film thickness has to be a minimum of about ten times the pitch ($d \geq 10p$). (The film preparation is described in detail in references[12,13].) The films are normally formed with the helix standing perpendicular to the film surfaces (*homeotropic helix geometry*) and thus with the smectic layers parallel to the boundaries, a geometry which gives possibility for measurements of selective reflection of light propagating along the helix axis. To measure the transmittance of the film as a function of the wavelength, we inserted the films in a Shimadzu 3101PC spectrophotometer.

Figure 4 shows the length of the pitch as a function of temperature for free-standing films of the materials A4 and CG-50, where each point has

been obtained by analysing a spectrum at the specific temperature. The spectra, which were obtained on increasing the temperature, show more or less distinct dips where the selective reflection takes place. The pitch in the SmC_A^* phase seems to diverge for low temperatures, at the same time as the reflection becomes weaker and weaker. In the SmC* phase, there is a general increase in the pitch with increasing temperatures, but at temperatures close to the SmA* phase, the pitch starts to decrease again.
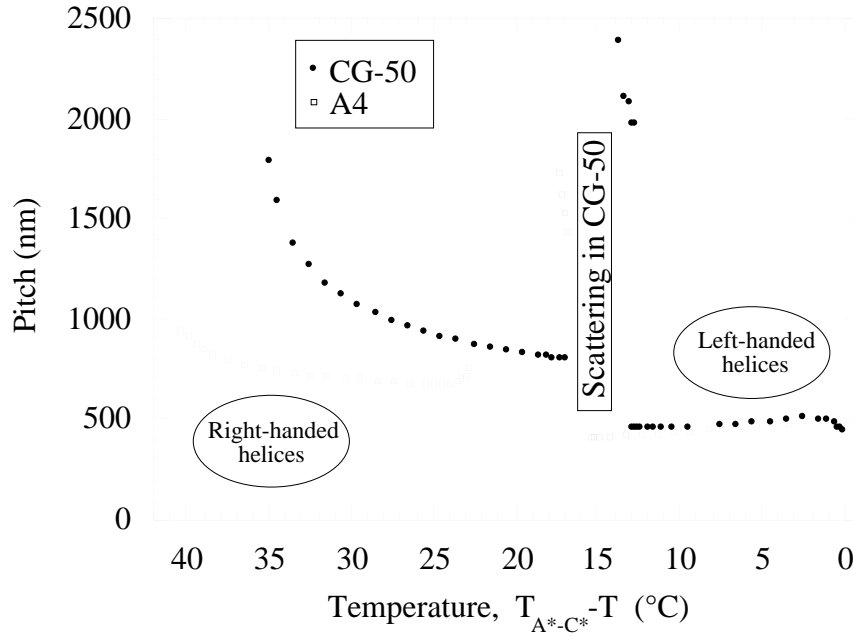

FIGURE 4: Pitch (not compensated for n) as a function of temperature measured in free-standing films of the materials A4 and CG-50. The film thicknesses are approximately 20 μm. There is a temperature interval where also the material A4 scatters light, but due to limited space it has been omitted in this figure.

In-between the SmC_A^* phase and the SmC* phase in figure 4, there is an interesting region which contains at least the SmC_γ^* phase and possibly also other SmC* sub-phases. In going from the SmC_A^* phase across the phase transition, we first observe a strongly scattering state where the light over a broad wavelength range is scattered from the film. For slightly higher temperatures within the range of the SmC_γ^* phase, the scattering shown in figure 4 disappears and a reflection at long

wavelengths becomes visible. As the temperature increases, the pitch corresponding to this reflection decreases from approximately 2500 nm to 2000 nm. There is a small interval where this reflection at long wavelengths is present as well as the reflection coming from the SmC* phase, which can be interpreted as coexistence of the SmC$_\gamma$* phase and the SmC* phase. In a thin film spectrum, the previously described scattering state as well as this long pitch reflection is missing. The plausible reason for the absence of a long pitch reflection is that the films were too thin to give any detectable reflection in the long pitch limit (note that the film thickness only corresponds to a few full turns in this limit) even if, in principle, the helix might also be absent due to the surface forces which affect the pitch more strongly in a thin film.

To find the handedness of the pitch, we analysed the transmittance of circularly (or almost circularly) polarised light through the film. Since the liquid crystal helix only reflects light with the same handedness as the pitch, the handedness can be determined as the one which gives lowest transmittance at the reflection wavelength. The measurements show that the pitch is right-handed in the SmC$_A$* phase, changes sign somewhere in the SmC$_\gamma$* phase(s) and is left-handed in the SmC* phase.

DIELECTRIC SPECTROSCOPY MEASUREMENTS

The dielectric response of the compounds was investigated using an HP4192A dielectric bridge. All results described below were obtained in planar orientation.

Behaviour in thick (50 μm) cells
On cooling, both materials feature normal SmA* and SmC* spectra, while the SmC$_\gamma$* phase is distinguished by a surprisingly weak absorption. On heating, a strong low-frequency absorption, not present in the cooling runs, appears in the vicinity of the SmC$_\gamma$*-SmC* transition (figure 5). This absorption has the characteristics typical of a SmC$_\gamma$* azimuthal mode[14], but in CG50 it seems to appear first *after* the transition to the SmC* phase since the azimuthal mode of the SmC* phase (Goldstone mode) appears at the same temperature. A possible explanation is that there is some degree of phase coexistence between SmC$_\gamma$* and SmC*.

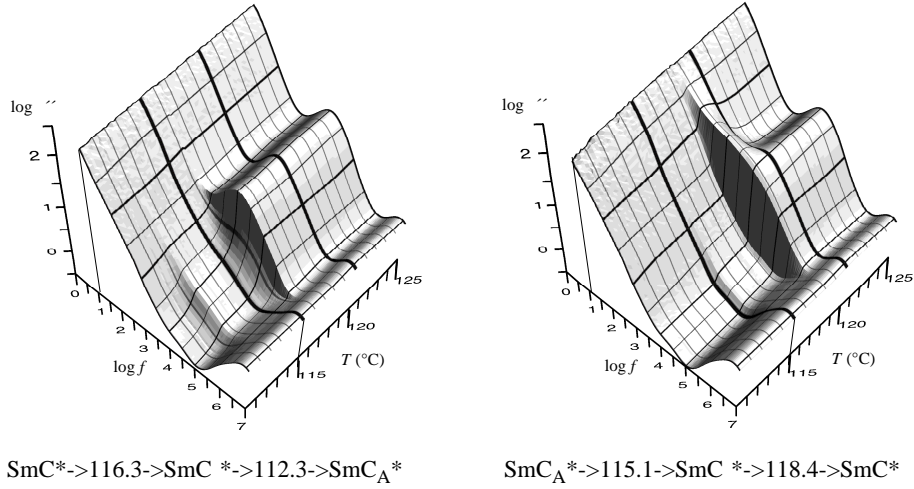SmC*->116.3->SmC *->112.3->SmC$_A$*   SmC$_A$*->115.1->SmC *->118.4->SmC*

FIGURE 5: 3D dielectric absorption spectra for CG50 in the vicinity of the SmC * phase, on cooling (left) and heating (right) in a 50 μm cell. A4 behaves similarly.

By applying a DC-bias of 0.7V/μm over the sample, the SmC * phase spectra are drastically altered. The strong low-frequency absorption mentioned above now appears both on cooling and on heating, and in CG50 it is present throughout the whole SmC * phase. In A4 the absorption is absent in the centre of the SmC * phase, but close to the low-temperature boundary of the phase it reappears (figure 6). This supports the idea that the absorption is due to a helix-related SmC * azimuthal mode. The applied DC field then seems to be enough to unwind the helix in the centre of the A4 SmC * phase, but not in CG50. However, with this model it is difficult to explain the absence of the mode when no DC bias field is applied.

The SmC$_A$* phase spectra are in both compounds without anomalies. In the high temperature end of the SmI$_A$* phase a single absorption is observed (figure 6). However, as f_R quickly decreases with decreasing temperature, the mode is soon covered by the ionic tail and can thus not be resolved some 10°C below the SmC$_A$*-SmI$_A$* transition.

Around 45°C in A4, and 50°C in CG50, a transition from SmI$_A$* to another smectic phase is observed. This is characterised by a weak absorption with an Arrhenius-like temperature dependence of f_R. We attribute this absorption to the reorientation around the molecular long axis, which can be expected to exhibit such low frequencies in a smectic

phase with very high order. On heating, the transition to the SmI$_A$* phase does not occur until at approximately 80˚C. The transition between these two phases thus features a hysteresis in the range of 30˚C in both materials.
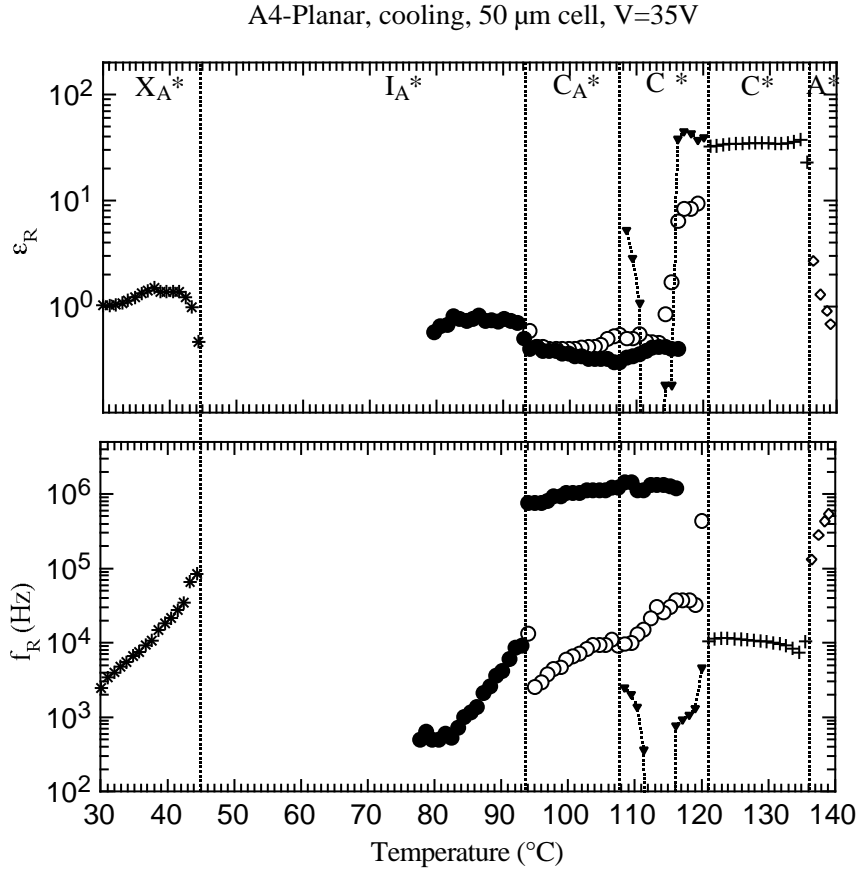
A4-Planar, cooling, 50 μm cell, V=35V

FIGURE 6: A4 in a 50 μm cell on cooling with 0.7V/μm DC-bias. Cole-Cole equations have been fitted to the experimental data in order to extract the relaxation frequencies and dielectric constant contributions.

Results from thin (2 μm) cells

The spectra obtained in 2 μm cells differ markedly from those of the thick cells. The main difference is the absence of a SmC * phase, and the very large degree of SmC* supercooling, see figure 7. On cooling A4, the SmC* azimuthal mode remains with undiminished intensity all the

way down to 109˚C (approximately 12˚C below the SmC*-SmC * transition in the 50 μm cell) and then it gradually decreases through a region of phase coexistence down to the onset of the SmI$_A$* phase. On heating (figure 7, right part), a weak SmC* azimuthal mode is observed immediately after the transition from SmI$_A$*, and this gradually increases in intensity up to the fully developed SmC* phase. CG50 features a similar behaviour. The large broadening of the SmC* temperature range in thin cells is a clear indication of how surface influence promotes the SmC* phase relative to SmC * and SmC$_A$* [15].
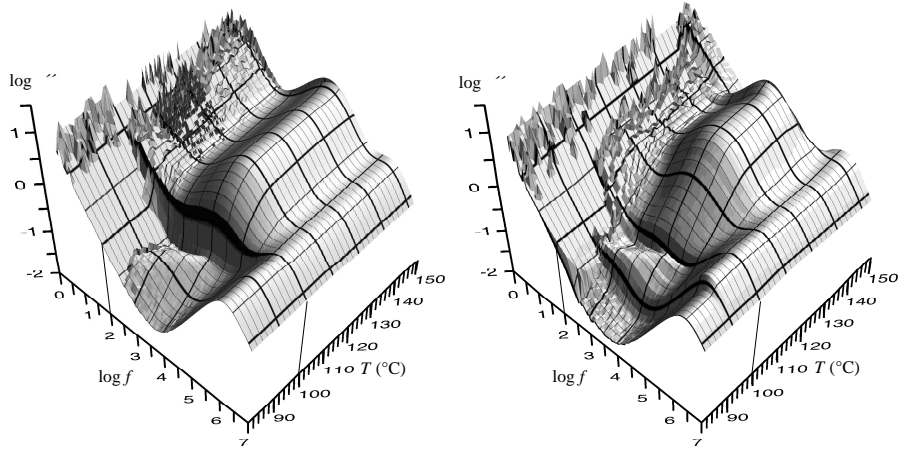

FIGURE 7: 3D dielectric absorption spectra for A4 in a 2 μm cell, on cooling (left) and on heating (right). No clear sign of a SmC * phase can be seen in either spectrum.

CONCLUSIONS

We have synthesised and characterised the two antiferroelectric liquid crystalline materials A4 and CG-50. Despite their non-linear molecular architecture, the materials exhibit wide SmC*, SmC * and SmC$_A$* phases. Pitch measurements and dielectric spectroscopy reveal that there is a strong hysterisis in the phase sequence on cooling and heating and that the phase temperature intervals depend on the sample thickness. In fact, the SmC * phase may be totally suppressed by surface interactions in thin cells. We have also seen that a long pitch absorption, interpreted as coming from the SmC * phase, is partially co-existing with the SmC* phase.

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