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Incommensurate smectic-A phase in the general model of frustrated smectic phases

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An incommensurate smectic-A phase (SA_i) made of two collinear independent density modulations at two incommensurate wave vectors is found to be stable in the phenomenological model of frustrated smectic phases of Prost in mean-field theory. The N-SA_1-SA_d-SA_2-SA_i phase diagram is computed; its representation in appropriate axis (i.e., temperature, incommensurability) is fully compatible with the experimental topology recently reported in a binary mixture of 4-n-heptyloxyphenyl-4′-cyanobenzoyloxybenzoate (DB7OCN) and 4-octyloxy-4′-cyanobiphenyl (8OCB).

INTRODUCTION

The rich smectic polymorphism of strongly polar smectogenic compounds[1] is now fairly well understood in the frame of the phenomenological model of frustration of Prost.[2,3] Uniaxial SA_1, SA_d, SA_2 (Refs. 4 and 5) as well as biaxial $S\tilde{A}$, $S\tilde{C}$ (Ref. 3) phases are described in a unified way by two coupled order parameters [usually, but not necessarily referred to as a mass density wave $\rho(\mathbf{r})$ and a polarization wave $Pz(\mathbf{r})$] having a tendency to condense at two incommensurate wave vectors $\mathbf{q}_1$ and $\mathbf{q}_2$, the ratio q_2/q_1 ranging experimentally from 1 to 2. Although incommensurate smectic-A phases were among the first to be predicted by the model,[2] none of them had been discovered until very recently when Ratna, Shashidar, and Raja[6] reported the first experimental observation of two collinear incommensurate density modulations coexisting in a smectic-A phase in a binary mixture of 4-octyloxy-4′-cyanobiphenyl (8OCB) and 4-n-heptyloxyphenyl-4′-cyanobenzoyloxy-benzoate (DB7OCN).

The aim of this Rapid Communication is to show how the interpretation of this experiment as the first observation of an incommensurate smectic-A phase is compatible with the Prost model of frustrated smectic phases in mean-field theory. Unlike in Ref. 2, fourth-order terms are included in the free energy so that the relative stabilities of the incommensurate smectic A and of other uniaxial phases N, SA_1, SA_d, and SA_2 can be compared.

THE MODEL

As discussed in Ref. 5, uniaxial frustrated smectic phases can be described by two one-dimensionally modulated order parameters:

$$Pz(\mathbf{r}) = \mathrm{Re}[\Psi_1(\mathbf{r})] = \mathrm{Re}[|\Psi_1|\exp(iq_p z)] \ ,$$

$$\rho(\mathbf{r}) = \mathrm{Re}[|\Psi_2|(\mathbf{r})] = \mathrm{Re}[|\Psi_2|\exp(iq_\rho z)] \ .$$

The z axis is chosen parallel to the nematic director $\mathbf{n}$, perpendicular to the smectic layers. $\rho(\mathbf{r})$ is the center-of-mass density of the constituent molecules, while $Pz(\mathbf{r})$ describes long-range head-to-tail correlations of polar molecules along the z axis. In the absence of coupling between ρ and Pz, ρ would develop spatial modulations at wave vector $\mathbf{q}_2 = 2\pi/l\mathbf{n}$, where l is of the order of a molecular length, whereas Pz would develop modulations at wave vector $\mathbf{q}_1 = 2\pi/l'\mathbf{n}$, where $l'(>l)$ is a length associated with the pair of antiparallel molecules. In terms of these fields, the Landau free energy of the Prost model reduces in one dimension to

$$\Delta F[\Psi_1,\Psi_2] = \int dz \left(\frac{r_1}{2}|\Psi_1|^2 + \frac{D_1}{2}|(\Delta + q_1^2)\Psi_1|^2 + \frac{u_1}{2}|\Psi_1|^4 + \frac{r_2}{2}|\Psi_2|^2 + \frac{D_2}{2}|(\Delta + q_2^2)\Psi_2|^2 + \frac{u_2}{4}|\Psi_2|^4 + \frac{u_{12}}{2}|\Psi_1|^2|\Psi_2|^2 - w\,\mathrm{Re}(\Psi_1^2\Psi_2^*) \right) \ , \quad (1)$$

where $r_1 = a_1(T - T1)$ and $r_2 = a_2(T - T2)$ and $T1$ and $T2$ are the noninteracting mean-field transition temperatures of the fields $\Psi_1(\mathbf{r})$ and $\Psi_2(\mathbf{r})$, which are expected to depend upon concentration in a binary mixture. The third-order coupling term $-w\,\mathrm{Re}(\Psi_1^2\Psi_2^*)$ is only relevant if we restrict our attention to slightly overlapping molecules ($1.5 < l'/l < 2$) [a harmonic coupling term $-w'\mathrm{Re}(\Psi_1\Psi_2^*)$ is required in the other limit $1 < l'/l < 1.5$ (Ref. 2)].

In addition to the three phases discussed in Ref. 5, namely, the nematic (N) with $|\Psi_1| = |\Psi_2| = 0$, the monolayer smectic A (SA_1) with $|\Psi_1| = 0$, $|\Psi_2| \neq 0$, and the bilayer smectic A (SA_2) with $|\Psi_1| \neq 0$, $|\Psi_2| \neq 0$, and $q_p = q_0$, $q_\rho = 2q_0$, we now look for the simplest incommensurate structure (SA_i) defined by $|\Psi_1| \neq 0$, $|\Psi_2| \neq 0$, and $q_\rho \neq 2q_p$, i.e., only two modes coexisting at incommensurate wave vectors. It follows immediately from the incommensurability of q_ρ and q_p that the coupling term $-w\,\mathrm{Re}(\Psi_1^2\Psi_2^*)$ oscillates along the z axis, and thus averages to zero in the SA_i phase. The minimization with respect to wave vectors is then straightforward and gives $q_p = q_1$ and $q_\rho = q_2$. After an appropriate rescaling of variables,[5] we are left with a reduced free energy analogous to the one describing the bicritical-tetracritical problem:[7]

$$f(SA_i) = y_1 x_1^2 + (1 + \delta u_1)x_1^4 + y_2 x_2^2 + (1 + \delta u_2)x_2^4 + 2x_1^2 x_1^2 \ , \quad (2)$$

with

$$x_1=\frac{u_{12}}{8w}\left(\frac{D_1}{D_2}\right)^{1/2}|\Psi_1|,\quad y_1=\frac{r_1}{2}\frac{u_{12}}{w^2},\quad (1+\delta u_1)=\frac{16u_1}{u_{12}}\frac{D_2}{D_1},$$

$$x_2=\frac{u_{12}}{2w}|\Psi_2|,\quad y_2=\frac{r_2}{32}\frac{u_{12}}{w^2}\frac{D_1}{D_2},\quad (1+\delta u_2)=\frac{u_2}{16u_{12}}\frac{D_1}{D_2}.$$

In mean field, the stability of the incommensurate (or intermediate) phase ($x_1=0$ and $x_2=0$) in the third quadrant $y_1<0$, $y_2<0$ depends on the coefficients of the fourth-order terms. The case $(1+\delta u_1)(1+\delta u_2)>1$ (i.e., $u_1u_2<u_{12}^2$) will only be investigated since the other condition allows no incommensurate phase[7] to appear in mean-field theory and obviously corresponds to Ref. 5.

The phase ($x_1=0$, $x_2\neq 0$) is stable in the $y_1>0$, $y_2<0$ region and clearly identifies to SA_1, whereas a phase ($x_1\neq 0$, $x_2=0$) that we call SA_x appears in the $y_2>0$, $y_1<0$ region. We know from Ref. 5 that SA_x is always of higher energy than SA_2 because of the third-order coupling term,[4,5] but close to SA_d (i.e., SA_2 with $x_1>>x_2$). The incommensurate phase is stable in the third quadrant in a region limited by two second-order transition lines: $y_1=y_2/(1+\delta u_2)$ SA_1-SA_i line and $y_1=(1+\delta u_1)y_2$ SA_i-SA_x line. The free-energy density of the incommensurate phase is easily minimized to

$$f(SA_i)=\frac{2y_1y_2-y_1^2(1+\delta u_2)-y_2^2(1+\delta u_1)}{4[(1+\delta u_1)(1+\delta u_2)-1]}$$

and the phase diagrams are finally obtained by comparing $f(SA_i)$ to $f(N)=0$, $f(SA_1)=-y_2^2/[4(1+\delta u_2)]$, and the computed value of $f(SA_2)$ in the same rescaled dimensionless units.[5]

PHASE DIAGRAMS

We choose $\delta u_1=9$, $\delta u_2=0$. The strength of the incommensurability is measured as in Ref. 5 by the reduced parameter

$$z=(u_{12}D_1/2)^{1/2}(q_1^2-q_2^2/4)/w$$

proportional to the difference of natural wave vectors over the coupling constant w. For small incommensurability parameter z (Fig. 1), the origin $y_1=0$, $y_2=0$ is deep in the SA_2 phase, there is no bicritical point, and SA_2 is always found to be of lower energy than SA_i. The diagram is qualitatively similar to Fig. 3(b) of Ref. 5. Rotated axes $(y_1,y_2)\rightarrow(t,x)$ are introduced to show the close agreement with the experimental diagram of the DBnOCN series (Fig. 1 of Ref. 8) as it was already noticed in Refs. 3 and 4.

For higher incommensurability parameter $z>zc$ given in Ref. 5 [$zc=1/(6)^{1/2}$ here] (Fig. 2), the bicritical point B appears and SA_i is found to be stable in a quasitriangular domain which grows when increasing z. The SA_1-SA_i second-order line is given by Eq. (2) $y_1=y_2/(1+\delta u_2)$, while SA_2-SA_i and SA_d-SA_i are first order. Of course, SA_x and the SA_x-SA_i line never appear. Even with rotated axis, the topology of the theoretical diagram in the (y_1,y_2) plane at constant z (Fig. 2) is far from the experimental one in the (DB7OCN-8OCB) plane. Moreover, the discontinuity at the SA_d-SA_2 transition unambiguously grows when moving along the line towards the SA_i phase, whereas it decreases in the experiment.[6] It is in fact clear that the (y_1,y_2) (or rotated t,x) representation at constant incommensurability

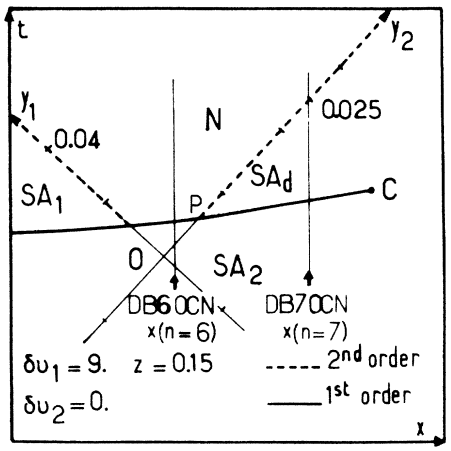

FIG. 1. N-SA_1-SA_d-SA_2 phase diagram in the case of a small incommensurability parameter z. The incommensurate phase does not appear. Rotated axes (t,x) are introduced to emphasize the close topological similarity with the experimental diagram of the DBnOCN series (Ref. 8): t corresponds to the temperature and x to the concentration in binary mixtures of successive homologous compounds. Pure products $n=6$, $n=7$ can be easily located on both sides of the critical end point P, whereas calorimetric and x-ray data of Ref. 8 allow one to estimate that the critical point C is not far from $n=8$. The pure DB7OCN axis $(t,n=7)$ is thus defined as $t=2(5)^{-1/2}(y_2-0.025)+(5)^{-1/2}y_1$.

parameter z is not appropriate to describe a DB7OCN-8OCB mixture, since the ratio of the two natural lengths $l'/l=q_2/q_1$ considerably varies from DB7OCN (l'/l close to 2) to 8OCB (l'/l close to 1). It follows from its definition that the incommensurability parameter z must increase significantly from DB7OCN to 8OCB.

We thus suggest that a theoretical phase diagram should be represented in a (t,z) coordinate system to be compared to the experimental one.[6] Such a diagram is shown in Fig.

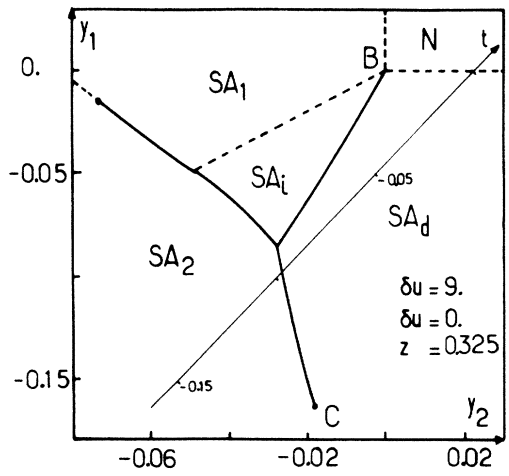

FIG. 2. N-SA_1-SA_d-SA_2-SA_i phase diagram in the case of higher incommensurability parameter ($z>zc$). The rotated $(t,n=7)$ axis of Fig. 1 is mentioned again, but the topology is quite different from that of the experimental diagam of Ref. 6. The nearly triangular SA_i domain grows when increasing z and crosses the above defined $(t,n=7)$ axis for $z>0.36$.

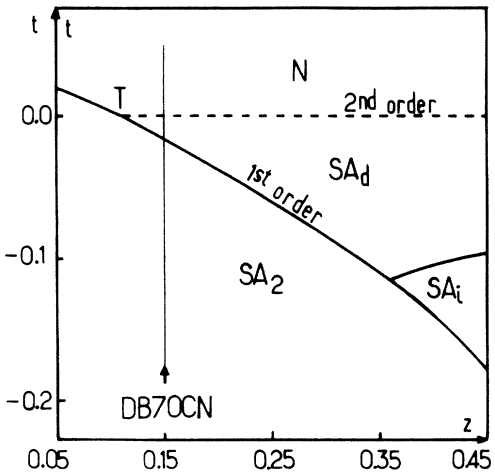

FIG. 3. N-SA_d-SA_2-SA_i diagram in the (t,z) plane. x has the constant value defined in Fig. 1 for $n=7$ so that pure DB7OCN is characterized by the same set of parameters in Figs. 1 and 3 ($z=0.15$). The z axis is clearly related to the experimental concentration of 8OCB in DB7OCN (Ref. 6).

3, with t defined by the same rotation as in Fig. 1 and $x(n=7)$ and $z(=0.15)$ corresponding to pure DB7OCN (i.e., the DB7OCN axis of Figs. 1 and 3 are common, as required). The topology is now in excellent agreement with the experiment.[6] Moreover, values of z lower than 0.15 are investigated to show the critical end point T where the three phases N, SA_d, SA_2 meet. This point does enter a $(t,z>0.15)$ representation at constant $x(n=6)$ (see Fig. 1), and thus should be reached in a DB6OCN-8OCB binary diagram.

CONCLUDING REMARKS

We have shown that the original observation of an incommensurate smectic-A phase is fully compatible with the topology computed from the Prost model of frustrated smectics in a temperature-incommensurability parameter cross section of the phase space. Other experimental features can be interpreted the following way:

(1) The lack of a harmonic coupling term in the free energy (1) makes it possible to describe the DB7OCN-rich part of the diagram only since it requires $1.5 < l'/l < 2$ as already mentioned. Fortunately, the experimental diagram of Ref. 6 corresponds to this limit [X(8OCB) $< 40\%$].

(2) The choice of the (t,x) coordinate system from the original (y_1,y_2) is not critical to get the topology of Fig. 3 provided that the t axis crosses the SA_2-SA_d line (as in Figs. 1 and 2). Depending on the exact definition of t (and of the value of other parameters $\delta u_1, \delta u_2$) the discontinuity (i.e., the latent heat) along the first-order SA_2-SA_d line can either increase or decrease, as experimentally seen,[6] when moving towards SA_i. Although it is not impossible *a priori*, an exact cancellation of the discontinuity at the triple point SA_d-SA_2-SA_i is, however, unlikely in the present approach.

(3) The SA_d-SA_i and SA_i-SA_2 lines are necessarily found to be first order because of the single-mode approximation of the incommensurate structure. For finite values of the coupling constant w, a modulated structure consisting of a periodic stack of discommensurations is known to be more stable[2] and allows the SA_i-SA_d and SA_i-SA_2 transitions to be continuous[9] as probably observed.[6] Moreover, the absence of any modulated structure in the x-ray scattering data[6] suggests that the coupling constant w is weak. Thus, if one forgets about the discontinuity, the evolution of wave vectors reported in Ref. 6 is in agreement with the present model (see formula 2-11 of Ref. 5): $q_0(SA_d)$ increases to q_1 at the SA_d-SA_i transition, $2q_0(SA_2)$ decreases to q_2 at the SA_2-SA_i transition.

At last, we must mention that the existence of the incommensurate phase close to the bicritical or tetracritical point B $(y_1=y_2=0)$ in the (y_1,y_2) plane (Fig. 2) is not correctly predicted by mean-field theory, but depends on the sign of the specific-heat exponents α associated with the second-order N-SA_1 and N-SA_d lines.[7,10] If α is negative as expected from theory (inverted XY universality class[11]), B is tetracritical and the incommensurate phase should always be present (i.e., the mean-field topology of Fig. 2 is valid close to B). If α is positive, B is bicritical and the incommensurate phase should not reach it. In both cases, however, the incommensurate SA_i domain of Fig. 3 is far enough from the origin B to believe that mean-field theory has some relevance.

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