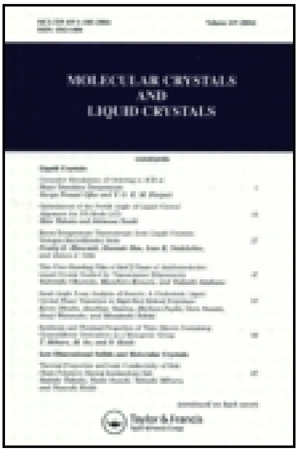

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A MODEL EXHIBITING DEVIL'S STAIRCASES PERTAINING TO FERRO- AND ANTIFERROELECTRIC SMECTECS

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Abstract Phase diagram of the ANNNI model with the third neighbour interaction is obtained to clarify the ferrielectric phases appearing in the sequences of phase transitions of certain ferroelectric smectic liquid crystals. While various mesophases are ferrielectric, those with wave number $q = 3/8$ and $3/10$ come out to exhibit the second order phase transition from antiferroelectric phase to ferrielectric one with decreasing temperature. The phases with $q = 4/13$ and $4/11$ are the candidates for the ferrielectric phases FI_H and FI_L observed just above and below the SmC_γ^*, respectively.

INTRODUCTION

In some liquid crystals, there appear many mesophases and accordingly various sequences of phase transitions can occur[1]. Certain ferroelectric smectics are truely such materials[2-4]. In practice, Fukuda-Takezoe group has reported the successive phase transitions, for example, at the mixture of MHPOCBC with MHPOOCBC in rather narrow temperature range[5-6]. The typical sequence is SmA-SmC_α^*-SmC^*-AF-SmC_γ^*-SmC_A^*, where AF and SmC_A^* are antiferroelectric phases with period 4 ($++--$) and period 2 ($+-$), respectively, and SmC_γ^* the ferrielectric one with period 3 ($++-$). In the present stage, the nature of SmC_α^* is not known clearly[7]. In addition to those, two ferrielectric phases FI_H and FI_L are found[5-6] at the temperature above and below SmC_γ^*. They suggested that these sequences of phase transitions are the parts of the devil's staircases which should occur in such materials[5-7].

In order to study the phenomena the present author and his co-worker[8] introduced the axial next nearest neighbour Ising model (ANNNI model[9-10]) with the third neighbour interaction[11], and showed that such type of successive phase transition occurs at the order in agreement with the observations[8]. The aim of the present study is to clarify the mesophases FI_H and FI_L theoretically, because the properties of those are not known well.

This article is composed of 5 sections; Introduction, Model, General Formulation, Results and Summary. In Results, the phase diagram is obtained by solving the minimum conditions of thermodynamical potential. Though many phases appear and construct the devil's staircases, only 10 phases (q = 0, 1/4, 2/7, 3/10, 4/13, 1/3, 4/11, 3/8, 2/5, 1/2) which seem to be the main sub-phases among them are practically taken into account. The properties of those phases are clarified. These results suggest that the mesophases with q = 4/13 and 4/11 are the candidates for the ferrielectric ones FI_H and FI_L, respectively.

MODEL

In the chiral smectic phases mentioned above except for SmC_{α}^*, the tilt angle of molecule to the smectic layer normal is sufficiently large and the state of each layer is described mainly by the direction of tilt[8,12]. On the coordinate system adjusted to the helix of chiral smectics, the direction is confined to right and left (or, + and −) , which is described by Ising spin, not by planer-rotator. Various phases are characterized by the stacking of layers. The signs ++− , and so on mentioned in Introduction show such stackings and also units of periodicities.

While the devil's staircases are known to occur in the original ANNNI model[10], the ferrielectric phase ++− with q = 1/3 never appears. On the other hand, the phase SmC_{γ}^* known to have q = 1/3 is considered to be the fundamental one besides SmC* and SmC_A^* in the observed successive phase transitions. To stabilize SmC_{γ}^* we only add the third neighbour interaction in the axial direction to the ANNNI model. Thus, the Hamiltonian is expressed as[8,11]

$$H = -J\,\Sigma\, s(i)\, s(i') - J_1 \Sigma^A s(i)\, s(i+1) - J_2 \Sigma^A s(i)\, s(i+2) - J_3 \Sigma^A s(i)\, s(i+3) \qquad (1)$$

where the Ising spin $s(i)$ (= ±1) represents the state of a molecule in the i-th layer, the first terms in the r.h.s. of Eq. (1) show the sum of all nearest neighbouring pairs in the same layer and second, third and fourth terms the sums of all nearest pairs between nearest, second and third neighbouring layers, respectively. As to the interaction parameters, J_2 should be negative and J is positive. J_1 comes from the steric interaction and also from electric one, and accordingly takes the following form given by[8]

$$J_1 = S\,T - J_0, \tag{2}$$

where T denote the temperature and S, $T_0 > 0$. From the T - J_1 phase diagram and $J_1(T)$ given by Eq. (2), the sequence of phase transition, SmC*-AF-SmC$_\gamma$*-SmC$_A$* is explained[8].

GENERAL FORMULATION

At the second order phase transition point from disorder phase to ordered one, there appears a sinusoidal order with no higher harmonics. The critical temperature T_c is given by[8,11]

$$T_c = 2\{ 3J + J_1 X - (2X^2 - 1) + J_3(4X^3 - 3X)\}, \tag{3}$$

where the Boltzmann constant is taken to be unity, $J_2 = -1$ (e.g. every energy parameter is scaled in the unit $|J_2|$) and X is given by

$$X = \frac{1 - \sqrt{3J_3(3J_3 - J_1) + 1}}{6J_3}, \tag{4}$$

and the wave number of the order q is obtained as

$$q = \frac{1}{2\pi} \cos^{-1} X. \tag{5}$$

To study the ordered phase and to obtain the phase diagram, it is required to evaluate the thermodynamical potential. The thermodynamical potential Φ_p with period p is given by[10]

$$\begin{aligned}\Phi_p = \frac{1}{p}\sum_{i=1}^{p}[& -J(z/2-1)\sigma_i^2 - J_1\sigma_i\sigma_{i+1} \\ & + \sigma_i\sigma_{i+2} - J_3\sigma_i\sigma_{i+3} \\ & + \frac{T}{2}\{(1+\sigma_i)\ln(1+\sigma_i) + (1-\sigma_i)\ln(1-\sigma_i)\}],\end{aligned} \tag{6}$$

where σ_i is the average of s (i) and $\sigma_{i\pm p} = \sigma_i$, z the mean of the coordination number. The stational values of σ_i are determined from the minimum condition of Φ_p shown in the followings

$$-J(z-2)\sigma_i - J_1(\sigma_{i+1}+\sigma_{i-1}) + \sigma_{i+2}+\sigma_{i-2} - J_3(\sigma_{i+3}+\sigma_{i-3})$$
$$+\frac{T}{2}\ln\{(1+\sigma_i)/(1-\sigma_i)\} = 0, \quad (i = 1, 2, \ldots, p). \tag{7}$$

RESULTS

Eqs. (7) are solved numerically, where we restrict the phases within main 10 phases ($q = 0$, 1/4, 2/7, 3/10, 4/13, 1/3, 4/11, 3/8, 2/5, 1/2), z=8 and the values of parameters are taken as $J = 1.0$ and $J_3 = 0.3$, exclusively in this article.

Phase Diagram

The critical temperature T_c for each phase with the fixed wave number q is given by Eq. (3) with X detemined from Eq. (5) instead of (4). T_c's are the linear functions of J_1 and tangential to the critical curve given by Eqs. (3)-(5) at the points shown in Figure 1 by ● with wave numbers concerned. So, the critical

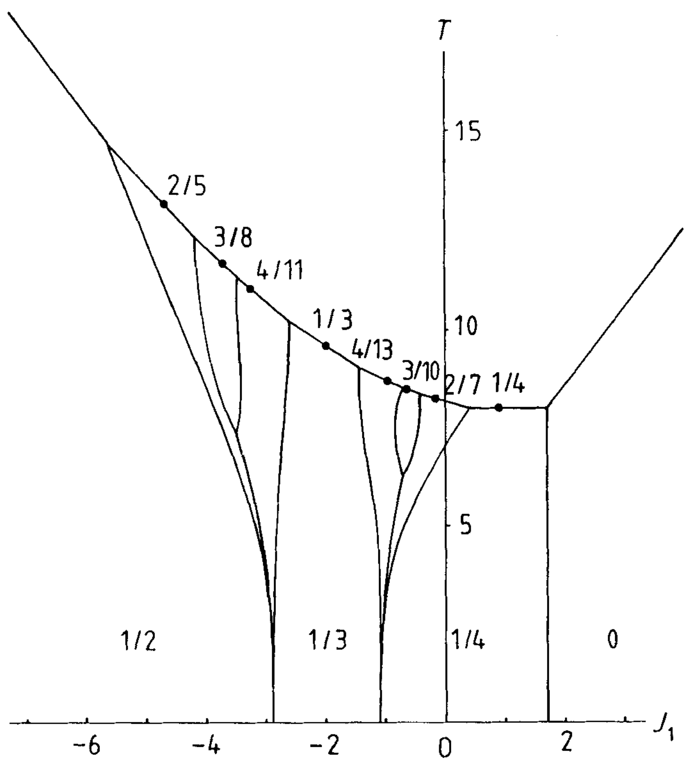

FIGURE 1. Phase diagram.

curve is an envelope ot these critical lines, though it is not drawn explicitly in Figure 1. The transitions between phases with different values of q are the first order ones and the coexisting curves are determined by numerical method.

Sub-phases

The phases with $q = 2/5$ and $2/7$ are ferrielectric and the stackings of the layers are such ones $++-+-$ and $++--++-$, respectively. While those with $q = 3/8$ and $3/10$ in the Figure 1 are antiferroelectric, there occur the second order phase transitions to the ferrielectric ones in case the neighbouring phases are neglected. The spin configurations for $q = 3/8$ are shown in Figure 2; $J_1 = -3.6$, $T = 7.1$ (a) and 6.6 (b). The antiferroelectric phase (a) is obtained by the continuous deformation from the sinusoidal form, and we can say that this phase and the sinusoidal one belong to the same symmetry class. As seen in (a) the average value of spins labelled by ∇ is vanishing. In this respect this phase may be called as the partially ordered phase. The spin configuration is antisymmetric with respect to these spins, while the antisymmetry is broken in (b) (the symmetry with respect to spins labelled by $\bigcirc$ exists in both phases).

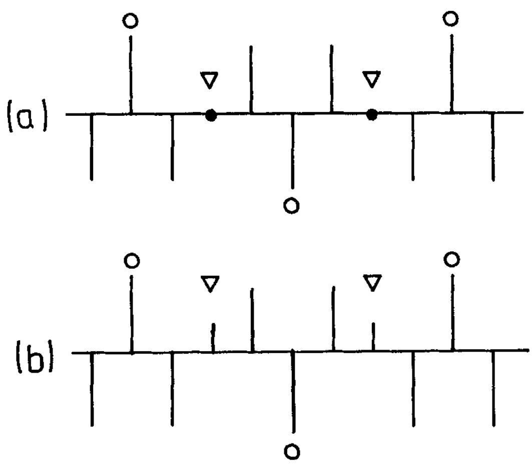

FIGURE 2 Spin configurations with $q = 3/8$.

By denoting the σ_i concerned by σ_1 ($= \sigma$), the thermodynamical potential is rewritten as

$$\Phi_p = \Phi(\sigma)/p + \Phi_p(\sigma = 0), \tag{8}$$

$$\Phi(\sigma) = -3J\sigma^2 - J_1(\sigma_8 + \sigma_2)\sigma + (\sigma_7 + \sigma_3)\sigma - J_3(\sigma_6 + \sigma_4)\sigma$$

$$+\frac{T}{2}\{(1+\sigma)\ln(1+\sigma)+(1-\sigma)\ln(1-\sigma)\}. \qquad (9)$$

If the antisymmetry is satisfied, the couplings between σ and other spins vanish as seen in Eq. (9), and then the transition occurs at $T=6$. However, the antisymmetry is violated due to the couplings given by Eq. (7) at low temperature region and so near the transition point the following relations with constants c_i are obtained as

$$\sigma_i = \sigma_i^{(0)} + c_i\,\sigma, \qquad (i=2, 3, \ldots, 8) \qquad (10)$$

where $\sigma_i^{(0)}$ is the value of σ_i at the antisymmetric configuration, that is $\sigma=0$. By substituting Eqs. (10) to (6), the transition temperature is obtained, which is larger than 6 as shown in Figure 3. Similar phenomena are also shown to occur for $q=3/10$.

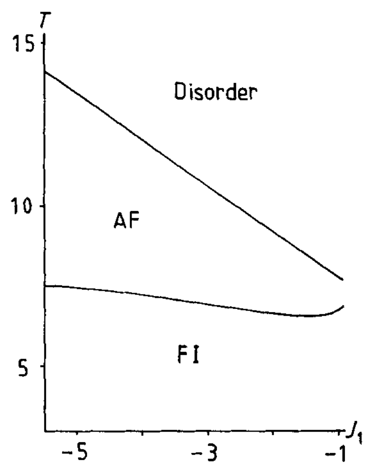

FIGURE 3 Phase transition between phases with $q = 3/8$.

As to the phases with $q = 4/11$ and $4/13$, two kinds of spin configurations are obtained which are shown in Figure 4 ($q=4/13$, $J_1=-1.05$, $T=5.5$). Both of them are ferrielectric and symmetric with respect to the spins labelled by ○. The phase shown in (a) belongs to the symmetry class of the sinusoidal order in the meaning mentioned above. On the other hand the phase shown in (b) is constructed of three blocks of type $++-$ and one $++--$. By inversing the sign of spins labelled by ▽, both phases exchanges to each other in respect of the configurations of $+$ and $-$. However the positions of centre of the symmetry change at that inversion. Accordingly, if the transition between those phases exists, then it is necessarily the first order one. In the numerical result the free

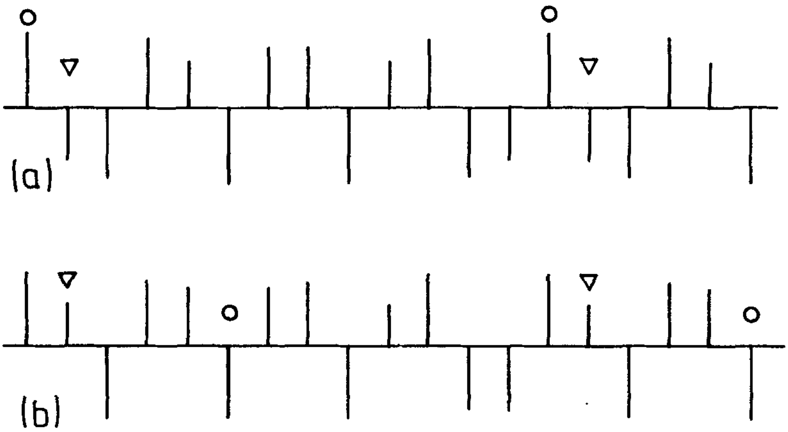

FIGURE 4 Spin configurations with $q = 4/13$.

energy of the former F_s is smaller than the latter one F_b as shown in Figure 5 ($\Delta F = F_b - F_s$; $q = 4/13$, $J_1 = -1.05$), while the mean of σ_i, $<\sigma>$ ($= \Sigma_i \sigma_i / p$) of the latter is larger than the former one. In any way, such transition never occurs and the phase belonging to the sinusoidal class is stable at finite temperature. It is noticed that at zero temperature the spin configurations are antisymmetric up to the third neighbours with respect to the spins labelled by ▽ and the energy is irrespective of state of the these spins. Due to this frustration effect the gain of the energy is not effective and so the existing area shrinks to only a point at zero temperature as shown in Figure 1. Similar phenomena also occur at the phase with $q = 4/11$.

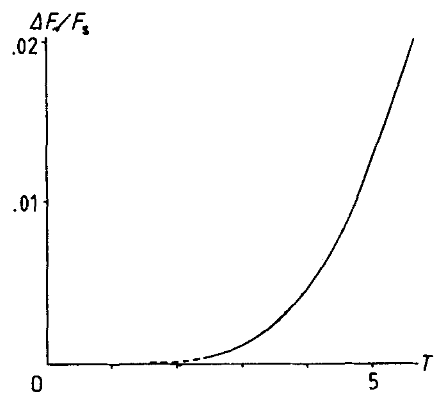

FIGURE 5 Defferences of the free energies of two spin configuration with $q = 4/13$.

SAMMARY AND DISCUSSIONS

The phase diagram of the ANNNI model with the third neighbour interaction is obtained, where the antiferroelectric phases with $q = 3/8$ and $3/10$ are shown to appear in addition to various ferrielectric ones. Moreover, the areas they occur are rather narrow. As for the ferrielectric phases with $q = 2/5$ and $2/7$, such area is also narrow for $q = 2/5$ though $< \sigma >$ is large in both phases. In contrast with above mentioned phases, the areas are wide for both of those with $q = 4/11$ and $4/13$, while $< \sigma >$ is comparably small.

These results indicate that the phase with $q = 4/11$ corresponds to FI_L. As to FI_H it is plausible to consider that the phase with $q = 4/13$ is fit to it, but the phase with $q = 2/7$ is yet a candidate. At the temperature near 5.0 and $J_1 = -1.0$, the ratio of the value $< \sigma >$ to that of $q = 1/3$ is about 0.23 for $q = 4/13$, while for $q = 2/7$ it is 0.43 and about twice of the former. If such quantity is measured experimentally, we can obtain the definite conclusion. In this context it is notable that the ratio is about 0.27 for $q = 4/11$ and 0.6 for $q = 2/5$ near the point $T = 5.0$ and $J_1 = -3.0$.

In this article the calculations are carried out for the value $J = 1.0$ exclusively. The effect of the intralayer interaction enhances the order σ_i of each layer and accordingly suppresses the sub-phases fully frustrated. In the practical situation J is considered to be larger than 1.0, and for quantitative discussion the caluculations shoud be required for wide range of value of J.

The behaviour of the present system in the electric field is also interesting because the experimental results are already available[4,5]. These will be reported in the near future.

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