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LONG RANGE INTERACTIONS, MANY BODY FORCE AND MESOPHASES IN FERROELECTRIC SMECTICS

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Abstract

The four body force has been shown to be induced in the course to certify the assumptions in the ANNNI model with the third nearest neighbour interaction. The effect of the force at finite temperature is studied, from which this model is shown to be the effective model for the successive phase transitions in ferroelectric smectics. The structures of mesophases appearing in such phase transitions are discussed and the effect of the fluctuation of the tilt angle is examined.

INTRODUCTION

The successive phase transitions appearing in ferro- and antiferroelectric smectics are one of the most fascinating phenomena.[1,2] For the purpose to clarify the mechanism of such phase transitions the axial next nearest neighbour Ising model (ANNNI model)[3,4] with the third nearest neighbour interaction J_3 was introduced,[5] on the basis of which fruitful results have been derived.[5-7] The underlying assumptions of this model are the negative definiteness of the second nearest neighbour interaction J_2 and the existence (or, positiveness) of J_3. The Hamiltonian of this model is expressed as

$$H = -J \sum_{(i,j)} s_i s_j - J_1 \sum_i^A s_i s_{i+1} - J_2 \sum_i^A s_i s_{i+2} - J_3 \sum_i^A s_i s_{i+3}, \tag{1}$$

where J denotes the nearest neighbour interaction parameter in the same layer, s_i is the Ising spin which takes plus and minus unities representing the direction of the molecular tilt, the summation $\Sigma_{(i,j)}$ are taken over nearest neighbouring molecular pairs in the same smectic layer and those Σ^A are only in the axial direction parallel to the layer normal.

In order to assure the assumptions mentioned above a model with sense of molecular long axis has been introduced,[8] whose Hamiltonian is given by

$$H = -J \sum_{(i,j)} s_i s_j - J_1^{(0)} \sum_i^A s_i s_{i+1} - \sum_i^A \{(E_1 s_i s_{i+1} + E_3) t_{i+1} + E_2 (s_{i-1} - s_{i+1}) s_i \} t_i, \tag{2}$$

where t_i is the Ising variable representing the up (+1) or down (-1) directions of the molecular sense, the parameter $J_1^{(0)}$ comes from the t_i-independent interaction and $J_1^{(0)}$ and E_i (i = 1, 2 and 3) are the linear combinations of bare ones representing pair states of molecules.[8] By carrying out the summation over all states of t_i in the partition function, long range interactions and many body forces are shown to be induced.[8] In the minimal theory where the interactions up to the third nearest neighbour interactions are taken into account the above assumptions are certified.[8] The mechanism to stabilise the ferrielectric phase (SmC*$_\gamma$) and intermediate antiferro- electric one (AF) is also clarified.[9,10]

In the process where J_3 is derived the four body interaction is shown to be induced.[8] Then, the resultant Hamiltonian is expressed as

$$H = -J\sum_{(i,j)} s_i s_j - J_1\sum_i^A s_i s_{i+1} - J_2\sum_i^A s_i s_{i+2} - J_3\sum_i^A s_i s_{i+3} - J_{4b}\sum_i^A s_i s_{i+1} s_{i+2} s_{i+3}. \quad (3)$$

The ground state of this model is already examined.[9] In this article the effect of J_{4b} is studied, from which the Hamiltonian (1) is shown to be the effective Hamiltonian for the phenomena of the successive phase transitions concerned.

We also give some comments on the structures of the mesophases and on the ferrielectric phase FI observed between the ferroelectric phase (SmC*) and AF,[11] about which we have already suggested.[5] The effect of the fluctuation of the tilt angle is also tested.

PHASE DIAGRAM

In the mean field approximation the thermodynamical potential of the system (3) is obtained with the coordination number z (= 6) in the layer as

$$\Phi_p = \frac{1}{p}\sum_{i=1}^{p} [-\frac{Jz}{2}\sigma_i^2 - J_1\,\sigma_i\,\sigma_{i+1} - J_2\,\sigma_i\,\sigma_{i+2} - J_3\,\sigma_i\,\sigma_{i+3} - J_{4b}\,\sigma_i\,\sigma_{i+1}\sigma_{i+2}\sigma_{i+3} + \frac{T}{2}\{ (1+\sigma_i) \ln (1+\sigma_i) + (1-\sigma_i) \ln (1-\sigma_i) \}], \quad (4)$$

where σ_i is the thermal average of s_i ($\sigma_{i\pm p} = \sigma_i$) and p denotes the period of the ordered structure. The critical temperature T_c is independent of the value J_{4b} in the mean field theory, because the contribution of J_{4b} to the thermodynamical potential appears in the fourth power of the order parameters. The critical temperature T_c and the wave number q are obtained as functions of J_1 with parameter X as[5]

$$T_c = 2\{ \frac{Jz}{2} + J_1X - (2X^2 - 1) + J_3(4X^2 - 3) \}, \quad (5)$$

$$q = \frac{1}{2\pi}\cos^{-1}X, \quad (6)$$

$$X = \frac{1 - \sqrt{3J_3(3J_3 - J_1) + 1}}{6J_3}, \quad (7)$$

where energy parameters are scaled in the unit $|J_2|$. The conditions for thermal equilibrium are given by

$$\begin{aligned} &-Jz\sigma_i - J_1(\sigma_{i+1}+\sigma_{i-1}) + \sigma_{i-2}+\sigma_{i+2} - J_3(\sigma_{i-3}+\sigma_{i+3}) \\ &- J_{4b}(\sigma_{i+1}\sigma_{i+2}\sigma_{i+3} + \sigma_{i-1}\sigma_{i+1}\sigma_{i+2} + \sigma_{i-2}\sigma_{i-1}\sigma_{i+1} + \sigma_{i-3}\sigma_{i-2}\sigma_{i-1}) \\ &+ \frac{T}{2}\ln\frac{1+\sigma_i}{1-\sigma_i} = 0 \qquad (i=1,2,\ldots,p). \end{aligned} \tag{8}$$

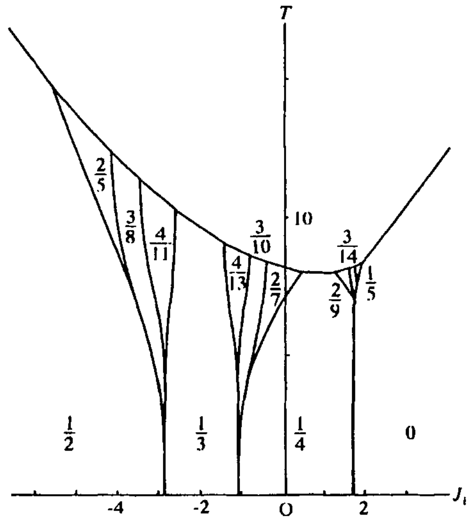
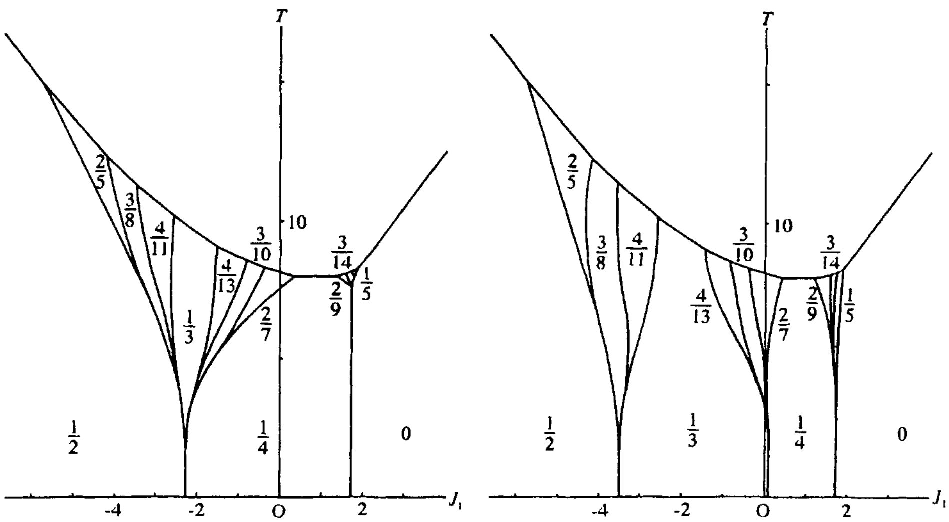


FIGURE 1 Phase diagram without the four body interaction.



(a) $J_{4b} = 0.3$ (b) $J_{4b} = -0.3$

FIGURE 2 The effect of J_{4b} on the phase diagram.

The 13 phases with wave number $q = 1/2$ (SmC^*_A), 2/5, 3/8, 4/11, 1/3 (SmC^*_γ), 4/13, 3/10, 2/7, 1/4 (AF), 2/9, 3/14, 1/5 and 0 (SmC^*) are taken into account. The values of the parameters are chosen as $J = 1$, $J_3 = 0.3$, and $z = 6$.

The phase diagram for the case $J_{4b} = 0$ is shown in Figure 1, where mesophases with wave number 2/9 and 1/5 are ferrielectric phases and that with 3/14 is the antiferroelectric one. In Figure 2 the effect of the four body force is examined where $J_{4b} = 0.3$ in (a) and $J_{4b} = -0.3$ in (b). By comparing these results with the one shown in Figure 1, we see that J_{4b} works rather at lower temperature region as predicted previously,[9] while in the high temperature region any remarkable effect is not observed. As to the ferroelectric smectic materials the successive phase transitions occur in the temperature range roughly 300K ~ 380K,[1,2] to which the rather higher temperature portions of the ordered phases in phase diagrams should be applied. Accordingly the effect of J_{4b} on this successive phase transitions is secondary, and so the Hamiltonian (1) is considered to be the effective Hamiltonian at the phenomena concerned.

Average of the Order σ_i and the Apparent Tilt Angle

In the present theory an observable quantity is only the average of the ordering, σ (= $\sum_{i=1}^{p} \sigma_i \,/\, p$), which is assumed to be proportional to the apparent tilt angle.[6,7] The ratio of this value to the one in SmC^*_γ is obtained roughly as 0.6 for the phase with $q = 2/5$ and 0.27 for the one with $q = 4/11$.[7] At the ferrielectric phase (FI_L) the ratio of the apparent tilt angles is estimated experimentally to be about 0.6,[12] and from this correspondence the structure of FI_L is suggested to be the type with $q = 2/5$.

As to the another ferrielectric phase (FI_H) the ratio is derived as 0.43 for phase $q = 2/7$ and 0.23 for $q = 4/13$.[7] These two values are expected to be distinguishable experimentally, though any observation on this quantity has not been reported yet.

Mesophase between SmC* and AF

In addition to the devil's staircases between SmC^*_A and SmC^*_γ and between SmC^*_γ and AF, another type of devil's staircase has been predicted between AF and SmC*.[5] After that a ferrielectric phase FI is observed among them.[11] With this phase in mind the phases with $q = 2/9$, 3/14 and 1/5 have been taken into account in Figures 1 and 2. We see that these phases appear in rather narrow area near the critical temperature, which is considered as the reason why FI is not observed commonly in various materials. It is noticed that these phases exist in some wide temperature range in Figure 2(b), where J_{4b} = -0.3.

In order to study the structure of FI the average σ of the order σ_i is calculated at ferrielectric phases with $q = 2/9$ and 1/5. Because those are stable near the critical temperature the ratio of σ to the one for SmC* changes considerably. Near the triple point in Figure 1 where $J_1 = 1.7$ and $T = 7.25 \sim 7.0$, the ratio is $0.043 \sim 0.057$ for $q = 1/5$ and $0.018 \sim 0.027$ for $q = 2/9$. This value for the complete ordering at $T = 0$ is 0.2 and 0.111 for these phases, respectively. The dependencies of the ratio on J_{4b} are also observed. In this respect it is not appropriate to derive some concrete conclusion in the present stage. The experimental study is expected.

FLUCTUATION OF THE TILT ANGLE

As for the observable quantity the layer spacing is promising. By generalizing the Ising spin to the one with large magnitude we can discuss the changes of the layer spacing within our model. The simplest is the one with spin magnitude $S = 3/2$, where s_i takes ± 1 and $\pm 1/3$ corresponding to large and small tilt angles, respectively. The thermal average of the thickness of the i-th layer d_i is expressed as

$$d_i = < d_1 \frac{s_i^2 - 1}{\frac{1}{9} - 1} + d_2 \frac{s_i^2 - \frac{1}{9}}{1 - \frac{1}{9}} >$$
$$= \frac{9}{8} \{ (d_2 - d_1) Q_i + d_1 - \frac{d_2}{9} \}, \tag{9}$$

where Q_i is the thermal average $< s_i^2 >$ and the parameters d_1 and d_2 are the layer spacing with complete ordering $Q_i = 1/9$ and 1, respectively. The average over a period p, d ($= \Sigma_i d_i / p$) is considered to be observable. In general terms $W\Sigma_i s_i^2$ should be added to the Hamiltonian (1), or (3).

We obtained the phase diagram for the case $J_{4b} = 0$ and $W = 0$, where 13 phases studied in the above are also taken into account. In the phase diagram any remarkable change by this generalization is not observed, although we do not show it here for want of space. The jumps of value Q_i at the phase transitions are also obtained, which is not so large. The experimental informations are required for the comparison.

SUMMARY AND DISCUSSIONS

We have summarized the three models concerning to the successive phase transitions in ferroelectric smectic liquid crystals, the ANNNI model with J_3, the model with freedom of sense of molecular long axis and the resultant model derived from this by decimation transformation. The last one is the same to the first model combined with the four body interaction J_{4b}. The effect of J_{4b} at finite temperature is examined, from which any qualitatively new properties are not found except for the ground state. In this respect the ANNNI model with J_3 is considered as the effective Hamiltonian for the successive phase transitions under discussion. By comparing the average of the layer order with the experimental report on the apparent tilt angle the mesophase FI_L is suggested to have a period 5. The ferrielectric phase observed between SmC* and AF, and the effect of the fluctuation of the tilt angle are also studied.

The fundamental assumption of these model is the Ising property, which is based on the conoscopic observations,[1,2] *i.e.*, all molecules are in one plane twisted with the helical structure. Recently, thresholdless transition between SmC^*_A and SmC* induced by the external field is reported and possibility of XY-like motion of the molecules is discussed.[13] Details on this phenomenon are hoped for. The magnitude of the tilt angle is considered to be relevant to those phenomena.

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