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On Intermediate Phases Appearing in Antiferroelectric Smectics

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Block-spin model (or ANNNI model) characterized by frustration due to competing interaction and 4-state model in which each chiral molecule takes four states of molecular orientation are considered in order to clarify a mechanism of appearance of intermediate phases in antiferroelectric smectics. It is concluded that the intermediate phases are caused not only by the frustrated interactions but also by unsymmetrical interaction energy in adjacent block-spin or in adjacent chiral molecule along layer normal.

Keywords: block-spin; chiral molecule; correlation function; intermediate phases; transfer matrix method

INTRODUCTION

In antiferroelectric smectics, it is well-known that various type of phases such as AF, FI_H, FI_L, SmC^*_γ appear among antiferroelectric and ferroelectric phases [1–6]. As an approach to explanation for the successive phase transitions, ANNNI model with the third nearest neighbor interaction J_3 is proposed [7,8] and is successful in the recent experimental results on the structures of the mesophases [9–11]. The ANNNI model [12,13] is characterized by frustration among the nearest neighbor interaction J_1 (>0) and the next nearest neighbor one J_2 (<0) along layer normal. It is concluded that the result of the frustration by competing interactions causes the intermediate phases [14,15].

We have presented on the correlation in layered structure in this frustrated model [16], which was studied by the transfer matrix

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method [17,18] by introducing a block-spin composed of a couple of spins in the adjacent layer. Furthermore, we calculated the correlation functions with damped oscillation in several intermediate phases [19]. It is found that this oscillating correlation functions are caused by the non-Hermit property of transfer matrix.

On the other hand, as a non-frustrated model, we consider a chiral smectic material system in which each chiral molecule takes multiple states of molecular orientation [6]. In this system, the transfer matrix becomes the non-Hermitian as in the frustrated model and oscillating correlation functions between the chiral molecules along layer normal appear. Consequently, the successive phase transitions are exhibited in the chiral smectic system, like in the frustrated model.

It is suggested from these facts that the reason why the intermediate phases appear in antiferroelectric smectics, is not only the frustration by the competing interactions but also the non-Hermitian transfer matrix, which is derived by unsymmetrical interaction energy in adjacent block-spin or in adjacent chiral molecule along layer normal.

BLOCK-SPIN MODEL

Let us consider the one-dimensional ANNNI model without an external field. The Hamiltonian is given by

$$H = -J_1 \sum_i^A s_i s_{i+1} - J_2 \sum_i^A s_i s_{i+2}, \tag{1}$$

where s_i denotes the Ising spin (± 1) designating the directions of molecular tilt. It is possible to analyze statistically the ANNNI model by use of a block-spin model [19], in which a couple of spins in the successive two layers (say, block-layer) are combined into a block-spin $\boldsymbol{\sigma}$:

$$\begin{array}{ccccccc} (s_1,\ s_2), & (s_3,\ s_4), & \ldots, & (s_{2n-1},\ s_{2n}) & \ldots, \\ \Downarrow & \Downarrow & \Downarrow & \Downarrow & \Downarrow \\ \boldsymbol{\sigma}_1, & \boldsymbol{\sigma}_2, & \ldots, & \boldsymbol{\sigma}_n, & \ldots,. \end{array}$$

The n-th block-spin $\boldsymbol{\sigma}_n$ is defined by a vector with four components corresponding to states; $(\uparrow\uparrow)_n$, $(\uparrow\downarrow)_n$, $(\downarrow\uparrow)_n$ and $(\downarrow\downarrow)_n$ of succeeding couple of spins (s_{2n-1}, s_{2n}), as follows:

$$(\uparrow\uparrow)_n \Rightarrow \boldsymbol{\sigma}_n = \begin{pmatrix} 1 \\ 0 \\ 0 \\ 0 \end{pmatrix}, \quad (\uparrow\downarrow)_n \Rightarrow \boldsymbol{\sigma}_n = \begin{pmatrix} 0 \\ 1 \\ 0 \\ 0 \end{pmatrix},$$

$$(\downarrow\uparrow)_n \Rightarrow \boldsymbol{\sigma}_n = \begin{pmatrix} 0 \\ 0 \\ 1 \\ 0 \end{pmatrix}, \quad (\downarrow\downarrow)_n \Rightarrow \boldsymbol{\sigma}_n = \begin{pmatrix} 0 \\ 0 \\ 0 \\ 1 \end{pmatrix}.$$

Then, the Hamiltonian (1) is rewritten in terms of the block-spin as

$$H_b = \sum_n^A \{\boldsymbol{\sigma}_n^T \cdot \boldsymbol{J}_z \cdot \boldsymbol{\sigma}_{n+1} + \boldsymbol{\sigma}_n^T \cdot \boldsymbol{A} \cdot \boldsymbol{\sigma}_n\}, \tag{2}$$

where the matrix $\boldsymbol{J}_z$ is an interaction between neighboring block-spins on succeeding block-layers and $\boldsymbol{A}$ the one within each block-spin, which are given by

$$\boldsymbol{J}_z = \begin{pmatrix} -J_1 - 2J_2 & -J_1 & J_1 & J_1 + 2J_2 \\ J_1 & J_1 - 2J_2 & -J_1 + 2J_2 & -J_1 \\ -J_1 & -J_1 + 2J_2 & J_1 - 2J_2 & J_1 \\ J_1 + 2J_2 & J_1 & -J_1 & -J_1 - 2J_2 \end{pmatrix}, \tag{3}$$

$$\boldsymbol{A}_n = \begin{pmatrix} -J_1 & & & \infty \\ & J_1 & & \\ & & J_1 & \\ \infty & & & -J_1 \end{pmatrix}. \tag{4}$$

The block-spin Hamiltonian H_b in (2) is tractable by transfer matrix method, in which a transfer matrix $\boldsymbol{M}_b$ is obtained by

$$\boldsymbol{M}_b = \boldsymbol{L}\boldsymbol{K} \tag{5}$$

where

$$\boldsymbol{K}_{\alpha,\gamma} = \exp\{-\beta \boldsymbol{A}_{\alpha,\gamma}\} \quad \text{and} \quad \boldsymbol{L}_{\alpha,\gamma} = \exp\{-\beta(\boldsymbol{J}_z)_{\alpha,\gamma}\},$$

finally, is expressed as

$$\boldsymbol{M}_b = \begin{pmatrix} e^{2\beta(J_1+J_2)} & 1 & e^{-2\beta J_1} & e^{-2\beta J_2} \\ 1 & e^{-2\beta(J_1-J_2)} & e^{-2\beta J_2} & e^{2\beta J_1} \\ e^{2\beta J_1} & e^{-2\beta J_2} & e^{-2\beta(J_1-J_2)} & 1 \\ e^{-2\beta J_2} & e^{-2\beta J_1} & 1 & e^{2\beta(J_1+J_2)} \end{pmatrix}. \tag{6}$$

It is noted that the transfer matrix $\boldsymbol{M}_b$ becomes a non-Hermitian. Let us reconstruct an effective Hamiltonian H_{ef} corresponding to the transfer matrix $\boldsymbol{M}_b$, which is equivalent to H_b in (2). It is clear that the H_{ef} is represented as

$$H_{ef} = \sum_n^A \boldsymbol{\sigma}_n^T \cdot \hat{\boldsymbol{J}}_z \cdot \boldsymbol{\sigma}_{n+1} \tag{7}$$

by judgment from the transfer matrix $\boldsymbol{M}_b$, where $\hat{\boldsymbol{J}}_z$ is an interaction between neighboring block-spins:

$$\hat{\boldsymbol{J}}_z = \begin{pmatrix} -2(J_1+J_2) & 0 & 2J_1 & 2J_2 \\ 0 & 2(J_1-J_2) & 2J_2 & -2J_1 \\ -2J_1 & 2J_2 & 2(J_1-J_2) & 0 \\ 2J_2 & 2J_1 & 0 & -2(J_1+J_2) \end{pmatrix}. \tag{8}$$

The interaction $\boldsymbol{A}$ in H_b (2) is normalized in $\hat{\boldsymbol{J}}_z$. Here, it is remarkable that $\hat{\boldsymbol{J}}_z$ is unsymmetrical interaction, for instance, the interaction $(=-2J_1)$ between the state $(\uparrow\downarrow)_n$ of n-th block-spin and the state $(\uparrow\uparrow)_{n+1}$ of $(n+1)$-th block-spin is different from the one $(=2J_1)$ between $(\uparrow\uparrow)_n$ of n-th block-spin and $(\uparrow\downarrow)_{n+1}$ of $(n+1)$-th block-spin. As is mentioned hereafter, the interaction between neighboring chiral molecules also show the unsymmetrical interaction. Consequently, the unsymmetrical interaction $\hat{\boldsymbol{J}}_z$ derives the non-Hermitian transfer matrix $\boldsymbol{M}_b$, as the result, the incommensurate structure appears.

Now, the incommensurate structure is exhibited by block-spin correlation function along layer normal. We define here a group of correlation functions $\boldsymbol{\Gamma}(r)$ between n-th block-spin and $(n+r)$-th one, as follows:

$$\boldsymbol{\Gamma}(r) \equiv \begin{pmatrix} \ll\uparrow\uparrow;\uparrow\uparrow\gg_r & \ll\uparrow\uparrow;\uparrow\downarrow\gg_r & \ll\uparrow\uparrow;\downarrow\uparrow\gg_r & \ll\uparrow\uparrow;\downarrow\downarrow\gg_r \\ \ll\uparrow\downarrow;\uparrow\uparrow\gg_r & \ll\uparrow\downarrow;\uparrow\downarrow\gg_r & \ll\uparrow\downarrow;\downarrow\uparrow\gg_r & \ll\uparrow\downarrow;\downarrow\downarrow\gg_r \\ \ll\downarrow\uparrow;\uparrow\uparrow\gg_r & \ll\downarrow\uparrow;\uparrow\downarrow\gg_r & \ll\downarrow\uparrow;\downarrow\uparrow\gg_r & \ll\downarrow\uparrow;\downarrow\downarrow\gg_r \\ \ll\downarrow\downarrow;\uparrow\uparrow\gg_r & \ll\downarrow\downarrow;\uparrow\downarrow\gg_r & \ll\downarrow\downarrow;\downarrow\uparrow\gg_r & \ll\downarrow\downarrow;\downarrow\downarrow\gg_r \end{pmatrix}. \tag{9}$$

For an example

$$\boldsymbol{\Gamma}(r)_{1,4} \equiv \ll\uparrow\uparrow;\downarrow\downarrow\gg_r = <\uparrow\uparrow;\downarrow\downarrow>_r - <\uparrow\uparrow><\downarrow\downarrow>, \tag{10}$$

where $<\uparrow\uparrow;\downarrow\downarrow>_r$ means the joint probability for a couple of states that n-th block-spin takes $(\uparrow\uparrow)$ and $(n+r)$-th one $(\downarrow\downarrow)$ and $<\uparrow\uparrow>$ the probability that a state of block-spin takes $(\uparrow\uparrow)$. The $\boldsymbol{\Gamma}(r)_{\alpha,\beta}$ $(\alpha,\beta=1\sim4)$ is calculated exactly as:

$$\boldsymbol{\Gamma}(r)_{\alpha,\beta} = \boldsymbol{U}_{\beta,1}\boldsymbol{U}^{-1}_{1,\alpha}\sum_{k=2}^{4}\left(\frac{\lambda_k}{\lambda_1}\right)^r \boldsymbol{U}_{\alpha,k}\boldsymbol{U}^{-1}_{k,\beta}. \tag{11}$$

where $\boldsymbol{U}$ denotes an unitary matrix which diagonalises the transfer matrix $\boldsymbol{M}_b$. The λ_k $(k=1\sim4)$ are the eigenvalues of $\boldsymbol{M}_b$ which are obtained by

$$\lambda_1 = \xi_+ + \eta_+, \quad \lambda_2 = \xi_+ - \eta_+ \quad \text{and} \quad \lambda_3 = \lambda_4^* = \xi_- + \hat{\boldsymbol{i}}\eta_-, \tag{12}$$

where

$$\xi_{\pm} = \exp(2\beta J_2)\cosh(2\beta J_1) \pm \exp(-2\beta J_2),$$
$$\eta_{\pm} = \frac{1}{2}\sqrt{8\{\cosh(2\beta J_1) \pm 1\} \pm 2\exp(4\beta J_2)\{\cosh(4\beta J_1) \pm 1\}}.$$

The maximum eigenvalue is λ_1 and λ_3 and λ_4 are complex conjugate each other because of the non-Hermitian matrix $\boldsymbol{M}_b$. The correlation functions $\boldsymbol{\Gamma}(r)$ are characterised by the factor $(\lambda_k/\lambda_1)^r$ in (11). Because of the complex eigenvalues λ_3 and λ_4, $\boldsymbol{\Gamma}(r)$ shows the feature of damping oscillation. In order to observe concretely the behavior of $\boldsymbol{\Gamma}(r)$, let us rewrite λ_k in the form as,

$$\lambda_2 \equiv \lambda_1 \exp(-\gamma_2) \quad \lambda_3 = \lambda_4^* \equiv \lambda_1 \exp(-\gamma_3 + 2\pi\hat{i}q) \tag{13}$$

where γ_2 and γ_3 are damping factors and q the wave number of the correlation function $\boldsymbol{\Gamma}(r)$ showing the damping oscillation. Substituting (13) into (11), we obtain

$$\boldsymbol{\Gamma}(r)_{\alpha,\beta} = a_{2,\alpha,\beta}\exp(-\gamma_2 r) + 2a_{3,\alpha,\gamma}\exp(-\gamma_3 r)\cos(2\pi q r) \tag{14}$$

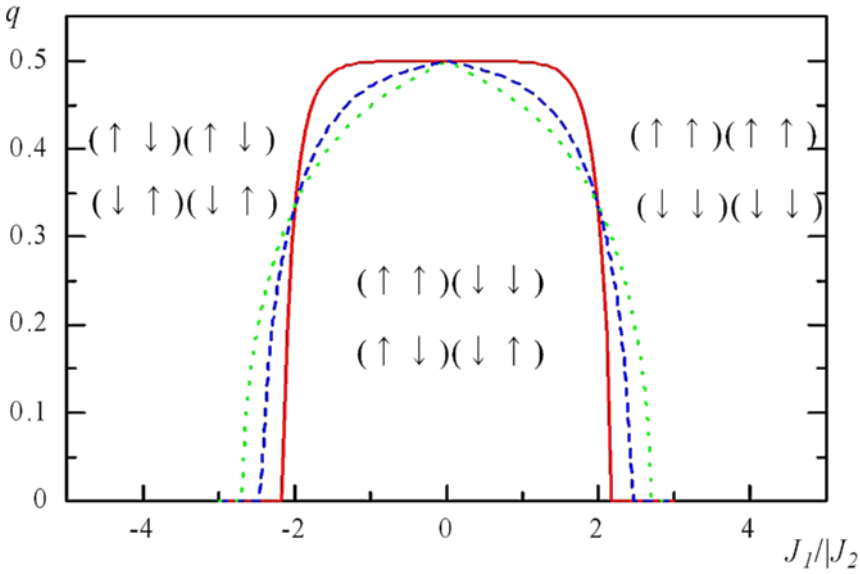


FIGURE 1 Incommensurate phase.

where $a_{k,\alpha,\beta}$ denotes a real part $\boldsymbol{U}_{\beta,1}\boldsymbol{U}_{1,\alpha}^{-1}\boldsymbol{U}_{\alpha,k}\boldsymbol{U}_{k,\beta}^{-1}$. The incommensurate structure along layer normal is exhibited by the oscillating correlation function with the wave number q.

Figure 1 shows q as a function of $J_1/|J_2|$ for $kT/|J_2| = 0.2$ (solid line), 0.6 (broken line) and 1.0 (dotted line).

At the absolute zero temperature, the phase transitionbetween ferroelectric phase $\big(q = 0 : (\uparrow\uparrow)(\uparrow\uparrow)\big)$ or antiferroelectric phase $(q = 0 : (\uparrow\downarrow)(\uparrow\downarrow))$, and AF phase $\big(q = 1/2 : (\uparrow\uparrow)(\downarrow\downarrow)\big)$ occurs at $J_1/|J_2| = \pm 2$, while no phase transition occurs at finite temperature because of one-dimensional system. However the remarkable change of q is observed even in finite temperature, that is, q changes from zero to the finite value (incommensurate phase) at a certain critical value of $J_1/|J_2|$, and q increases up to 1/2 (AF phase). The region of the incommensurate phase expands as the temperature increases.

Several block-spin = block-spin correlation functions are plotted as a function of "distance" r for ferroelectric phase (solid lines ; $J_1/|J_2| = 3.0$), antiferroelectric phase (broken lines ; $J_1/|J_2| = -3.0$) and AF phase (dotted lines ; $J_1/|J_2| = 0.01$) at $kT/|J_2| = 0.5$ in Figure 2. In

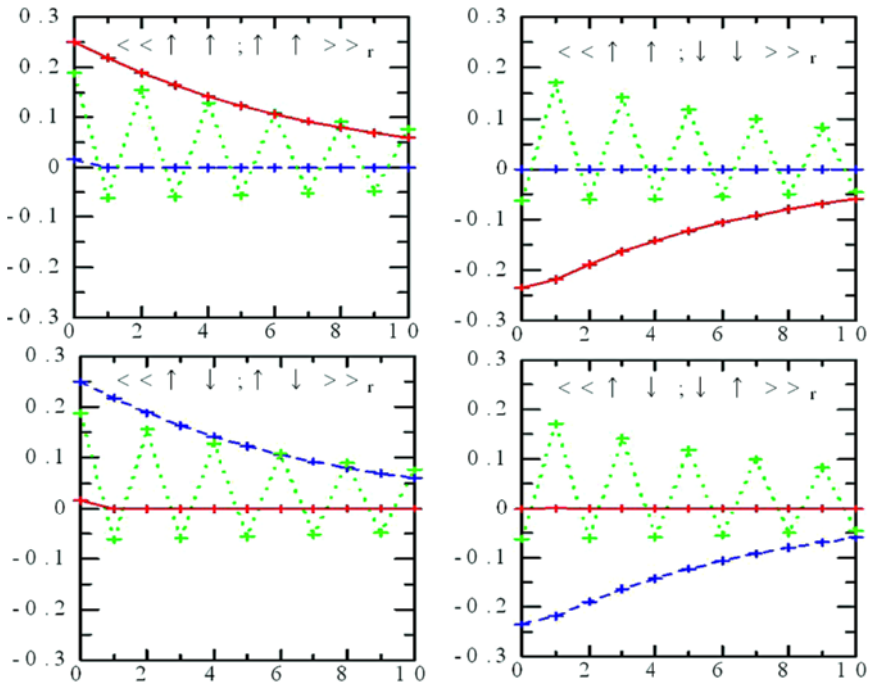


FIGURE 2 Correlation functions for block-spin.

the ferroelectric phase, $\ll\uparrow\uparrow;\uparrow\uparrow\gg_r$ shows the damping correlation, while $\ll\uparrow\uparrow;\downarrow\downarrow\gg_r$ comes to negative value which means that the joint probability for a couple of states $(\uparrow\uparrow)$ and $(\downarrow\downarrow)$ becomes almost zero in the ferroelectric phase. In the ferroelectric phase, the correlations $\ll\uparrow\downarrow;\uparrow\downarrow\gg_r$ and $\ll\uparrow\downarrow;\downarrow\uparrow\gg_r$ disappear. In antiferroelectric phase, $\ll\uparrow\downarrow;\uparrow\downarrow\gg_r$ exhibits a similar damping correlation to $\ll\uparrow\uparrow;\uparrow\uparrow\gg_r$ in the ferroelectric phase and $\ll\uparrow\downarrow;\downarrow\uparrow\gg_r$ shows negative correlation. In AF phase, as is clear, the damping and oscillating feature with wave number $q = 1/2$ appears in these correlation functions. The period of oscillating correlation functions of $\ll\uparrow\uparrow;\uparrow\uparrow\gg_r$ and $\ll\uparrow\downarrow;\uparrow\downarrow\gg_r$ are shifted by half wave length against that of $\ll\uparrow\uparrow;\downarrow\downarrow\gg_r$ and $\ll\uparrow\downarrow;\downarrow\uparrow\gg_r$.

4-STATE MODEL

In contrast to the block-spin model with frustration, we consider a non-frustrated model, that is, one-dimensional system of chiral molecules along layer normal, in which each chiral molecule takes four states of molecular orientation. Hereafter, we call this model a 4-state model. In this section, it is expected that the incommensurate structure along layer normal appears even in the 4-states model without frustration.

Let us make the four states of molecular orientation; $\left(\diamond\right)$, $\left(\diamond\right)$, $\left(\diamond\right)$, $\left(\diamond\right)$ to correspond to four vectors of the block-spin $\boldsymbol{\sigma}$ introduced in the above section, as follows:

$$\left(\diamond\right)_n \Rightarrow \boldsymbol{\sigma}_n = \begin{pmatrix} 1 \\ 0 \\ 0 \\ 0 \end{pmatrix}, \quad \left(\diamond\right)_n \Rightarrow \boldsymbol{\sigma}_n = \begin{pmatrix} 0 \\ 1 \\ 0 \\ 0 \end{pmatrix},$$

$$\left(\diamond\right)_n \Rightarrow \boldsymbol{\sigma}_n = \begin{pmatrix} 0 \\ 0 \\ 1 \\ 0 \end{pmatrix}, \quad \left(\diamond\right)_n \Rightarrow \boldsymbol{\sigma}_n = \begin{pmatrix} 0 \\ 0 \\ 0 \\ 1 \end{pmatrix}.$$

Furthermore, we define a group of interactions between neighboring chiral molecules along layer normal:

	$\left(\quad\right)_{n+1}$	$\left(\quad\right)_{n+1}$	$\left(\quad\right)_{n+1}$	$\left(\quad\right)_{n+1}$
$\left(\quad\right)_n$	$-f_2$	$-a_2$	$-f_1$	$-a_1$
$\left(\quad\right)_n$	$-a_2$	$-f_2$	$-a_1$	$-f_1$
$\left(\quad\right)_n$	$-f_3$	$-a_3$	$-f_2$	$-a_2$
$\left(\quad\right)_n$	$-a_3$	$-f_3$	$-a_2$	$-f_2$

where $-f_i$, $-a_i$ $(i = 1 \sim 3)$ denote the interaction parameters between the state of n-th chiral molecule and the state of $(n+1)$-th one. Then, Hamiltonian H_s of the 4-state model is written in terms of $\boldsymbol{\sigma}_n$ and $\boldsymbol{\sigma}_{n+1}$ as

$$H_s = \sum_n^A \boldsymbol{\sigma}_n^T \cdot \boldsymbol{K}_z \cdot \boldsymbol{\sigma}_{n+1} \tag{15}$$

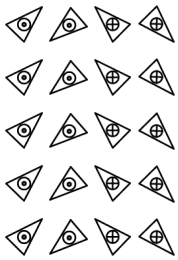
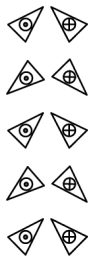
where the interaction matrix $\boldsymbol{K}_z$ is defined by

$$\boldsymbol{K}_z = \begin{pmatrix} -f_2 & -a_2 & -f_1 & -a_1 \\ -a_2 & -f_2 & -a_1 & -f_1 \\ -f_3 & -a_3 & -f_2 & -a_2 \\ -a_3 & -f_3 & -a_2 & -f_2 \end{pmatrix}, \tag{16}$$

and is also unsymmetrical one similar to the interaction matrix $\hat{\boldsymbol{J}}_z$ in (8) for the block-spin model. Then the transfer matrix derived from $\boldsymbol{K}_z$ comes to non-Hermitian. This fact suggests that the incommensurate structure appears even in the 4-state model without the frustration.

As a first step, we calculate the ground state of the 4-state model at absolute zero temperature. The results are classified in the cases of (1): $f_1 > a_1$, $f_3 > a_3$, (2): $a_1 > f_1$, $a_3 > f_3$, (3): $f_1 > a_1$, $a_3 > f_3$, and (4): $a_1 > f_1$, $f_3 > a_3$, as follows:

(1): $f_1 > a_1, f_3 > a_3$

$f_2 > a_2$ $f_2 > (f_1 + f_3)/2$ $E_0 = -Nf_2$	$a_2 > f_2$ $a_2 > (f_1 + f_3)/2$ $E_0 = -Na_2$	$(f_1 + f_3)/2 > a_2$ $(f_1 + f_3)/2 > f_2$ $E_0 = -N(f_1 + f_3)/2$
		
Ferro-1	Antiferro-1	Ferro-2

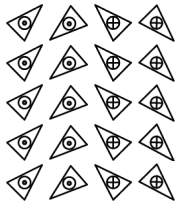
(2): $a_1 > f_1, a_3 > f_3$

$f_2 > a_2$ $f_2 > (a_1 + a_3)/2$ $E_0 = -Nf_2$	$a_2 > f_2$ $a_2 > (a_1 + a_3)/2$ $E_0 = -Na_2$	$(a_1 + a_3)/2 > f_2$ $(a_1 + a_3)/2 > a_2$ $E_0 = -N(a_1 + a_3)/2$
		
Ferro-1	Antiferro-1	Antiferro-2

(3): $f_1 > a_1, a_3 > f_3$

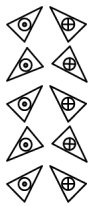
$f_2 > a_2$ $f_2 > (f_1 + a_3)/2$ $E_0 = -Nf_2$	$a_2 > f_2$ $a_2 > (f_1 + a_3)/2$ $E_0 = -Na_2$	$(f_1 + a_3)/2 > f_2$ $(f_1 + a_3)/2 > a_2$ $E_0 = -N(f_1 + a_3)/2$
		
Ferro-1	Antiferro-1	AF-1

(4): $a_1 > f_1, f_3 > a_3$

$f_2 > a_2$ $f_2 > (f_1 + a_3)/2$ $E_0 = -Nf_2$	$a_2 > f_2$ $a_2 > (f_1 + a_3)/2$ $E_0 = -Na_2$	$(a_1 + f_3)/2 > f_2$ $(a_1 + f_3)/2 > a_2$ $E_0 = -N(a_1 + f_3)/2$
		
Ferro-1	Antiferro-1	AF-2

At absolute zero temperature, there appear six phases; ferro-1, ferro-2, antiferro-1, antiferro-2, AF-1 and AF-2 phases depending on the interaction parameters, as is shown in the tables. When the interaction parameters $-f_2$ and $-a_2$ are large enough, a dimer of neighboring chiral molecules is constructed, then the ground state is given by

$f_2 = a_2 = -\infty$

$f_1 > a_1$ $f_3 > a_3$ $-(f_1 + f_3)/2$	$f_1 > a_1$ $f_3 < a_3$ $-(f_1 + a_3)/2$	$f_1 < a_1$ $f_3 > a_3$ $-(a_1 + f_3)/2$	$f_1 < a_1$ $f_3 < a_3$ $-(a_1 + a_3)/2$
			
Ferro-2	AF-1	AF-2	Antiferro-2

In this article, we consider only a dimer model ($-f_2 = -a_2 = -\infty$) for the simplicity and calculate the correlation functions for four phases shown in above table. Now, like the block-spin model, transfer matrix $\boldsymbol{M}_s$ derived from the interaction matrix $\boldsymbol{K}_z$ in (16) and the eigenvalues λ_i ($i = 1 \sim 4$) of $\boldsymbol{M}_s$ are calculated exactly as

$$\boldsymbol{M}_s = \begin{pmatrix} 0 & 0 & e^{\beta f_1} & e^{\beta a_1} \\ 0 & 0 & e^{\beta a_1} & e^{\beta f_1} \\ e^{\beta f_3} & e^{\beta a_3} & 0 & 0 \\ e^{\beta a_3} & e^{\beta f_3} & 0 & 0 \end{pmatrix} \tag{17}$$

and

$$\begin{aligned}
\lambda_1 &= 2\exp\left(\frac{y_1+y_3}{2t}\right)\sqrt{\cosh\left(\frac{x_1}{2t}\right)\cosh\left(\frac{x_3}{2t}\right)} \\
\lambda_2 &= -2\exp\left(\frac{y_1+y_3}{2t}\right)\sqrt{\cosh\left(\frac{x_1}{2t}\right)\cosh\left(\frac{x_3}{2t}\right)} \\
\lambda_3 &= 2\exp\left(\frac{y_1+y_3}{2t}\right)\sqrt{\sinh\left(\frac{x_1}{2t}\right)\sinh\left(\frac{x_3}{2t}\right)} \\
\lambda_4 &= -2\exp\left(\frac{y_1+y_3}{2t}\right)\sqrt{\sinh\left(\frac{x_1}{2t}\right)\sinh\left(\frac{x_3}{2t}\right)}
\end{aligned} \tag{18}$$

where

$$t=\frac{kT}{f_1+f_3} \quad x_1=\frac{f_1-a_1}{f_1+f_3} \quad x_3=\frac{f_3-a_3}{f_1+f_3}$$
$$y_1=\frac{f_1+a_1}{f_1+f_3} \quad y_3=\frac{f_3+a_3}{f_1+f_3}$$

The λ_1 is maximum eigenvalue. The eigenvalues λ_3 and λ_4 come to complex conjugate each other when $x_1x_3 < 0$ in which AF-1 phase or AF-2 one appears at the ground state as is shown in above table, at finite temperature, therefore, the appearance of incommensurate phase is expected. In order to observe the incommensurate structure of the 4-state model, we define a group of correlation functions $\mathbf{\Gamma}(r)$ between n-th chiral molecule and $(n+r)$-th one along layer normal, similar to the block-spin model, as follows,

$$\mathbf{\Gamma}(r) \equiv \begin{pmatrix} \ll ;\gg_r & \ll ;\gg_r & \ll ;\gg_r & \ll ;\gg_r \\ \ll ;\gg_r & \ll ;\gg_r & \ll ;\gg_r & \ll ;\gg_r \\ \ll ;\gg_r & \ll ;\gg_r & \ll ;\gg_r & \ll ;\gg_r \\ \ll ;\gg_r & \ll ;\gg_r & \ll ;\gg_r & \ll ;\gg_r \end{pmatrix} \tag{19}$$

For an example

$$\mathbf{\Gamma}(r)_{1,2} \equiv \ll ;\gg_r = < ;>_r - < >< >, \tag{20}$$

where $< ;>_r$ means the joint robability for a couple of states that n-th chiral molecule takes and $(n+r)$-th one and $< >$ the probability that a state of chiral molecule takes .

In Figure 3, the correlation functions of the 4-state model are plotted as a function of "distance" r along layer normal for ferro-2 phase (solid line; $x_1 = 0.5$, $x_3 = 1.5$), AF-2 phase (broken line; $x_1 = -0.5$, $x_3 = 0.5$),

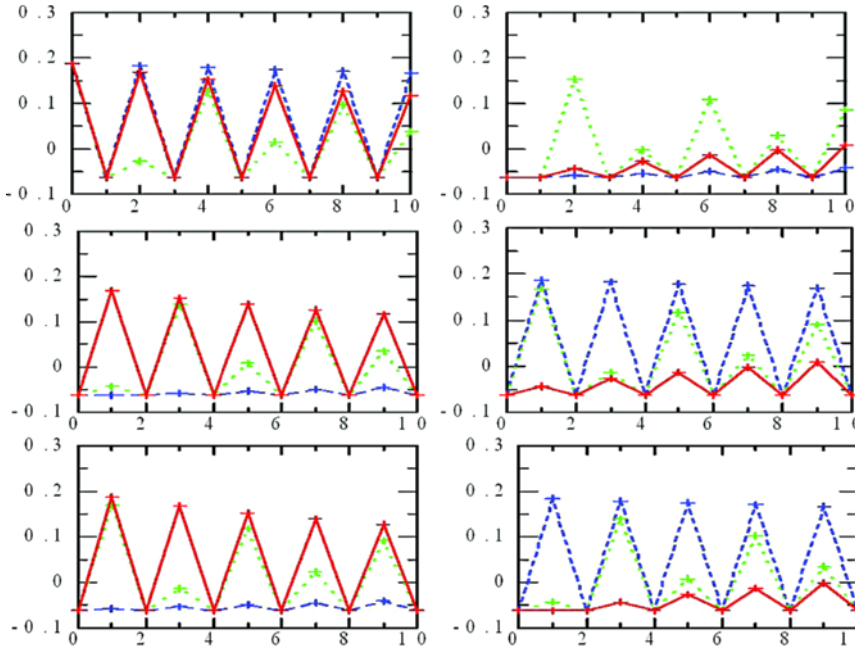


FIGURE 3 Correlation functions for 4-state model.

and antiferro-2 phase (dotted line; $x_1 = -1.8$, $x_3 = -0.8$) at $t = 0.2$. In the dimmer model, all of correlation functions show damping oscillation, because the joint probability that two neighboring chiral molecules take same state becomes zero at $-f_2 = -a_2 = \infty$. Then, for the ferro-2 phase and antiferro-2 one, the orientational structure with wave number $q = 1/2$ appear. For AF-2 phase, two kinds of the orientational structure with $q = 1/4$ are observed.

SUMMARY

In order to clear up the mechanism of incommensurate structure observed in antiferroelectric smectics, two different models have been considered and studied by the transfer matrix method. One is the block-spin model which is equivalent to the ANNNI model characterized by frustration due to competing interactions. Another is the 4-state model characterized by non-frustration, which is made up of the interactions between neighboring chiral molecules taking 4 states of orientational molecule. Both models are characterized by unsymmetrical interaction between neighboring block-spins or neighboring chiral molecules. The unsymmetrical interactions

establish non-Hermitian transfer matrix which causes the complex eigenvalues. As the result, correlation functions exhibit the feature of damping oscillation, that is, incommensurate structures along layer normal appear.

It is concluded that the incommensurate structures are caused not only by the frustration due to the competing interactions but also by the unsymmetrical interaction energy in adjacent block-spin or in adjacent chiral molecule along layer normal. In these models which are composed of four states of block-spin or orientational molecule, ferroelectric ($q = 0$), antiferroelectric ($q = 1/2$) and AF (q =1/4) phases are observed by the correlation functions, however more complicated phases such as SmC^*_γ (q =1/3) and FI_H ($q = 2/7$), which are observed in extended ANNNI model with third neighboring interaction J_3, are not exhibited. If we consider the system which consists of multiple states of chiral molecule or of block-spin made up successive three spin (s_i, s_{i+1}, s_{i+2}), it is expected that more complicated phases are observed in correlation functions. We may study the correlations for the complicated phases such as SmC^*_γ in near future.

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