Phase Transition Properties of a Ferroelectric Superlattice with Surface Modification

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The phase diagrams of a ferroelectric superlattice with finite alternating layers are investigated by using the transverse Ising model within the mean-field approximation. The effects of surface modification are introduced through a surface exchange interaction constant and a surface transverse field parameter. The results indicate that the features of the phase diagrams can be greatly modified by changing the transverse Ising model parameters. In addition, the crossover features of the inside transverse field parameters from the ferroelectric dominant phase diagram to the paraelectric dominant phase diagram are determined for a finite alternating superlattice.

Key words: Ferroelectrics; Phase Transitions.

1. Introduction

An exciting aspect of solid-state physics is the discovery or exploration of new classes of materials. During the past decades, much effort has been devoted to the study of artificially fabricated superlattices, because the physical properties of superlattices differ dramatically from simple solids. With the advancements of experimental techniques, which make it possible to obtain well characterized samples, ferroelectric superlattices have attracted considerable attention in recent years [1 – 6]. Theoretically, the static properties including polarization, susceptibility and pyroelectricity have been studied for ferroelectric superlattices using the Ginzburg-Landau phenomenological theory [7 – 10] and the transverse Ising model (TIM) [11 – 13]. Besides, by applying the mean-field approximation, Wang et al. [14, 15] investigated extensively the ferroelectric phase transition of superlattices. Zhou and Yang [16] used the effective field theory with correlations to calculate the Curie temperature of ferroelectric superlattices formed from two alternating materials. Kaneyoshi [17] studied the phase diagrams of a transverse Ising superlattice based on the decoupling approximation in the differential operator technique. In most of the above work, surface modifications on the systems were not discussed. However, the atoms in the surface region are in an environment which is different from that of the ones in the bulk of the ferroelectric superlattice, and consequently various parameters of the surface of the TIM used to describe the ferroelectric superlattice may differ from those of the bulk. In the earlier literature, Sy et al. [18, 19], have modified the surface layer to study the magnetic properties in an alternating superlattice.

In the present paper we investigate the phase transition properties of ferroelectric superlattices by modifying the transverse Ising model parameters of the surface layer. The phase diagrams are described in two ways, and the dependence of the phase diagrams on the TIM parameters is obtained by calculating the coefficient determinants.

2. Theory

We consider a finite ferroelectric superlattice with alternative slabs. A good description for H-bonded ferroelectric systems is generally believed to be the TIM within the framework of the pseudo-spin theory. The Hamiltonian of the model can be written as [14 – 19]

$$H = \sum_i \Omega_i S_i^x - \frac{1}{2} \sum_{ij} J_{ij} S_i^z S_j^z, \quad (1)$$

where $\Omega_i$ is the transverse field, $S_i^x$ and $S_i^z$ are the $x$ and $z$ components of a spin-$\frac{1}{2}$ operator at site $i$, and $J_{ij}$ is the exchange interaction constant between the $i$-th and $j$-th site, where $i$ and $j$ run over only the nearest-neighbouring sites. As shown in Fig. 1, we introduce...
the same values, the spin average along the assuming that the pseudo-spins in the same layer have

\[ J_{ij} \]

or

\[ \Omega \]

with the surface layer.

Fig. 1. Schematic illustration of a ferroelectric superlattice

\[ H_{1} = \sqrt{\Omega_{1}^{2} + (H_{1}^{2})} \] (4)

When the temperature approaches the Curie temperature, the spin average tends to zero. Therefore we can obtain from (2) – (4) the simple expressions for the finite alternating superlattice.

For the surface layers we have

\[ \tau_{S} S_{0} = 4JS_{S} S_{0} + JS_{B} \],

\[ \tau_{S} S_{2n+2} = 4JS_{S} S_{2n+2} + JS_{2n+2}, \] (5)

and for the other alternating layers

\[ \tau_{A} S_{i} = 4JA S_{i} + J (S_{i+1} + S_{i-1}) \ (i = 1, 3, \cdots, 2n + 1), \]

\[ \tau_{B} S_{i} = 4JB S_{i} + J (S_{i+1} + S_{i-1}) \ (i = 2, 4, \cdots, 2n), \] (6)

where \( S_{i} \) denotes \( \langle S_{i} \rangle \), and

\[ \tau_{S} = 2\Omega_{S} \coth \frac{\Omega_{S}}{2k_{B} T} \]

\[ \tau_{A} = 2\Omega_{A} \coth \frac{\Omega_{A}}{2k_{B} T} \]

\[ \tau_{B} = 2\Omega_{B} \coth \frac{\Omega_{B}}{2k_{B} T} \] (7)

Then, the following coefficient determinant equation can be obtained:

\[ \det \left[ \begin{array}{ccc} X_{S} - 1 & -1 & -1 \\ -1 & X_{A} - 1 & -1 \\ -1 & -1 & X_{B} - 1 \end{array} \right] = 0, \] (8)

where \( X_{S} = \frac{(\gamma - 4J_{S})}{J} \), \( X_{A} = \frac{(\gamma - 4J_{A})}{J} \), and \( X_{B} = \frac{(\gamma - 4J_{B})}{J} \). We expand the above equation as

\[ (\xi_{S}^{2} X_{A}/X_{B}) C_{2n+1} - 2X_{S} D_{2n} + C_{2n-1} = 0, \ n \geq 1, \] (9)

where the two determinants \( D_{2n} \) and \( C_{2n-1} \) are defined as

\[ D_{2n} = \det \left[ \begin{array}{ccc} X_{A} - 1 & -1 & -1 \\ -1 & X_{B} - 1 & -1 \\ -1 & -1 & X_{A} - 1 \end{array} \right] \] (10)

\[ C_{2n-1} = \det \left[ \begin{array}{ccc} X_{B} - 1 & -1 & -1 \\ -1 & X_{A} - 1 & -1 \\ -1 & -1 & X_{B} \end{array} \right] \] (2n-1)×(2n-1)
The solutions of (10) have been evaluated as [18] and here

\[ D_{2n} = \frac{\sinh(n + 1)\phi + \sinh(n\phi)}{\sinh\phi}, \]

\[ C_{2n-1} = \frac{2\sinh(n\phi)(\cosh\phi + 1)}{X_A \sinh\phi}, \]

and here

\[ 2\cosh\phi = X_A X_B - 2. \] (12)

### 3. Results and Discussion

In order to obtain a general view of the phase transition, we follow Teng and Sy’s [20, 21] definitions of
the ferroelectric dominant phase diagram (FPD) and the paraelectric dominant phase diagram (PPD) (see Fig. 2a). The FPD means that, while the temperature is below a certain value, the system is ferroelectric irrespective of any $J_S$. This is to say, any $J_S$ can result in a transition from a ferroelectric to a paraelectric phase with increasing the temperature. In contrast, the PPD means that, while $J_S$ is less than a certain value, the system is paraelectric irrespective of any temperature. In other words, only larger $J_S$ can result in a transition from a ferroelectric to a paraelectric phase with increasing the temperature [20, 21].

In most of the discussions of ferroelectric thin films, the phase diagrams are described in two ways: the re-
lations between the Curie temperature, $T_c$, and the surface exchange interaction, $J_S$ [18–23], as well as the Curie temperature and the surface transverse field, $\Omega_S$ [23–25]. In this paper we will discuss the effects of the TIM parameters on the phase diagrams for a finite alternating superlattice, with use of the definitions of the FPD and PPD. The numerical calculations for the two different sorts of phase diagrams in the TIM are given in the figures.

Figures 2, 3, 4 and 5 give the phase diagrams between the Curie temperature and the exchange interaction on the surface. Figures 2 and 3 give the curves of different values of the transverse field $\Omega_A$ or $\Omega_B$, and it is shown that the phase diagram depends sensitively on $\Omega_A$ or $\Omega_B$. The larger the transverse field $\Omega_A$ or $\Omega_B$, the larger is the range of the paraelectric phase; and the smaller the parameter $\Omega_A$ or $\Omega_B$, the larger is the range of the ferroelectric phase. The crossover feature from the FPD to PPD is also shown in Figure 2. It is obvious that, when $\Omega_A$ or $\Omega_B$ have less than the crossover value $\Omega_C^A$ or $\Omega_C^B$, the phase diagram is in the FPD, and any $J_S$ can result in a transition from the ferroelectric

![Fig. 4. The effect of $\Omega_A$ on the phase diagram ($\Omega_B < 2J_B$). All curves are for $\Omega_B/J = 1.8, J_A/J = 2, J_B/J = 1, \Omega_S/J = 2$, and $n = 2$.](image1)

![Fig. 5. The effect of the layer number $n$ on the phase diagram. All curves are for $\Omega_A/J = 4.6, \Omega_B/J = 3, J_A/J = 2, J_B/J = 1$, and $\Omega_S/J = 2$.](image2)
to the paraelectric phase with increasing the temperature. However, when $\Omega_A$ or $\Omega_B$ is larger than $\Omega^C_A$ or $\Omega^C_B$, the phase diagram is in the PPD, and only larger $J_S$ can result in a transition from the ferroelectric to the paraelectric phase with increasing the temperature. Figures 2a and 2b also reveal the effect of the layer number on the crossover value of the parameter $\Omega_A$. The thicker the superlattice, the larger is the crossover value $\Omega^C_A$. Figures 3a and 3b also show the effect of the surface transverse field $\Omega_S$ on the crossover value of the parameter $\Omega_B$. The larger the surface transverse field $\Omega_S$, the smaller is the crossover value $\Omega^C_B$. Simultaneously, we find that larger $\Omega_S$ will result in a larger range for the paraelectric state as well. In addition, the dependence of $\Omega_A$ on $\Omega_S$ is similar to that of $\Omega_B$, and the dependence of $\Omega_B$ on the superlattice thickness is also similar to that of $\Omega_A$; so we do not give a detailed discussion of these situations.

However, comparing Fig. 2 and Fig. 4, we find that the appearance of the crossover value of the parameter $\Omega_A$ is determined by the relation between the transverse field $\Omega_S$ and the exchange interaction $J_B$. Figures 2a and 2b indicate that, when $\Omega_B > 2J_B$, there exists a crossover value $\Omega^C_A$ from the FPD to PPD. Figure 4 shows that, when $\Omega_B < 2J_B$, the phase diagram is always in the FPD, irrespective of $\Omega_A$, and this is to say, there does not exist a crossover value $\Omega^C_A$. At the same time, it can be seen from Fig. 3 that in the region of $\Omega_A > 2J_A$ there always exists a crossover value $\Omega^C_B$ in the phase diagram. In fact, the numerical calculations reveal that in the region of $\Omega_A < 2J_A$, there does not exist a crossover value $\Omega^C_B$. These phase transition properties are similar to those of ferroelectric thin films [20, 23].

Figure 5 shows the dependence of the phase diagram on the thickness of the superlattice. It can be clearly seen that the five-layer superlattice has no phase transition, and it is always paraelectric in the entire temperature range, but only if the surface interaction strength $J_S$ is sufficiently weak. When the ferroelectric superlattice is thicker than five layers, the more layers the superlattice contains, the larger is the range of the ferroelectric phase.

Figures 6 and 7 are the phase diagrams showing the relations between the Curie temperature and the transverse field on the surface. Figure 6 shows the dependence of the phase diagram on the surface exchange interaction $J_S$: it can be seen that a larger $J_S/J$ will result in a larger range for the ferroelectric state. Figure 7 shows how the phase diagram depends on the exchange
interaction constants $J_A$ and $J_B$. One sees from Fig. 6 that the larger the ratio $J_A/J_B$, the larger is the ferroelectric range in the phase diagram. Obviously, the phase diagram depends sensitively on the exchange interaction $J_S$, $J_A$ and $J_B$.

4. Conclusion

In summary, we have studied the ferroelectric phase properties of a finite alternating superlattice described by the transverse Ising model. Although the mean-field approximation, compared with the effective field theory and the decoupling approximation in the differential operator technique, may exaggerate the ferroelectric feature of a superlattice, our numerical results can reveal explicitly how the phase diagram depends on the transverse Ising model parameters by using the mean-field approximation. Meanwhile, the crossover features of the parameters from the FPD to PPD are given for the ferroelectric superlattice. In fact, the surface modification may be similarly introduced into other transverse Ising superlattices for studying the ferroelectric phase transitions. We hope that these results may provide some useful information for theoretical and experimental work on ferroelectric superlattices, with the developments of the experimental techniques in this field.

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