The Effects of the Layer-Dependent Interaction Parameters on the Phase Diagrams and Polarizations of the Ferroelectric Thin Film

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Z. Naturforsch. **65a,** 725 – 732 (2010); received July 24, 2008 / revised Novmber 21, 2008

While the exchange interaction and the transverse field parameters are changed with the layers of the ferroelectric thin film, the properties of phase transition of the transverse field Ising model have been studied within the framework of the mean field approximation. The phase diagrams and polarizations of the ferroelectric thin film have been calculated numerically in the different situations of the interaction parameters changed with the layers. The results show that various layer-dependent parameters changed gradually layer by layer have sensitive effects on the phase diagrams and the polarizations of the *n*-layer ferroelectric thin film.

Key words: Ferroelectrics; Layer-dependent Parameters; Phase Diagrams.
PACS numbers: 68.65.Cd; 05.50.+q; 77.80.Bh

1. Introduction

Although the surface and size effects on the phase transitions in ferroelectrics have been known since the 1950's, it aroused a renewed interest in recent years due to the development of ferroelectric thin films and composites [1 – 7]. Owning to their special properties, the ferroelectric thin films and superlattices have been widely investigated both experimentally [8 – 11] and theoretically [12 – 23]. The transverse field Ising model (TFIM), introduced firstly by de Gennes [24], was believed to describe reasonably the phase transition properties in potassium dihydrogen posphate (KDP)-like ferroelectrics [25]. Because TFIM can not be solved exactly, many approximations have been applied to study the transition properties of this model [13 – 23]. Usually, TFIM can be treated with the mean field approximation [12 – 18], the effective-field theory with correlations [26, 27], the decoupling approximation in the differential operator technique [19, 28], and the Green function method [20 – 23]. However, in earlier papers for the transition properties of the ferroelectric thin film [13, 29 – 31], the three interaction parameters in TFIM (the intra-layer and the inter-layer interactions as well as the transverse field parameter) are usually considered as constant ones. In fact, impurities, vacancies, or dislocations etc, are widely present in the thin film. Therefore, the interaction parameters of the ferroelectric thin film materials should be changed with the layers. Recent researches have shown that these defect layers have considerable impact on the phase transformation properties, such as the polarizations, the lattice parameters, the Curie temperature, the spin-wave energies, and the elementary excitations [32 – 37]. The polarization gradients even have detrimental effects on the ferroelectric properties, especially of the ultrathin ferroelectric thin films, due to the coupling of the stress field of the dislocation and the polarization [32]. In this paper, we study the effects of the interaction parameters changed layer by layer on the properties of phase transition of the ferroelectric thin film. Firstly, we consider how the exchange interaction and the transverse field parameters are changed layer by layer and suppose the parameters decrease or increase gradually according to some identical functions from the surface to the interior of the thin film. Then we investigate the impacts of these gradually changed parameters on the properties of phase transition of the ferroelectric thin film. Because the layer-dependent interaction parameters are changed layer by layer, it refers that each layer in the ferroelectric thin film is equivalent to a different defect layer to some extent. Therefore, the investigation to the phase diagrams and polarizations of the *n*-layer ferroelectric thin film while changing the different exchange interactions and the transverse field gradually and layer by layer may be considered as the extension of the previous works [29,34,35].

2. Numerical Results for the Phase Diagrams and Polarizations

The Hamiltonian of the system based on the transverse field Ising model [12–17] is

$$H = -\sum_i \Omega_i S_{ix} - \sum_{\langle i,j\rangle} J_{ij} S_{iz} S_{jz}, \tag{1}$$

where Ω_i is the transverse field, S_{ix} and S_{iz} the x- and z-components of a spin-$\frac{1}{2}$ operator at site i, J_{ij} the two-spin exchange interaction between site i and site j, and $\sum_{\langle i,j\rangle}$ runs over only the nearest-neighbouring sites. The schematic illustration of the n-layer ferroelectric thin film is shown in Figure 1. Assuming that the z-direction is perpendicular to the interface and the polarization is along the z-direction, the spin average along the z-direction in the ith layer can be expressed by [12–17]

$$\langle S_{iz}\rangle = (H_{iz}/2|H_i|)\tanh(|H_i|/2k_B T), \tag{2}$$

where

$$H_{iz} = zJ_{ii}\langle S_{iz}\rangle + J_{i,i+1}\langle S_{i+1,z}\rangle + J_{i,i-1}\langle S_{i-1,z}\rangle, \tag{3}$$

$$|H_i| = \sqrt{\Omega_i{}^2 + H_{iz}{}^2}, \tag{4}$$

and z is the number of nearest-neighbours in the same layer of site i. Considering that $\langle S_{iz}\rangle$ will be small while the temperature is near the Curie temperature, we have a set of equations with respect to the reducing arbitrary parameters J:

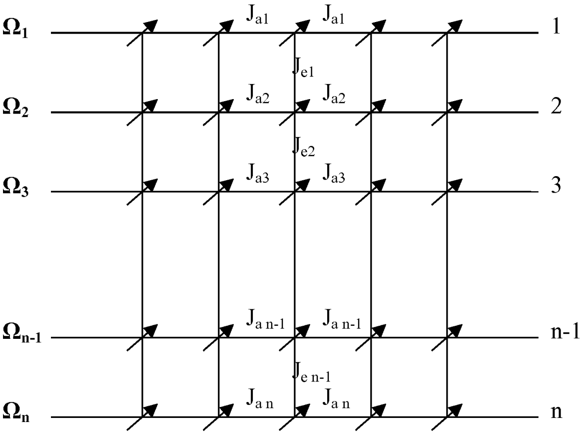

Fig. 1. Schematic illustration of the n-layer ferroelectric thin film.

$$\tau_i S_i = z j_{ii} S_i + j_{i,i+1} S_{i+1} + j_{i,i-1} S_i - 1, \tag{5}$$

where

$$\tau_i = \frac{2\Omega_i}{J}\coth\left(\frac{\Omega_i/J}{2t_\mathrm{c}}\right), \tag{6}$$

$$t_\mathrm{c} = \frac{k_\mathrm{B}T}{J}, \tag{7}$$

$$j_{ii} = \frac{J_{ii}}{J}, \tag{8}$$

$$j_{i,i+1} = \frac{J_{i,i+1}}{J}, \tag{9}$$

$$j_{i,i-1} = \frac{J_{i,i-1}}{J}, \tag{10}$$

In the following, we will study the phase diagrams and the polarizations while the exchange interactions and the transverse field are changed with the layers of the n-layer ferroelectric thin film. Because the interaction parameters in the film are layer-dependent, the coefficient determinant with respect to (5) can not be analytically calculated as usual. So we assume that the two exchange interactions and the transverse field are changed according to some identical functions with respect to the layer number n. Usually, the surface in a material can affect the interior gradually. That means that the parameters in each layer of the thin film are different. So we can assume the parameters in each layer decreasing or increasing from the surface to the interior. Meanwhile the farer the layer is away from the surface, the less the interaction parameters change. And finally the surface in a material has little effect on the most interior when the layer number is large. In order to describe the tendency that the interaction parameters vary layer by layer, we consider that the parameters are changed according to the following decreasing or increasing functions:

a) the slowly and fast decreasing functions:

$$F_\mathrm{DS} = D_0\Big(1 + \frac{\alpha_1}{n}\Big) \text{ and } F_\mathrm{DF} = D_0\left(1 + \frac{\alpha_2}{n^3}\right), \tag{11}$$

b) the slowly and fast increasing functions:

$$F_\mathrm{IS} = I_0\left(1 - \frac{\alpha_1}{n}\right) \text{ and } F_\mathrm{IF} = I_0\left(1 - \frac{\alpha_2}{n^3}\right), \tag{12}$$

where D_0 or I_0 denotes $J_{\mathrm{a}0}$, $J_{\mathrm{e}0}$ or Ω_0.

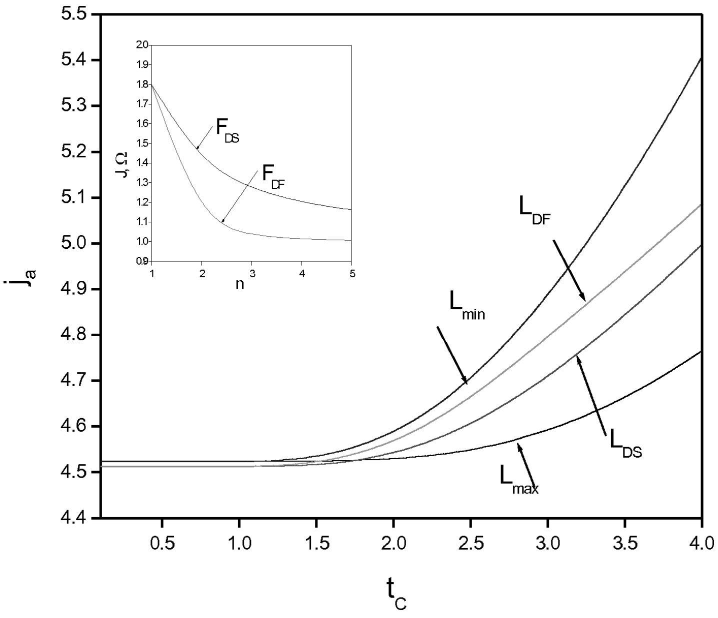

Fig. 2. Phase diagram for the intra-layer exchange interaction j_a and the Curie temperature t_C while the exchange interactions and the transverse field decrease with the layers. The interaction parameters in Line L_{DS} decrease slower than the ones in Line L_{DF}. The parameters in Line L_{max} is largest and the parameters in Line L_{min} is smallest. All curves are for $J_{e0}/J = 1$, $\Omega_0/J = 10$, $\alpha = \beta = \gamma = 0.5$. The inset figure shows the tendencies of the parameters decreased slowly or fast.

In this way, the phase diagrams and the polarizations for the n-layer ferroelectric thin film can be calculated when the interaction parameters are determined by the above functions. Defining three new parameters j_a, j_e and ω as $j_a = \frac{J_{a0}}{J}, j_e = \frac{J_{e0}}{J}, \omega = \frac{\Omega_0}{J}$, the phase diagrams which describe the relations between the Curie temperature and the exchange interactions or the transverse field ($j_a \sim t_C$, $j_e \sim t_C$ or $\omega \sim t_C$) can be calculated numerically as follows. For simplicity, we study the phase transition properties of a 9-layer ferroelectric thin film.

Based on (5)–(12), the Curie temperature can be derived from the coefficient determinant when the interactions vary according to the functions of F_{DS}, F_{DF}, F_{IS}, or F_{IF}. The following expressions refer to the situation of the slow decreasing function F_{DS}. Here the symmetry for the upper and lower surface is considered.

$$\det\begin{bmatrix} X_1 & -Y_1 & & & & & & & \\ -Y_1 & X_2 & -Y_2 & & & & & & \\ & -Y_2 & X_3 & -Y_3 & & & & & \\ & & -Y_3 & X_4 & -Y_4 & & & & \\ & & & -Y_4 & X_5 & -Y_4 & & & \\ & & & & -Y_4 & X_4 & -Y_3 & & \\ & & & & & -Y_3 & X_3 & -Y_2 & \\ & & & & & & -Y_2 & X_2 & -Y_1 \\ & & & & & & & -Y_1 & X_1 \end{bmatrix}_{9\times 9} = 0, \qquad (13)$$

where

$$X_1 = 2\cdot[\Omega_0\cdot(1+\gamma)]\cdot\coth\left[\Omega_0\cdot\frac{(1+\gamma)}{2\cdot t}\right] - 4\cdot J_{a0}(1+\alpha),$$

$$X_2 = 2\cdot\left[\Omega_0\cdot\left(1+\frac{\gamma}{2}\right)\right]\cdot\coth\left[\Omega_0\cdot\frac{\left(1+\frac{\gamma}{2}\right)}{2\cdot t}\right] - 4\cdot J_{a0}\cdot\left[1+\frac{\alpha}{2}\right],$$

$$X_3 = 2\cdot\left[\Omega_0\cdot\left(1+\frac{\gamma}{3}\right)\right]\cdot\coth\left[\Omega_0\cdot\frac{\left(1+\frac{\gamma}{3}\right)}{2\cdot t}\right] - 4\cdot J_{a0}\cdot\left[1+\frac{\alpha}{3}\right],$$

$$X_4 = 2\cdot\left[\Omega_0\cdot\left(1+\frac{\gamma}{4}\right)\right]\cdot\coth\left[\Omega_0\cdot\frac{\left(1+\frac{\gamma}{4}\right)}{2\cdot t}\right] - 4\cdot J_{a0}\cdot\left[1+\frac{\alpha}{4}\right],$$

$$X_5 = 2\cdot\left[\Omega_0\cdot\left(1+\frac{\gamma}{5}\right)\right]\cdot\coth\left[\Omega_0\cdot\frac{\left(1+\frac{\gamma}{5}\right)}{2\cdot t}\right] - 4\cdot J_{a0}\cdot\left[1+\frac{\alpha}{5}\right],$$

$$Y_1 = J_{e0}\cdot(1+\beta), \quad Y_2 = J_{e0}\cdot\left(1+\frac{\beta}{2}\right),$$

$$Y_3 = J_{e0}\cdot\left(1+\frac{\beta}{3}\right), \quad Y_4 = J_{e0}\cdot\left(1+\frac{\beta}{4}\right).$$

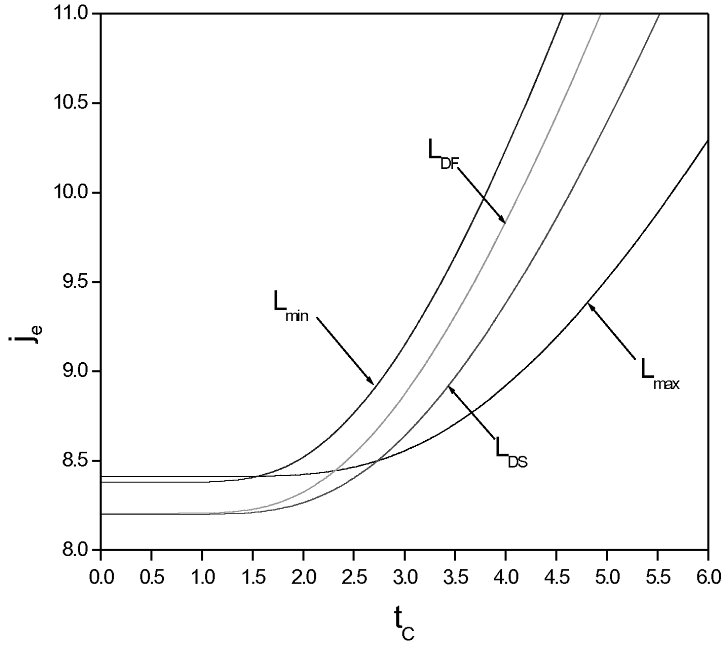

Fig. 3. Phase diagram for the inter-layer exchange interaction j_e and the Curie temperature t_C while the exchange interactions and the transverse field decrease with the layers. All curves are for $J_{a0}/J = 1$, $\Omega_0/J = 10$, $\alpha = \beta = \gamma = 0.5$.

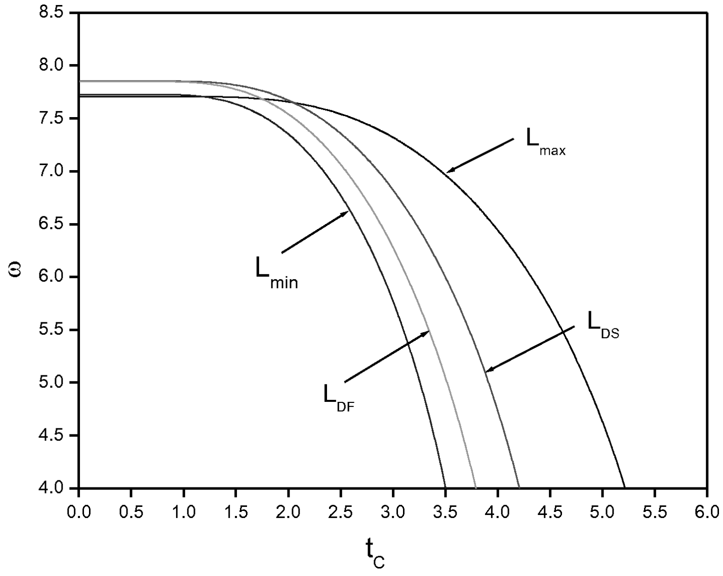

Fig. 4. Phase diagram for the transverse field ω and the Curie temperature t_C while the exchange interactions and the transverse field decrease with the layers. All curves are for $J_{a0}/J = 1$, $J_{e0}/J = 6$, $\alpha = \beta = \gamma = 0.5$.

Solving the determinant of (13) numerically, the phase diagrams described by the relations between the interaction parameters and the Curie temperature are shown in Figures 2–4. In the calculation we assume the interaction parameters decreasing slowly and fast with the layers, respectively. Obviously, the parameters are largest when the parameters take the values of the first layer from the function of F_{DS} or F_{DF} $(n = 1)$, and smallest when the parameters take the values of the fifth layer from the function of F_{DF} $(n = 5)$. In order to compare the effect of the layer-dependent parameters on the phase diagrams, we calculate firstly the phase diagrams while the parameters of the ferroelectric thin film are layer-independent. The lines L_{max} and L_{min} are referred to the results that the layer-independent parameters take the largest or the smallest ones, respectively. Then we calculate the phase diagrams while the three interaction parameters decrease

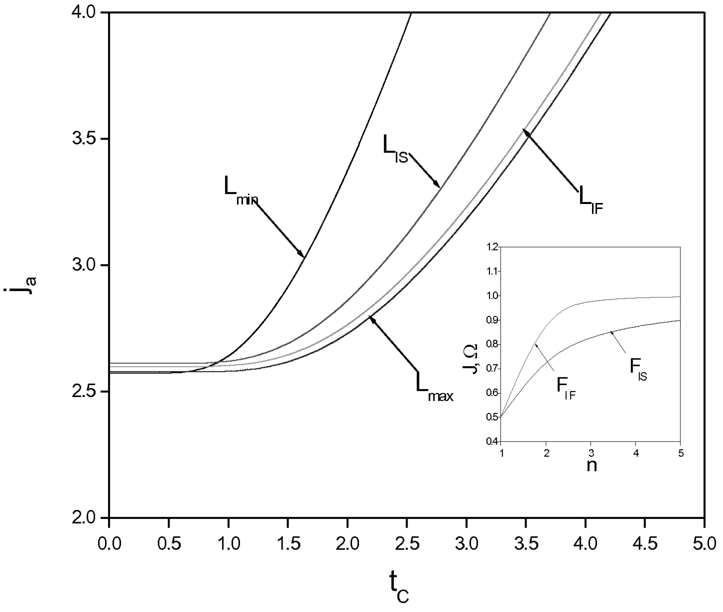

Fig. 5. Phase diagram for the intra-layer exchange interaction j_a and the Curie temperature t_C while the exchange interactions and the transverse field increase with the layers. The interaction parameters in Line $\mathrm{L_{IS}}$ increase slower than the ones in Line $\mathrm{L_{IF}}$. The parameters in Line $\mathrm{L_{max}}$ is largest and the parameters in Line $\mathrm{L_{min}}$ is smallest. All curves are for $J_{\mathrm{e}0}/J = 3$, $\Omega_0/J = 8$, $\alpha = \beta = \gamma = 0.4$. The inset figure shows the tendencies of the parameters increased slowly or fast.

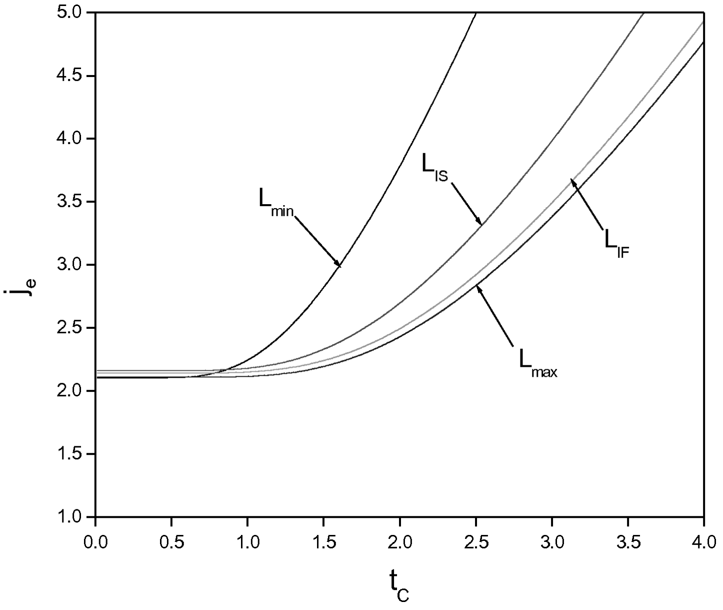

Fig. 6. Phase diagram for the inter-layer exchange interaction j_e and the Curie temperature t_C while the exchange interactions and the transverse field increase with the layers. All curves are for $J_{\mathrm{a}0}/J = 3$, $\Omega_0/J = 8$, $\alpha = \beta = \gamma = 0.4$.

with the layers slowly or fast. The results are shown as $\mathrm{L_{DS}}$ and $\mathrm{L_{DF}}$. We can see that for the given values of the parameters $J_{\mathrm{a}0}/J$, $J_{\mathrm{e}0}/J$, or Ω_0/J, the ferroelectric range with respect to $\mathrm{L_{max}}$ is largest and the one with respect to $\mathrm{L_{min}}$ is smallest. While the three parameters decrease with the layers, the ferroelectric range is changed synchronously. Meanwhile, the faster the parameters decrease, the smaller the ferroelectric range is. It indicates that the tendency of the changes for the three parameters has sensitive effects on the phase diagrams.

What effects have the layer-dependent parameters on the phase diagrams while the interaction parameters increase with the layers? The similar results to Figures 2–4 are given in Figures 5–7. Here the parameters are smallest when the parameters take the values of the first layer from the function of F_IS or F_IF $(n = 1)$, and largest when the parameters take the values of the

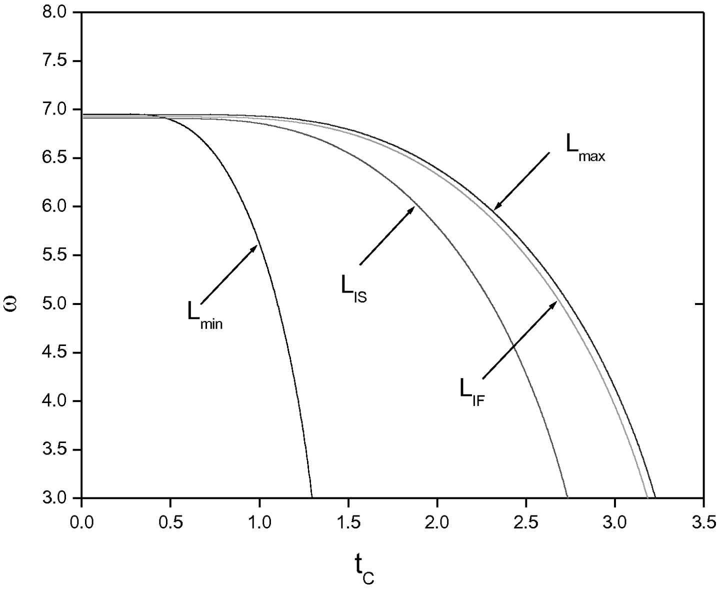

Fig. 7. Phase diagram for the transverse field ω and the Curie temperature t_C while the exchange interactions and the transverse field increase with the layers. All curves are for $J_{a0}/J = 3$, $J_{e0}/J = 1$, $\alpha = \beta = \gamma = 0.6$.

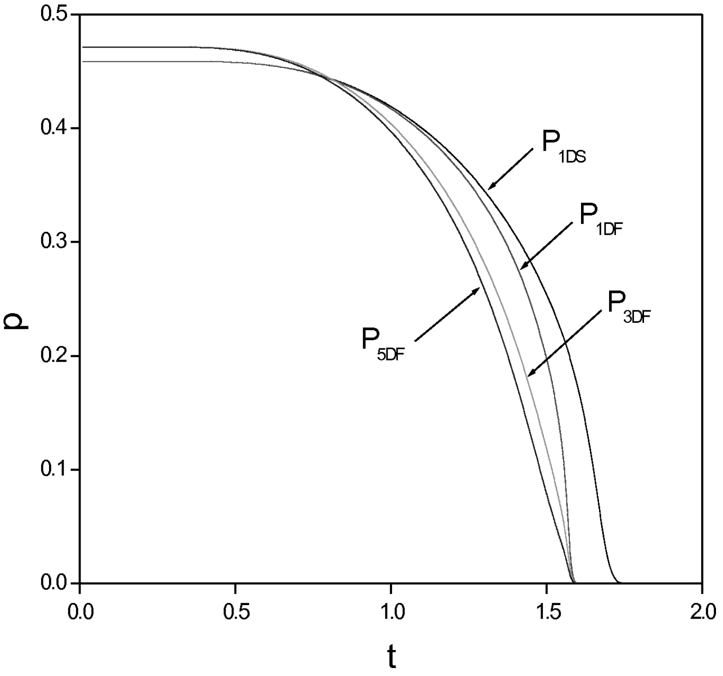

Fig. 8. Polarization versus the temperature t while the parameters decrease with the layers. P_{1DS} and P_{1DF} are the polarizations of the first layer while the parameters decrease slowly and fast with the layers, and P_{3DF} and P_{5DF} are the polarizations of the third layer and the fifth layer while the parameters decrease fast with the layers, respectively. All curves are for $\alpha = \beta = \gamma = 0.4$ and $J_{a0}/J = J_{e0}/J = \omega_0/J = 1$.

fifth layer from the function of F_{IF} $(n = 5)$. We calculate first the phase diagrams while the parameters of the ferroelectric thin film are layer-independent, and use the lines L_{max} and L_{min} to show the results that the layer-independent parameters take the largest or the smallest ones, respectively. Then the results for the phase diagrams while the three interaction parameters increase with the layers slowly or fast are shown as L_{IS} or L_{IF}. It is obvious that for the given values of the parameters J_{a0}/J, J_{e0}/J, or Ω_0/J, the ferroelectric range with respect to L_{max} is largest and the one with respect to L_{min} is smallest. Meanwhile the ferroelectric range is changed synchronously when the three parameters increase with the layers. That means,

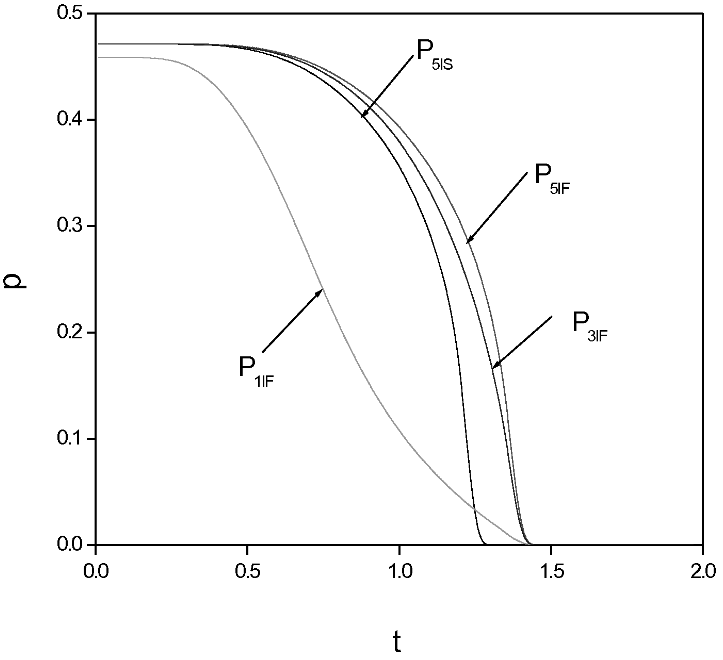

Fig. 9. Polarization versus the temperature t while the parameters increase with the layers. P_{5IS} and P_{5IF} are the polarizations of the fifth layer while the parameters increase slowly and fast with the layers, and P_{1IF} and P_{3IF} are the polarizations of the first layer and the third layer while the three parameters increase fast with the layers, respectively. All curves are for $\alpha = \beta = \gamma = 0.4$ and $J_{a0}/J = J_{e0}/J = \omega_0/J = 1$.

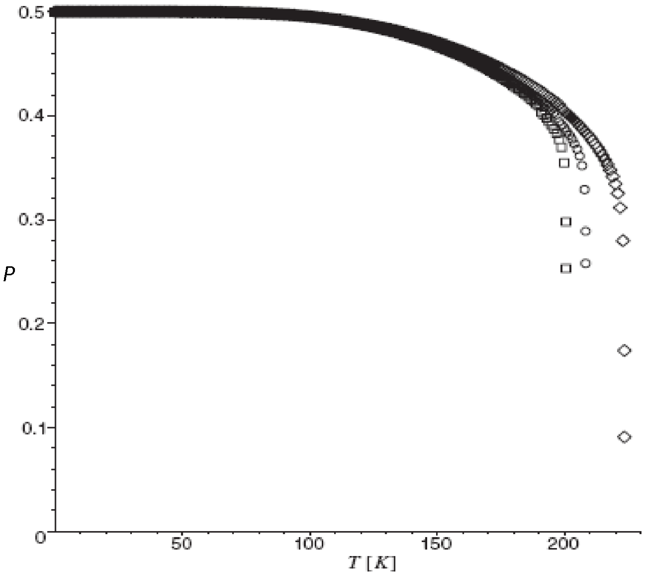

Fig. 10. Temperature dependence of the polarization P of the ferroelectric thin film with $J_b = 495$ K, $\omega_b = 20$ K, $J_s = 900$ K, $\omega_s = \omega_b$, $N = 9$, and different J_d-values: (1). $J_d = 300$ K, $T_C = 201$ K (□), (2). $J_d = 495$ K, $T_C = 208$ K (○), (3). $J_d = 1000$ K, $T_C = 224$ K (◇). This figure is cited from [35].

the faster the parameters increase, the larger the ferroelectric range is. Similar results as in Figures 2–4 are achieved. Namely, the tendencies of the changes for the three parameters have sensitive effects on the phase diagrams.

The polarizations can be obtained by the iterative calculation based on (2)–(4). First we give out polarizations of the first, the third, and the fifth layers while the parameters *decrease* fast with the layers. They are expressed as P_{1DF}, P_{3DF}, and P_{5DF} in Figure 8. Although the polarizations of each layer are different, they have a common Curie temperature. In order to compare the effects of different tendencies for layer-dependent parameters on the polarizations of the thin film, we then calculate the polarizations of each layer while the parameters decrease slowly with the layers. For simplicity, only the polarization P_{1DS} of the first layer is shown in Figure 8. It is obvious that for the given values, the faster the parameters decrease, the smaller the Curie temperature is. In contrast to the polarizations in Figure 8, we give the polarizations of each layer while the parameters *increase* fast or slowly with the layers in Figure 9. It comes to the similar result that the faster the parameters increase, the larger the Curie temperature is. Namely, the tendency of the changes for the three parameters has sensitive effects on the polarizations of the ferroelectric thin film, which are in good agreement with the results of Wesselinowa [34], see Figure 10. In fact, the above description of the effect of interaction parameters on the polarization is also qualitatively coincident with experiments. In experiment, with the increasing Sr concentration to $PbTiO_3$, the phase transition temperature decreases [36]. That means that the addition of Sr to $PbTiO_3$ may result in sensitive change for interaction parameters with layers.

3. Conclusions

In summary, we have calculated numerically the phase diagrams and polarizations while the three parameters decrease or increase monotonically with the layers. The results show that various layer-dependent parameters have sensitive effects on the phase diagrams and the polarizations of the n-layer ferroelectric thin film. While the interaction parameters vary layer by layer fast, the ferroelectric range in the phase diagram and the Curie temperature are changed promptly, which are in accordance with the results of the predecessors. It indicates that if the properties of phase transition of the ferroelectric thin film are investigated in the future, the layer-dependent parameters should be involved carefully and some experiments may be explained reasonably.

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