The influence of layer defect in the Ferroelectric films

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Abstract : Using the modified transverse Ising model, and the effective field theory based on the probability distribution technique, the phase transition temperature, the polarization and susceptibility for ferroelectric thin films with structural defects are studied. It is shown that the defect layers in ferroelectric thin films can induce strong increase or decrease of the critical temperature of ferroelectric phase transition due to different exchange interactions in the defect layers. The obtained results are in qualitative agreement with experimental data for thin ferroelectric film with different thickness.

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I. Introduction

Recent developments in the fabrication of thin films have been applied to the research of ferroelectric thin films. Oxide thin films with perovskite-type structure, such as $BaTiO_3$ and $SrTiO_3$, have been fabricated and they have revealed some novel physics [1-3]. The transverse Ising Model was first applied by De Gennes et al. [4], Blinc et al [5] to describe order-disorder type ferroelectrics. But later the TIM is applied to displacive type FE's such as $BaTiO_3$ [6]. Despite its simplicity, the transverse Ising model is successful in studying the microscopic properties of finite-size ferroelectrics. Modelling of ferroelectric films has bloomed since Pertsev's landmark paper [7]. Since then, a lot has been accomplished. A very recent review paper discusses these in detail has been published recently by Schlom et al. [8]. The dynamical properties of this model film were explored within the random-phase approximation by Wang and Smith [9] ignoring the effects of damping. It was shown that for films with reduced surface interaction (compared to the bulk), the soft mode corresponds to a surface-like mode in the ferroelectric phase but to a bulk-like mode in the paraelectric phase. Conversely, for films with an enhanced surface interaction, the soft mode is a bulk-like mode in the ferroelectric phase and a surface-like mode in the paraelectric phase.

Based on the Ising model in a transverse field and using the Green's function theory Wesselinowa et al [10] had been successfully in calculating the spin wave energies, the polarization and the phase transition temperature for a FE thin film with different structural defect layers. Our aim in the present letter is to study the influence of defect in ferroelectric thin films with different structural defect layers, based on the Ising model described by the transverse field in the framework of the effective filed theory, with a probability distribution technique, in particular the phase transition and dielectric properties FE films. It was obtained that with increasing film thickness the defect is larger for thin films than for the bulk material. This is in agreement with different experimental observations [11-12]. The outline of our paper is as follows. The formalism of the problem within an effective field treatment is presented in section 2. Presentation of the numerical results and theirs discussion is contained in section. 3, where the last section 4 is devoted to a brief conclusion.

II. Formalism

We Consider a number L of *xy*-layers of simple cubic lattice in the (*xyz*) space. Distinguishing one of the three cubic axes, say, the *z*-axis; these planes are identified by the values of z (z = 1, 2, …L): The geometry of the film requires two free surfaces, say (z = 1 and z = L) and periodic boundary conditions in the *xy*-directions are implemented for each film layers. The Hamiltonian of the system is given by:

$$H = \sum_{ij} J_{ij} S_{iz} S_{jz} - \Omega_b \sum_i S_{ix} - \Omega_s \sum_i S_{ix} - 2\mu E \sum_i S_{iz} \qquad (1)$$

Where S_{iz} and S_{ix} denote the z and x components of a quantum spin $\overrightarrow{S_i}$ of magnitude $S = 1/2$ at site i. E represents the external electric field, the Ω_b and Ω_s represent transverse fields in the bulk and surface layers (for H-bond ferroelectrics it represents the Proton tunnelling between the two equilibrium positions on the H-bond). For simplicity but without loss of generality, we assume that the z-direction is perpendicular to the surface; the polarization is along the z-direction. J_{ij} is the two-spins exchange interaction constant between the spins at the neighbouring sites i and j; and $J_{ij} = J_s$ between spins on the surface layer, otherwise it is J_b. We assume that one or more of the layers can be defect, since J_d and Ω_d denote the exchange interaction and the transverse field of the defect layer.

The method we use is the effective-field theory, fully described in [13], that employed the probability distribution technique to account for the single-site spin correlations. Following that procedure, we find in the current situation for a fixed configuration of neighbouring spins that the layer longitudinal polarizations are given by

$$p_{nz} = \langle S_{nz} \rangle = \left\langle f_z\left(\sum_j J_{ij} S_{jz} + 2\mu E, \Omega_n\right) \right\rangle \qquad (2)$$

Where n is the layer index. The function f_z is given by

$$f_z\left(\sum_j J_{ij} S_{jz} + 2\mu E, \Omega_n\right) = \frac{1}{2} \frac{\sum_j (J_{ij} S_{jz} + 2\mu E)}{\sqrt{(\sum_j J_{ij} S_{jz} + 2\mu E)^2 + \Omega_n^2}} \qquad (3)$$

$$than\left(\frac{1}{2} \sqrt{(\sum_j J_{ij} S_{jz} + 2\mu E)^2 + \Omega_n^2} \right)$$

With $\beta = 1/k_B T$ and T is the temperature. In Eq. (2), $\langle \ldots \rangle$ indicates the usual canonical ensemble thermal average for a given configuration and the sum runs over all nearest neighbors of the spin S_i.

To perform thermal averaging on the right hand side of Eq. (2), we follow the general approach described in [13]. First of all, in the spirit of the effective field theory, multi-spins correlation functions are approximated by products of single spin averages. We then take advantage of the integral representation of the Dirac's delta distribution, in order to write Eq. (2) in the following form

$$p_{nz} = \int dw f_z(w, \Omega_n) \frac{1}{2\pi} \int \left[dt \exp(iwt) \prod_j \langle \exp(itJ_{ij}\sigma_{jz}) \rangle \right] \qquad (4)$$

Now, we introduce the probability distribution of the spin variables (for details see Ref. [13])

$$p_{nz} = \frac{1}{2}\left[(1 - 2p_{nz})\delta\left(S_{nz} + \frac{1}{2}\right) + \left((1 + 2p_{nz})\delta\left(S_{nz} - \frac{1}{2}\right)\right)\right] \qquad (5)$$

Using the four previous equations, we get the following equations for the layer polarizations

$$p_{1z} = 2^{-N-N_0} \sum_{\mu_1}^{N} \sum_{\mu_2}^{N_0} \{ C_{\mu_1}^{N} C_{\mu_2}^{N_0} (1 - 2p_{1z})^{\mu_1} (1 + 2p_{1z})^{N-\mu_1} \qquad (6)$$

$$(1 - 2p_{2z})^{\mu_2} (1 + 2p_{2z})^{N_0 - \mu_{12}} f_z(y_1, \Omega_s)$$

With

$$y_1 = \frac{1}{2}\left[J_s(N - 2\mu_1) + J_b(N_0 - 2\mu_2) \right] + 2\mu E \qquad (7)$$

$$p_{k,z} = 2^{-N-2N_0} \sum_{\mu_1}^{N} \sum_{\mu_2}^{N_0} \sum_{\mu_3}^{N_0} \{ C_{\mu_1}^{N} C_{\mu_2}^{N_0} C_{\mu_3}^{N_0} (1 - 2p_{kz})^{\mu_1} (1 + 2p_{kz})^{N-\mu_1}$$

$$(1 - 2p_{k-1,z})^{\mu_2} (1 + 2p_{k-1,z})^{N_0 - \mu_{12}} \qquad (8)$$

$$(1 - 2p_{k+1,z})^{\mu_3} (1 + 2p_{k+1,z})^{N_0 - \mu_3} f_z(y_k, \Omega_b) \}$$

With $y_k = \frac{1}{2}[J(N - 2\mu_1) + J(N_0 - 2\mu_2) + J(N_0 - 2\mu_3)] + 2\mu E$; (9)

$2 \le k \le L - 1$

$$p_{L,z} = 2^{-N-2N_0} \sum_{\mu_1}^{N} \sum_{\mu_2}^{N_0} \{ C_{\mu_1}^{N} C_{\mu_2}^{N_0} (1 - 2p_{Lz})^{\mu_1} (1 + 2p_{Lz})^{N-\mu_1} \qquad (10)$$

$$(1 - 2p_{L-1,z})^{\mu_2} (1 + 2p_{L-1,z})^{N_0 - \mu_{12}} f_z(y_L, \Omega_s)$$

With

$$y_L = \frac{1}{2}\left[J_s(N - 2\mu_1) + J_b(N_0 - 2\mu_2) \right] + 2\mu E \qquad (11)$$

In these equations, N and N_0 denote respectively the coordination numbers on the parallel planes and inter-planes and for the case of a simple cubic lattice which is considered here one has $N = 4$ and $N_0 = 1$ and C_l^k are the binomial coefficients, $C_l^k = \frac{k!}{l!(k-l)!}$. We have thus obtained the self-consistent equations (6), (8) and (10) for the layer longitudinal polarizations p_{nz} that can be solved directly by numerical iteration. The average longitudinal polarization of the film is defined by

$$p_{av} = p_z = \frac{2\mu}{L} \sum_{n=1}^{L} p_{nz} \qquad (12)$$

And the susceptibility of the films can be evaluated by

$$\chi = \left. \frac{\partial p_{av}}{\partial E} \right)_{E=0} \qquad (13)$$

We are interested in the calculation of the Curie transition temperature of the film.

The usual argument that the layer longitudinal polarization p_{nz} tends to zero as the temperature approaches its critical value, allows us to consider only terms linear in p_{nz} on approaching a critical temperature. Consequently, all terms of the order higher than the linear terms in Eqs. (6), (8) and (10) can be neglected. The system is of the form

$$M\overrightarrow{p_z} = 0 \qquad (14)$$

and $\overrightarrow{p_z}$ is a vector of components

$(p_{1z}, p_{2z}, \ldots.., p_{Lz})$ All the informations about the critical temperature of the system is contained in Eq.(14).

Up to now we did not assign precise values of the exchange coupling constants and the transverse field, the terms in matrix Eq. (14) are general ones. In a general case; for arbitrary coupling constants, transverse field and film thickness; the evaluation of the critical temperature relies on numerical solution of the system of linear equations (Eq. (14)). This equation can be satisfied by nonzero polarization vectors p_z only if

$$\det M = 0 \qquad (15)$$

The film critical temperature T_c depends on the parameter $R_d = J_d / J_b$ that reflects the degree of dilution, $R_s = J_s / J_b$, R_b, Ω_s and Ω_b

III. Results And Discussion

In this paper, we take the ratio $R_d = J_d / J_b$ and two ratio $R_s = J_s / J_b, R_b = 1$ represent the reduced exchange interaction near the surface (in the bulk) respectively.

In this section we shall present the numerical calculations of our theoretical results taking the following model parameters: J_b = 495 and Ω_b/J_b=Ω_s/J_b=0.04. We have calculated the temperature dependence of the ratio R_d for a simple cubic thin film and for different values of the exchange interaction constants. The numerical results expose some interesting and novel characteristics in the dilution values (film with defect) in comparison to the case of FE thin films without defects. The results for film thickness N = 7 and different exchange interaction parameters in the defect layer J_d are presented in Fig.1.

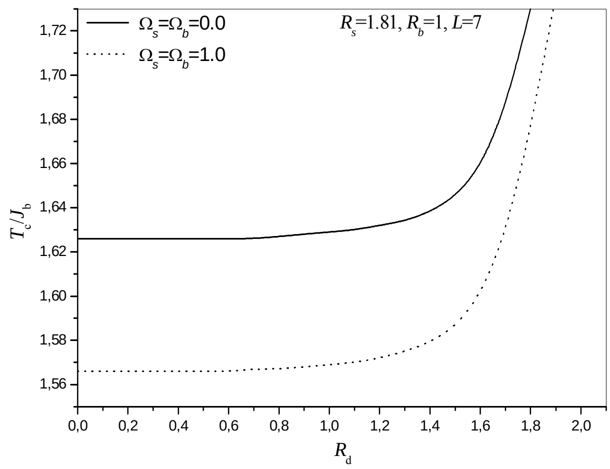

Fig. 1. Dependence of the Curie temperature on the ratio R_d for a seven layers film with different values of Ω_s and Ω_b.

We consider firstly the case where the middle layers is defect, which is possibly the case when the layer has vacancies or impurities with smaller radius and larger distances between them. In this figure, we can see that the ratio R_d increases with increasing the critical temperature, and the behavior changed from the larger value of the ratio R_d, and we shows that a transverse

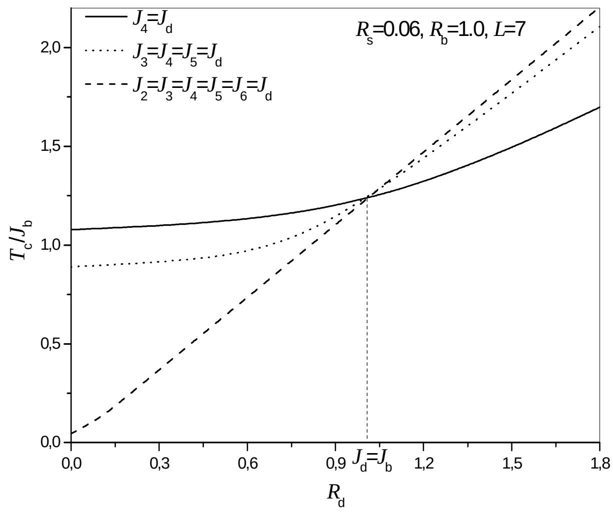

Fig. 2. Dependence of the Curie temperature on the ratio R_d for a seven layers film and Ω_s=Ω_b= 0.04

field in the surface and bulk layers causes the critical value of temperature and to move to a lower values.

In Fig. 2, we have plotted the temperature dependence of the ratio R_d for a FE thin film. Tree cases of figures are studied. In the first for one layer is defect $(J_4 = J_d)$, in the second tree layers are defect $(J_3 = J_4 = J_5 = J_d)$, in the end five layers are defect $(J_2 = J_3 = J_4 = J_5 = J_6 = J_d)$.We can see that the diluted case depend also on the number of inner defect layers and it is demonstrated that for $R_s = 0.06$, the

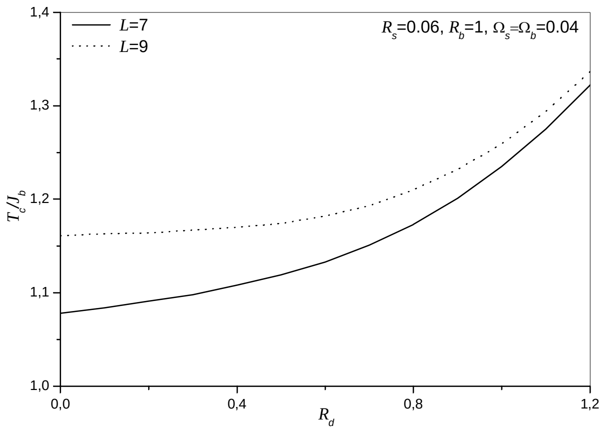

Fig. 3. Dependence of the Curie temperature on the ratio R_d for different number of layers.

increasing the value of ratio R_d , the critical temperature increases, and for the particular point where $J_d = J_b$ the tree curves intersect, and reflect the case without defect (dotted line in Fig. 2).

In Fig. 3 we have studied a ferroelectric thin film with different film thickness where one layer, the middle is defect (N = 7, solid line) and (N = 9, dotted line 2). The ratio of dilution increases with increasing the critical temperature, and theirs value move to higher value when the film thickness decreases. That is in agreement with the experimental data of [11].

In Fig. 4, we have plotted the temperature dependence of the polarization for a film thickness N = 7, where one layer, the middle, is defect and for tree layers $(J_3 = J_4 = J_5 = J_d)$ are defect. The results show that

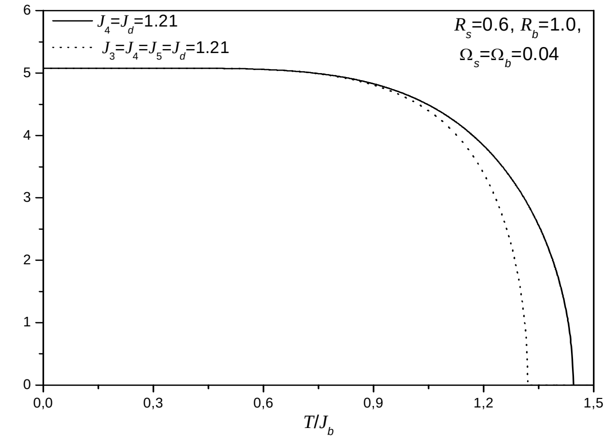

Fig. 4. Temperature dependence of the polarization for seven layers film.

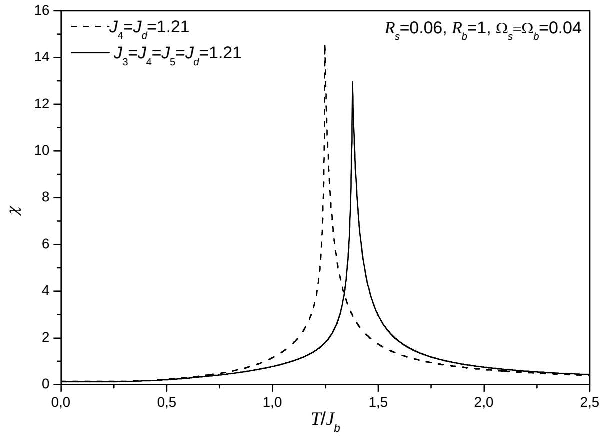

Fig. 5. Temperature dependence of the Susceptibility for seven layers film

for some typical value of R_s, R_b, Ω_s and Ω_b, the polarization decreases monotonically from the value of saturation and reaches zero at the critical temperature T_c. And we have demonstrated that with an increasing number of defect layers, the critical temperatures increases.

For the same values of parameters R_s, R_b, Ω_s and Ω_b, we have plotted in Fig. 5, the temperature dependence of the susceptibility for two case, $(J_4 = J_d)$ and $(J_3 = J_4 = J_5 = J_d)$. We can see that number of defect layers is an important factor

influencing the film properties. With the increasing this number of defect layers , the susceptibility peak shifts to higher temperature and the peak value decreases, which is predicted from Fig. 4. This could explain the observed experimental results from ferroelectric thin films that the line shapes of the film become broad as the temperatures approaches T [11,12].

IV. Conclusion

In conclusion, we have studied the phase diagrams and the dielectric properties of the ferroelectric thin film with different structural defects, using the transverse Ising model with the effective field theory based on probability distribution technique. From this study, we have demonstrated that the defect layers in ferroelectric thin films increase or decrease of the critical temperature of ferroelectric phase transition due to different exchange interactions in the defect layers. And we have demonstrated that the number of defect layers is an important factor influencing the film properties. The obtained results are in qualitative agreement with experimental data for thin ferroelectric film with different thickness.

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V. References

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