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Phase diagram of ferroelectric thin film with diluted surface

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ABSTRACT

We study the influence of the surface of the ferroelectric films on the properties of the intrinsic ferroelectric polarization state in frame of statistical Transverse Ising Model (TIM). The quality of the surface is modelled by the dilution parameter q that reflects the relative weight of the paraelectric impurities vs. ferroelectric ions. Using the effective field approach the variation of the average value of spontaneous polarization as function of temperature for different film thicknesses has been investigated as function of dilution parameter q. The phase diagram of the system and crossover from the ferroelectric to the paraelectric phase is discussed.

1. Introduction

Fabrication of nano-scale ferroelectric memory storage devices initiated a great deal of interest to study ferroelectric materials confined to the restrictive geometry of a microelectronic environment. A special emphasis is given to understanding the properties of thin ferroelectric films and to the role of the surface and interface effects on the average spontaneous polarization [1–3]. Modelling of ferroelectric systems is usually based on the complimentary methods: statistical physics approach, ab initio simulations and minimization of the phenomenological Ginzburg–Landau functional.

In the current article, we apply the microscopic statistical approach to investigate the influence of the surface effects on the ferroelectric phase in thin films. The consideration is based on the pseudo-spin Transverse Ising Model (TIM) that is the adequate tool to investigate the bulk properties of KH_2PO_4-type ferroelectrics. This model has also been applied to study the critical properties of ferroelectric thin films [4–12]. Particularly, in [4] the surface properties were taking into account by

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surface variation of the transverse field coupling constant. It is however more realistic to consider the film surface as the ensemble of diluted ferro/paraelectric ions. Phase diagram of such a system will be obtained in the present work.

The outline of this work is as follows. A brief formulation of the effective field theory which is based on the introduction of a differential operator technique [13] is given in Section 2. The numerical results are obtained and discussed in Section 3. In Section 4 we present the principal conclusions.

2. The model

We consider a surface-diluted transverse Ising thin film with a thickness L having simple cubic symmetry in which each layer is parallel to the diluted (001) surfaces. The Hamiltonian of the system is given by:

$$H = -\sum_{(ij)} J_{ij} S_i^z S_j^z \xi_i \xi_j - \sum_i \Omega_i \xi_i S_i^x. \tag{1}$$

Here S_i^z and S_i^x are the z and x components of spin-1/2 operator at site i, the transverse field Ω_i represents a quantum tunnelling between potential minima, and J_{ij} is the interaction between nearest-neighbor dipoles. Physically J_{ij} describes both the direct electrostatic dipolar interaction and the indirect dipolar interaction provided by the lattice deformation potential, screened at large distances. Unlike magnetic systems the numerical value of phenomenological constants J_{ij} can be found only from ab initio calculations. Approximately they are estimated as ferroelectric transition temperature i.e. several hundreds of K (∼0.1–1 eV). The tunnelling integrals Ω_i are of the order of 200 cm^{-1} (0.03 eV) for proton ions [14] and much lower for more heavy ions.

We assume that parameters J_{ij}, Ω_i takes the value J and Ω in the bulk layers and J_s and Ω_s at the surface layer. Parameter ξ_i is the site occupancy parameter equal to one or zero, depending on whether the site is occupied or not by ferroelectric ion. Since only the surfaces are considered to be diluted in the present system, $\xi_i = 1$ with a probability q when the surface site i is ferroelectric and $\xi_i = 0$ with a probability $(1 - q)$ when the surface site i is paraelectric. In bulk $\xi_i = 1$.

The standard effective field method of treatment of such system is based on the differential operator technique [13] in which the spatial distribution of polarization across the ferroelectric layers is based on the system of coupled equations, that in application to our case can be written as:

For first and last layer with ($k = 1$, $i = 2$ or $k = L$, $i = L - 1$)

$$p_k = \left[q\left\{\cosh\left(J_s D\right) + p_k \sinh\left(J_s D\right)\right\} + (1 - q)\right]^4 \left[\cosh\left(JD\right) + p_i \sinh\left(JD\right)\right] F_s(x)|_{x=0}. \tag{2}$$

For the second or the $(L - 1)$ layer

$$\begin{aligned} p_2 \;=\; & \left[\cosh\left(J_s D\right) + p_2 \sinh\left(J_s D\right)\right]^4 \left[q\left\{\cosh\left(JD\right) + p_1 \sinh\left(JD\right)\right\} + (1 - q)\right] \\ & \times \left[\cosh\left(JD\right) + p_3 \sinh\left(JD\right)\right] F(x)|_{x=0} \end{aligned} \tag{3}$$

$$\begin{aligned} p_{(l-1)} \;=\; & \left[\cosh\left(J_s D\right) + p_{(l-1)} \sinh\left(J_s D\right)\right]^4 \left[q\left\{\cosh\left(J_s D\right) + p_1 \sinh\left(J_s D\right)\right\} + (1 - q)\right] \\ & \times \left[\cosh\left(JD\right) + p_{l-2} \sinh\left(JD\right)\right] F(x)|_{x=0}. \end{aligned} \tag{4}$$

For each layer with polarization p_L $3 \leq k \leq L - 2$

$$\begin{aligned} p_k \;=\; & \left[\cosh\left(JD\right) + p_k \sinh\left(JD\right)\right]^4 \left[\cosh\left(JD\right) + p_{k-1} \sinh\left(JD\right)\right] \\ & \times \left[\cosh\left(JD\right) + p_{k+1} \sinh\left(JD\right)\right] F(x)|_{x=0}. \end{aligned} \tag{5}$$

Here the differential operator $D = \mathrm{d}/\mathrm{d}x$ acts on the generating functions $F_s(x)$ and $F(x)$ that are defined by:

$$F_S(x) = \left(\frac{x}{y_s}\right) \tanh\left(\beta y\right) \quad \text{and} \quad F(x) = \left(\frac{x}{y}\right) \tanh\left(\beta y\right)$$

with

$$y_s = \left(x^2 + \Omega_s^2\right)^{1/2}, \qquad y = \left(x^2 + \Omega^2\right)^{1/2}.$$