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The Curie temperature of ultra-thin ferroelectric films

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Abstract. The Curie temperature of ferroelectric films described by the transverse Ising model was studied under the mean-field theory. The film layer number, the surface interaction and the surface layer number dependence of the Curie temperature were obtained. There is a critical surface interaction strength, which is $J_{sc} = 1.25J$ for single-surface-layer films, and $J_{sc} = 1.078J$ for multiple-surface-layer films. If the surface interaction strength exceeds the critical value, there exists an optimum film thickness which possesses the maximum Curie temperature; then the surface interaction strength is weaker than the critical value, the Curie temperature decreases monotonically with increasing film thickness, and there exist critical sizes or critical thicknesses at which the ferroelectricity will disappear if the surface interaction is weak enough.

1. Introduction

The effects of size on ferroelectricity have been investigated for a long time since Känzig and co-workers [1, 2] studied the dielectric properties of ferroelectric fine particles. An early study on KDP fine particles embedded in an insulating medium showed no ferroelectric phase transition when the size of the particles was less than 150 nm [1]. The transition temperature of $BaTiO_3$ increases as the particle size decreases [2]. Recently controversial results obtained from $BaTiO_3$ fine particles [3] and $PbTiO_3$ fine particles [4], shown a decrease in Curie temperature with decrease in grain size.

In recent years, there has been considerable interest, both theoretical [5–13] and experimental [4, 13, 14], in the effects of the surface and size on the ferroelectric phase transitions. Much work has been done on the Landau theory [8, 9, 12, 13] of phase transition in ferroelectric films. When the surface polarization is reduced, the polarization approaches its bulk value away from the surface. When the surface polarization is enhanced, there is a surface phase transition above the bulk transition temperature, and the polarization approaches zero away from surface. At the bulk transition temperature, there is a second phase transition; below this transition temperature, the polarization approaches its bulk value away from the surface. Recent research by Scott *et al* [13] showed that the transition temperature approaches the bulk value with increase in film thickness if the surface polarization is reduced; otherwise it decreases with increasing film thickness and approaches a certain temperature high above the bulk transition temperature as the film thickness increases to infinite. On the other hand, study of the phase transition in ultra-thin Ising films indicates the appearance of a peak transition temperature in the two-layer films [15].

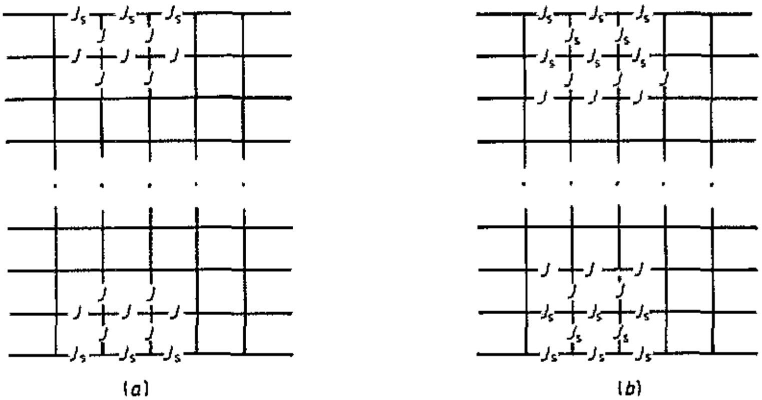


Figure 1. A model of the films, where J_s is the surface interaction strength and J is the bulk interaction strength: (*a*) one-surface-layer film; (*b*) two-surface-layer film.

The transverse Ising model (TIM) was introduced by de Gennes [16] to describe the phase transition properties in KDP-like ferroelectrics [17]; then this model was applied to other systems successfully [18, 19]. It has been proved that in the semi-infinite TIM, there is a localized surface spin wave [20]. The surface diagram [21] and the surface magnetism in the presence of a disordered surface [22] were also obtained from this model.

In this paper, we have studied the ferroelectric films described by the TIM and obtained the Curie temperature of the film for different layers, different surface layers and different surface interactions. In the following section, the general expression for the film Curie temperature is formalized; the results are obtained under the mean-field approximation and are discussed in section 3; the last section contains the conclusion.

2. The general formalism of film Curie temperatures

The Hamiltonian of the TIM [17] is

$$H = -\Omega \sum_i S_i^x - \tfrac{1}{2} \sum_{ij} J_{ij} S_i^z S_j^z \tag{1}$$

where Ω is the transverse field (for H-bond ferroelectrics it represents the proton tunnelling between the two equilibrium positions on the H bonds), S_i^x and S_i^z are the x and z component of pseudo-spin (the thermal average of S_i^z is related to the polarization) and J_{ij} is the interaction between the ith and jth site, where i, j run over all sites. Under the mean-field approximation, the Hamiltonian (1) predicates a second-order phase transition; the bulk Curie temperature T_b can be determined from [17]

$$\tanh(\Omega/2k_B T_b) = 2\Omega/n_0 J \tag{2}$$

where $J = J_{ij}$ is the nearest interaction, and n_0 is the coordinate number.

The model used to describe the ferroelectric properties of the thin film is shown in figure 1; only a one-surface-layer film and a two-surface-layer film are illustrated. In general the lowering of symmetry at the surface may lead to a modification of Ω and J_{ij} compared with their bulk values. The simplest assumption is to take J_{ij} non-zero only for nearest-neighbour sites i and j, with $J_{ij} = J_s$ if both sites are in the surface layers and $J_{ij} = J$ otherwise. In order to examine their behaviour in more detail we consider the case where spins lie on a simple cubic lattice with the coordinate axes parallel to the cube edges.

The spin average $\boldsymbol{R}_i = \langle S_i \rangle$, which is obtained from the mean field theory [12], is

$$\boldsymbol{R}_i = \boldsymbol{H}_i/|\boldsymbol{H}_i| \tanh(|\boldsymbol{H}_i|/2k_B T) \tag{3}$$

where $\boldsymbol{H}_i\,(\Omega, 0, \Sigma_j J_{ij} R_j^z)$ is the mean field acting on the ith spin. For single-surface-layer films, from the above equation, R_n, which denotes the value of R_i^z in the layer n from the uppermost surface, satisfies

$$R_1 = [(4J_s R_1 + JR_2)/2\tau_1] \tanh(\tau_1/2k_B T)$$

at the surface and

$$R_n = [J(4R_n + R_{n+1} + R_{n-1})/2\tau_n] \tanh(\tau_n/2k_B T)$$

elsewhere, where

$$\tau_1 = \sqrt{\Omega^2 + (4J_s R_1 + JR_2)^2}$$
$$\tau_n = \sqrt{\Omega^2 + J^2(4R_n + R_{n+1} + R_{n-1})^2}.$$

At a temperature sufficiently close to and below the Curie temperature, the R_n-values are small. In this limit, the above equations reduce to the following set of linear equations:

$$(4J_s/J - x)R_1 + R_2 = 0$$

at the surface and

$$(4 - x)R_n + J(R_{n+1} + R_{n-1}) = 0$$

elsewhere, where

$$x = (2\Omega/J)\coth(\Omega/2k_B T_C).$$

Under the symmetry condition, i.e. $R_i = R_{N-i-1}$, the above N equations reduce to $N/2$ equations for even-number-layer films and $N/2 + 1$ equations for odd-number-layer films. The Curie temperature can be obtained by solving the secular equation of the coefficients. For one-layer to four-layer films, there are explicit expressions for the film Curie temperature; for films thicker than four layers, there is only an implicit expression from which the film Curie temperature can be obtained by numerical calculation. The expressions for the Curie temperature of N-layer film with a single surface layer are

$N = 1$ $\quad x = 4J_s/J$

$N = 2$ $\quad x = 1 + 4J_s/J$

$N = 3$ $\quad x = 2(1 + J_s/J) + \sqrt{2 + 4(1 - J_s/J)^2}$

$N = 4$ $\quad x = (5 + 4J_s/J)/2 + \sqrt{4 + (5 - 4J_s/J)^2/2}$

$N = 5$ $\quad (4J_s/J - x)(4 - x)^2 - (4 - x) - 2(4J_s/J - x) = 0$

$N = 6$ $\quad (4J_s/J - x)(4 - x)(5 - x) + (2x - 5 - 4J_s/J) = 0$

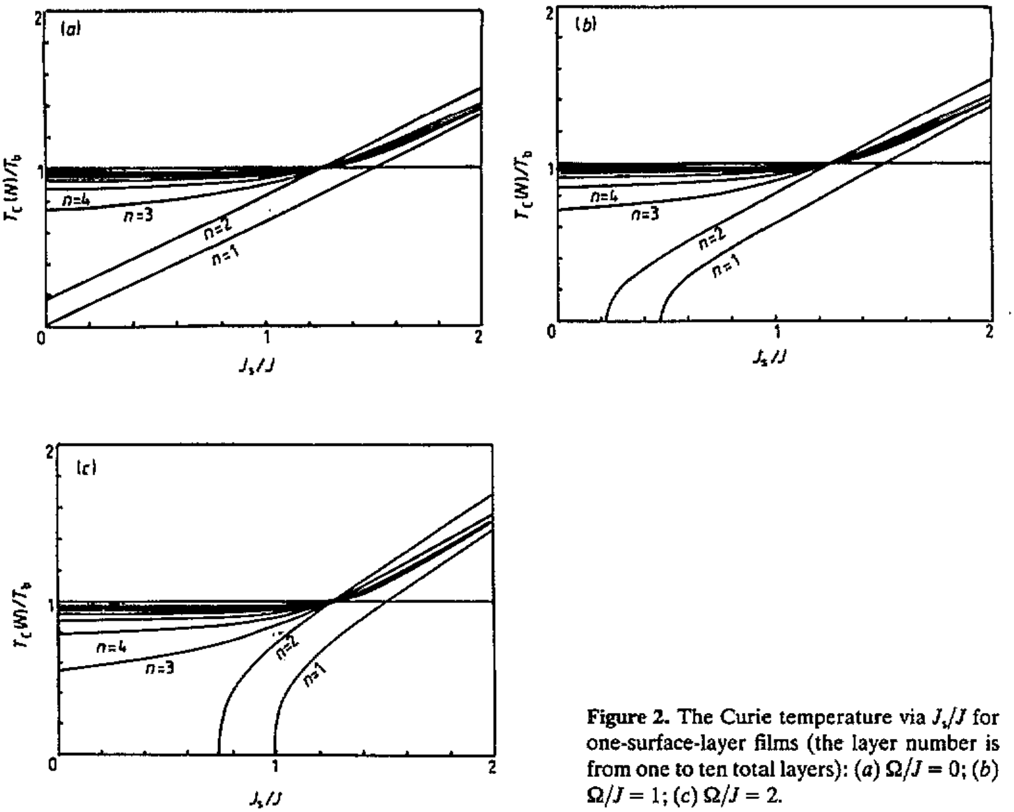


Figure 2. The Curie temperature via J_s/J for one-surface-layer films (the layer number is from one to ten total layers): (*a*) $\Omega/J = 0$; (*b*) $\Omega/J = 1$; (*c*) $\Omega/J = 2$.

$$N = 7 \qquad (4J_s/J - x)(4 - x)((4 - x)^2 - 3) - [(4 - x)^2 - 2] = 0$$

$$N = 8 \qquad (4J_s/J - x)[(4 - x)^2(5 - x) - (9 - 2x)] - (4 - x)(5 - x) + 1 = 0$$

$$N = 9 \qquad [(4J_s/J - x)(4 - x) - 1](4 - x)[(4 - x)^2 - 3] - (4J_s/J - x)[(4 - x)2 - 2] = 0$$

$$N = 10 \qquad [(4J_s/J - x)(4 - x) - 1][(4 - x)^2(5 - x) - (9 - 2x)] - (4J_s/J - x)[(4 - x)(5 - x) - 1] = 0.$$

Similar equations can also be obtained for multiple-surface-layer films.

3. Results and discussion

The Curie temperatures for single-surface-layer films are shown in figure 2. There exists a critical surface interaction strength J_{sc} ($J_{sc}/J = 1.25$) which is in agreement with previous calculations [12, 20, 23]. Figure 2(*a*) corresponds to the Ising model; it is easy to see that, if the surface interaction is not trivial, there is always a phase transition. If the transverse field Ω is non-zero, as shown in figures 2(*b*) and 2(*c*), the one-layer film and the two-layer film have no phase transition when J_s is sufficiently weak. The film

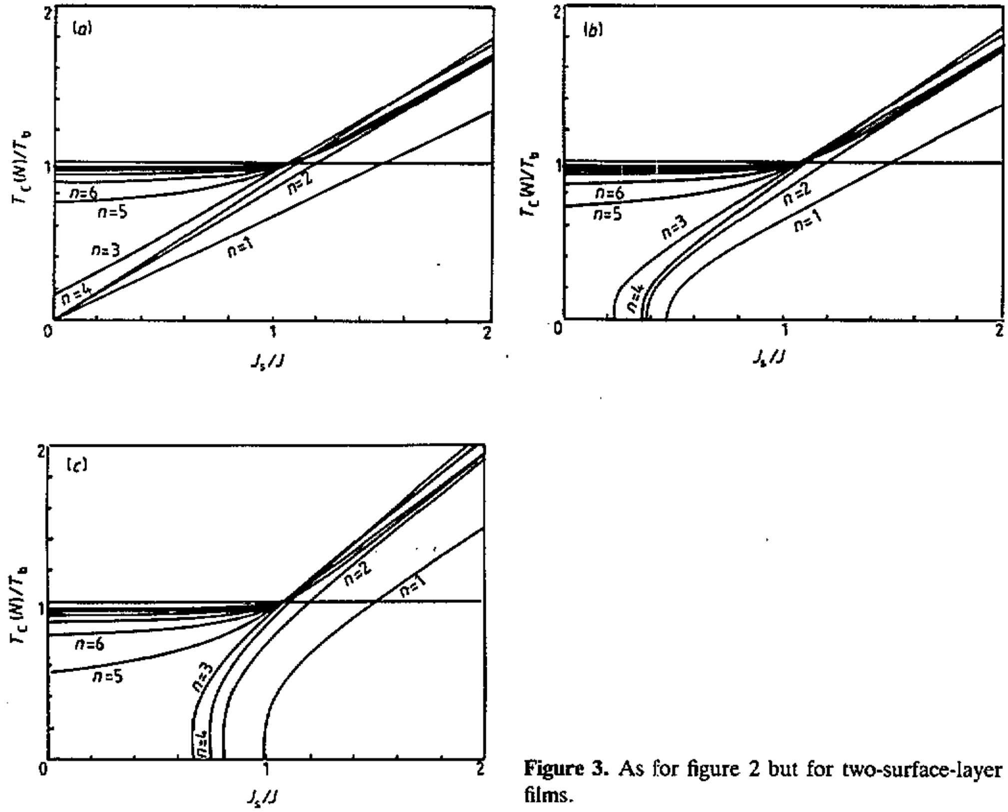
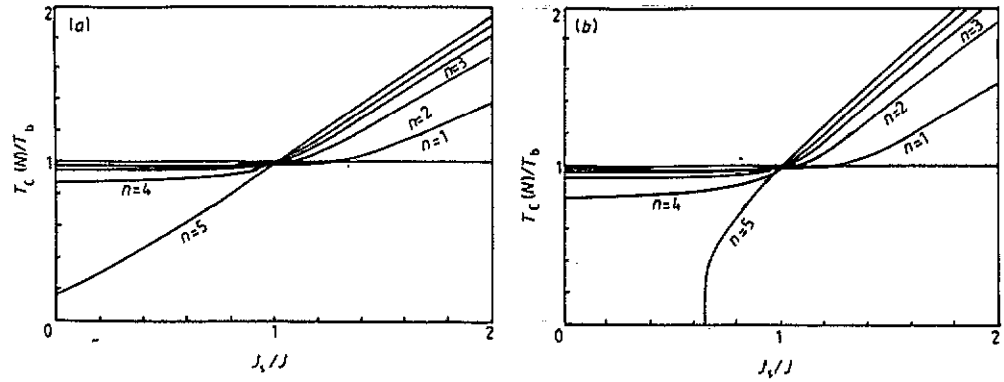


Figure 3. As for figure 2 but for two-surface-layer films.

Curie temperature approaches the bulk value as the film thickness increases. When $J_s > J_{sc}$, the film Curie temperature is always higher than the bulk value and lies between that of the one-layer film and that of the two-layer film. As the layer number N increases (i.e. the film becomes thicker), the film Curie temperature approaches that of the one-layer film. The above statements are in agreement with the results obtained for an ultrathin ferromagnetic film [15], which are calculated from the Ising model.

The behaviour of the two-surface-layer film is shown in figure 3; it seems similar to but a little more complicated than that of the single-surface-layer films. First, there is also a critical surface interaction strength, which is lower than that of the single-surface-layer film strength ($J_{sc}/J = 1.078$) and this is also the critical surface interaction strength for multiple-surface-layer films as shown in figure 4. In the Ising limit (i.e. $\Omega = 0$) a ferroelectric phase always exists if the temperature is low enough and the surface interaction strength is non-zero. When the surface interaction strength is weaker than the critical value, the film Curie temperature approaches the bulk value as the film thickness increases. When the film is thinner than four layers, there may be no ferroelectricity in the entire temperature range for any non-zero Ω, but only if the surface interaction strength is weak enough. This can be easily seen from figures 3(*b*) and 3(*c*). When the surface interaction strength is stronger than the critical value, the four-layer films have the maximum Curie temperature. As the film thickness increases, the film Curie temperature is little lower than that of four-layer films, but higher than that of the bulk system.



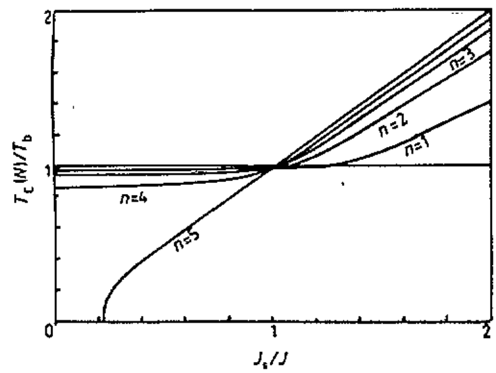


Figure 4. The Curie temperature via J_s/J for ten-layer films with surface layer numbers from 1 to 5: (*a*) $\Omega/J = 0$; (*b*) $\Omega/J = 1$; (*c*) $\Omega/J = 2$.

For multiple-surface-layer films, we consider only ten-layer films; the results are shown in figure 4. Except for the single-surface-layer film which has the critical surface interaction strength given by $J_{sc}/J = 1.25$, the critical surface interaction strength of the multi-surface-layer films is given by $J_{sc}/J = 1.078$. From the figure, it is easy to see that the increase in the surface layer thickness makes the film Curie temperature deviate further from the bulk value, i.e., when the surface interaction strength is weaker than the critical value, the higher the surface layer number, the lower is the film Curie temperature; when the surface interaction strength is stronger than the critical value, the highest Curie temperature for a definite film thickness corresponds to the thickest surface layer film.

4. Conclusion

The surface interaction strength and surface layer thickness dependence of the Curie temperatures of ultra-thin ferroelectric films described by the TIM were obtained under the mean-field theory. There is a critical surface interaction which is higher than the bulk interaction; beyond that value the film Curie temperature increases as the film thickness decreases; otherwise the Curie temperature decreases with decreasing film thickness. For a weak surface interaction, there will be no ferroelectricity in the ultra-thin films;

for a strong surface interaction, an optimum film thickness exists at which the film reaches the maximum Curie temperature.

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