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Surface modification in ferroelectric transitions

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Abstract. We study the phase transitions of finite and infinite ferroelectric systems using the Ising model in a transverse field. The mean-field layer approximation is used and the results for the Curie temperature are expressed in terms of general determinants. The effects of surface modification are introduced through a surface exchange constant J_0 and a surface transverse field Ω_0. It is shown that above a critical curve in J_0–Ω_0 space, surface polarization is possible, even when there is no phase transition in the bulk. The dependence of the Curie temperature on the film thickness is obtained for two types of surface modification.

1. Introduction

The effects of size on the ferroelectric phase transition have been investigated for a long time. Känzig and co-workers [1, 2] found that KDP fine particles embedded in an insulating medium show no ferroelectric phase transition if their size is less than 150 nm, while the transition (Curie) temperature of $BaTiO_3$ fine particles [3] and $PbTiO_3$ fine particles [4] demonstrated that the Curie temperatures decrease with decrease in grain size.

For ferroelectric TGS films, Hadni and Thomas [5] observed that the Curie temperature increases with decreasing thickness, whereas Batra and Silverman [6] earlier reported a decrease with decreasing thickness. For the case of ceramic KNO_3 thin films, Scott *et al* [7] have found that some samples exhibit an increase of Curie temperature with increasing film thickness, whereas others show a decrease.

Theoretically, much work has been done on the Landau phenomenological theory of phase transition in ferroelectric films [7–10]. When the surface polarization is reduced, the polarization away from the surface approaches its bulk value. On the other hand, when the surface polarization is enhanced, there is a surface transition temperature above the bulk transition temperature, and the polarization approaches zero away from the surface. At the bulk transition temperature, there is a second phase transition, and below this temperature the polarization approaches its bulk value away from the surface.

On the microscopic level, the pseudo-spin theory based on the Ising model in a transverse field (TIM) was first introduced by de Gennes [11] to describe the phase transition of KDP-like ferroelectrics. It has since been applied to many other systems in studying surface effects on the Curie temperature and the spin waves [10–17]. In most of the discussions, the semi-infinite system is used, and the surface modification is introduced through a surface exchange constant J_0. In a recent work [17], the dependence of the Curie temperature on the thickness (number of layers) of a thin

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film is studied numerically, by considering two types of surface modification to the exchange constant. The possible surface modification to the transverse field Ω is however not discussed.

In this article, we consider the TIM for a ferroelectric film of arbitrary thickness (n: number of bulk layers). Changes to both the exchange constant J_0 and the transverse field Ω_0 at the surface layer(s) are included. We study the Curie temperature as a function of n, as well as the values of J and Ω for the bulk and surface layers. By making use of determinants introduced for finite magnetic films [18–20], explicit equations for the Curie temperature are obtained for arbitrary thickness n. In the semi-infinite limit, it is shown that surface polarization, decaying into the bulk, is possible for J_0 and Ω_0 above a critical curve. We also show that for $2\Omega \geqslant Jn_0$ (n_0 = number of neighbours), although no bulk transition is allowed, surface phase transition is still possible for certain regions of Ω_0–J_0 space. Finally, the dependence of the Curie temperature on J_0 and n is obtained numerically for typical values of J, Ω and Ω_0.

2. The Curie temperature in the transverse Ising model

We start with the TIM [10–12]

$$\mathcal{H} = -\sum_{i,r} \Omega_i s_{ir}^x - \frac{1}{2}\sum_{i,r}\sum_{j,r'} J_{ij} s_{ir}^z s_{jr'}^z \tag{1}$$

where Ω is the transverse field in the x direction and s_{ir}^x, s_{ir}^z are the x and z components of the pseudo-spin at the site specified by layer index i and position index r on the same plane (layer). We will allow the exchange constants J_{ij} and the transverse field Ω_i to depend only on the layer index i. Physically, Ω_i represents the ability of a proton (in a hydrogen bond) to tunnel from one position to the other, and J_{ij} represents a correlation energy. Both of these can be changed at the surface layers.

Let $\langle s_i^z\rangle$, $\langle s_i^x\rangle$ be the spin average in the mean-field layer approximation,

$$\langle s_i^x\rangle = \left(\Omega_i/2|\langle \boldsymbol{H}_i\rangle|\right)\tanh\left(|\langle \boldsymbol{H}_i\rangle|/2k_BT\right) \tag{2}$$

$$\langle s_i^z\rangle = \left(\langle H_i^z\rangle/2|\langle \boldsymbol{H}_i\rangle|\right)\tanh\left(|\langle \boldsymbol{H}_i\rangle|/2k_BT\right) \tag{3}$$

and

$$\langle H_i^z\rangle = z_0 J_{ii}\langle s_i^z\rangle + z\left(J_{i,i+1}\langle s_{i+1}^z\rangle + J_{i,i-1}\langle s_{i-1}^z\rangle\right) \tag{4}$$

where z_0, z are the numbers of nearest neighbours in the same plane and between successive planes respectively;

$$|\langle \boldsymbol{H}_i\rangle| = \sqrt{\left(\Omega_i^2 + \langle H_i^z\rangle^2\right)}. \tag{5}$$

We will be studying regions near the transition temperature; then $\langle s_i^z\rangle$ are small, $|\langle \boldsymbol{H}_i\rangle| = \Omega_i$, and equations (2) and (3) become

$$\langle s_i^z\rangle = \tfrac{1}{2}\tanh\left(\Omega_i/2k_BT\right) \tag{6}$$

$$\langle s_i^z\rangle = \left[z_0 J_{ii}\langle s_i^z\rangle + z\left(J_{i,i+1}\langle s_{i+1}^z\rangle + J_{i,i-1}\langle s_{i-1}^z\rangle\right)\right](1/2\Omega_i)\tanh\left(\Omega_i/2k_BT\right). \tag{7}$$

Let J be the interlayer exchange constant in the bulk, then, using the notations from [19,20], $j_i = z_0 J_{ii}/(zJ)$, $j_{ij} = J_{ij}/J$, $\omega_i = \Omega_i/zJ$, $m_i = \langle s_i^z \rangle$ and $\tau_i = 2\omega_i \coth(\Omega_i/2k_BT)$, equation (7) can be written as

$$m_i(\tau_i - j_i) - (j_{i,i+1}m_{i+1} + j_{i,i-1}m_{i-1}) = 0 \tag{8}$$

where $j_{i,i-1}$ and $j_{i,i+1}$ are zero for the first and last layers respectively.

For a uniform system of n layers, with $j_i = j_A$ and $\Omega_i = \Omega$, the Curie temperature is given by the determinant equation

$$B_n = \begin{vmatrix} x_A & -1 & & & \\ -1 & x_A & -1 & & \\ & & \ddots & & \\ & & & x_A & \end{vmatrix}_n = 0. \tag{9}$$

The determinant [18–20] has been earlier evaluated to be

$$B_n = \sinh[(m+1)\phi]/\sinh\phi \qquad x_A = \tau - j_A \qquad \tau = (2\Omega/zJ)\coth(\Omega/2k_BT)$$
$$\cosh\phi = x_A/2 \qquad x_A \geqslant 2. \tag{10}$$

For $x_A \leqslant 2$, ϕ becomes $i\theta$, and the hyperbolic functions become trigonometric functions of θ.

Equation (9) gives $2\Omega \coth(\Omega/2k_BT) = z_0J_A + 2zJ\cos(\pi/(n+1))$. In the limit $n \to \infty$ the bulk Curie temperature T_0 is given by

$$2\Omega \coth(\Omega/2k_BT_0) = z_0J_A + 2zJ. \tag{11}$$

This equation has a solution only if

$$z_0J_A + 2zJ \geqslant 2\Omega.$$

For $J_A = J$, this is simply $n_0J \geqslant 2\Omega$, where n_0 is the total number of neighbours.

3. Surface polarization and the critical curve

To study the surface effects on the ferroelectric transition, we consider two models. In model I (figure 1(*a*)), we consider a system of $n+1$ layers; all the interlayer J_{ij} are equal to J, J_{ii} is equal to J_0 for layer $i = 0$, and J_A otherwise. All the Ω_i are equal to Ω except for layer $i = 0$;

$$\begin{aligned} &m_0(\tau_0 - j_0) - m_1 = 0 \\ &m_i(\tau - j_A) - (m_{i+1} + m_{i-1}) = 0 \qquad i \neq 0, n \\ &m_n(\tau - j_A) - m_{n-1} = 0. \end{aligned} \tag{12}$$

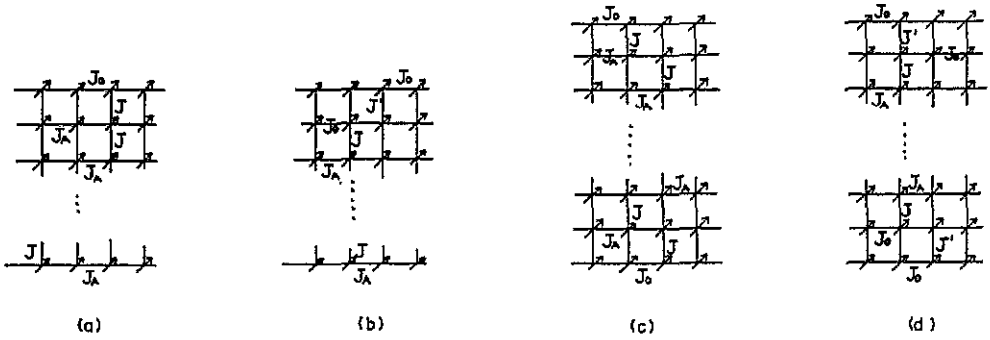

Figure 1. (*a*) Ising model of $n + 1$ layers with one top surface layer. (*b*) Model of $n + 2$ layers with two top surface layers. (*c*) Model of $n + 2$ layers with one top and one bottom layer. (*d*) Model of $n + 4$ layers with two top and two bottom layers.

where $\tau_0 = 2\omega_0 \coth(\Omega_0/2k_BT)$, $x_0 = \tau_0 - j_0$.

The Curie temperature is given [18, 19] by the determinant equation

$$x_0 B_n - B_{n-1} = 0 \qquad n \geqslant 1 \tag{13}$$

where values of B_m are given in (10).

In the semi-infinite limit, if there is a surface transition, $B_{n-1}/B_n = \gamma$, where the decay factor γ is given [19, 20] by

$$\gamma + \gamma^{-1} = x_A \tag{14}$$

then

$$x_0 = \gamma. \tag{15}$$

Equations (15) and (14) give the surface transition temperature $T_s \geqslant T_0$. The equality holds when $\gamma = 1$ or

$$\tau_0 - j_0 = 1. \tag{16}$$

This gives the relation between j_0 and Ω_0, or the critical curve. For the special case $\Omega_0 = \Omega$, $\tau_0 = \tau = 2 + j_A$ and hence $j_0 = j_A + 1$ and is equal to five for a simple cubic structure with $j_A = J$, $j_A = 4$ [10].

In general for $\Omega_0 \neq \Omega$, equation (16) must be solved numerically. We have shown the relation between ω_0 and j_0 for a simple cubic structure with $j_A = 4$ in figure 2(*a*). The different curves are for $\omega = 0$, 1, 2 and 3. Surface transition is allowed above the curves. Note that for $\omega > \frac{1}{2}(z_0 + 2z)$, no phase transition is possible in the bulk. With surface modification, a non-zero surface transition temperature can still occur for the region above the curve given by (14) and (15) with $T = 0$. This is shown by the broken curve with $\omega = 3.5$. In [10], equations similar to (14) and (15) are obtained for this model, and equivalent curves obtained, but the cases $\omega > 3.0$ are not investigated.

We now consider model II (figure 1(*b*)). This is a system of $n + 2$ layers. All the bulk interaction constants are the same as before. For the first two surface layers,

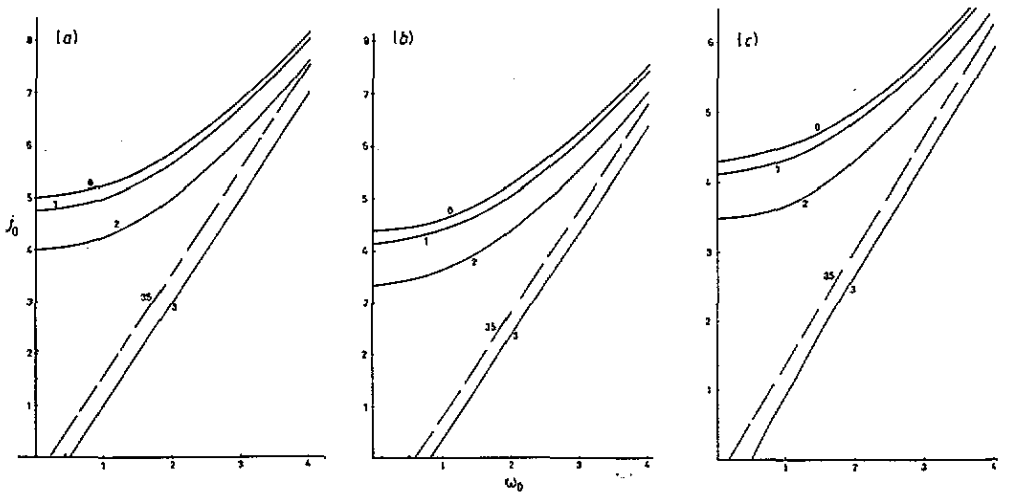

Figure 2. Critical curves for $\omega = 0$, 1, 2, 3 and 3.5: (*a*) model I; (*b*) model II with $c = 1$; (*c*) model II with $c = j_0/j_A$.

$J_{ii} = J_0$, $\Omega_i = \Omega_0$, and the interlayer exchange is $J' = cJ$. In this model, the determinant equation is

$$\begin{bmatrix} x_0 & -c & & & \\ -c & x_0 & -1 & & \\ & -1 & x_A & -1 & \\ & & & \ddots & \\ & & & -1 & x_A \end{bmatrix}_{n+2} = 0$$

which can be written as

$$\left(x_0^2 - c^2\right) B_n - x_0 B_{n-1} = 0. \tag{17}$$

Again in the semi-infinite limit $n \to \infty$,

$$\left(x_0^2 - c^2\right) - x_0 \gamma = 0. \tag{18}$$

Equations (18) and (14) give the surface transition temperature.

The critical curve is obtained by putting $T = T_0$ and $\gamma = 1$.

In figure 2(*b*), we have shown the relations between ω_0 and j_0 for the same choice of j_A and ω. We have taken $c = 1$, which means that the surface interlayer exchange is not changed. For the case $\omega = 3.5$, where the bulk transition is not possible, we have shown the broken curve above which surface transition is allowed.

In figure 2(*c*), we have shown similar results for $c = j_0/j_A$. This means that the interlayer exchange is affected the same way as the intralayer exchange, and is the same case considered in [17]. We have used the same parameter for the bulk. We find results similar to 2(*a*) and 2(*b*), but very different from the case $\Omega_0 = \Omega$ considered previously [10–12].

4. Ferroelectric films

We now consider finite ferroelectric systems of arbitrary thickness. The first system is shown in figure 1(*c*). This is an extension of model I with one top and one bottom surface. All the values of J and Ω are the same except for the first and last layers. Using equation (12), the Curie temperature is seen to be given by the determinant

$$\begin{bmatrix} x_0 & -1 & & & \\ -1 & x_A & -1 & & \\ & & \ddots & & \\ & & -1 & x_A & -1 \\ & & & -1 & x_0 \end{bmatrix}_{n+2} = 0$$

which can be shown to be

$$x_0^2 B_n - 2x_0 B_{n-1} + B_{n-2} = 0 \qquad n \geqslant 2. \tag{19}$$

Here n is the number of bulk layers. The special cases of $n = 0$ and 1 can be written down simply from the determinant. Equation (19) is the general equation for the Curie temperature for arbitrary n. The expressions for the first few values of n have been written down in [17].

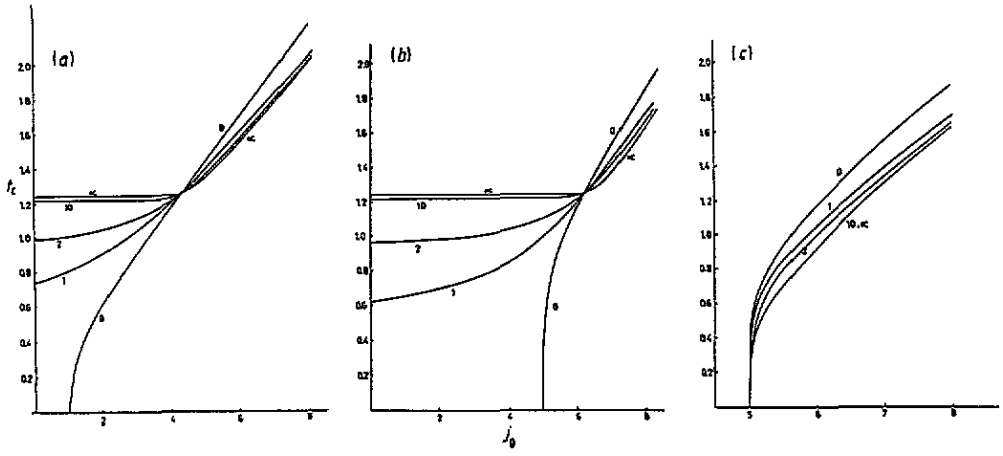

Figure 3. The Curie temperature t_C as a function of j_0 for different layer number n for the system in figure 1(*c*): (*a*) $\omega = 2$, $\omega_0 = 1$; (*b*) $\omega = 2$, $\omega_0 = 3$; (*c*) $\omega = 3$, $\omega_0 = 3$.

In figure 3, we have shown the Curie temperature $t_C = k_B T_C / zJ$ as a function of j_0. We have used $j_A = 4$. The transverse fields chosen are: $\omega = 2$, $\omega_0 = 1$ in figure 3(*a*); $\omega = 2$, $\omega_0 = 3$ in figure 3(*b*) and $\omega = 3$, $\omega_0 = 3$ in figure 3(*c*). The different curves correspond to different numbers of bulk layers n. The case $n = \infty$ is that given by (14) and (15). In figures 3(*a*) and 3(*b*), the $n = 0$ case has no solution for small j_0. In general the Curie temperature decreases with decreasing n for small j_0. However, when j_0 is larger than the critical values, t_C increases with decreasing

n; the maximum is reached at $n = 0$, when there are no bulk layers. In figure 3(*c*), where $\Omega = 3$, no bulk transition is possible for non-zero temperature. There is no solution for t_C for $j_0 < 5$ for any n. Above the critical j_0, the Curie temperature starts from zero, and the value increases for decreasing n. In this case, only surface transition is possible, as the bulk system does not order. Similar results are obtained for $\Omega > 3$.

We next consider a finite system with two top and two bottom surface layers as in figure 1(*d*). This is an extension of model II where the first and last two layers have different exchange constants and transverse field. In this case, the transition is given by the determinant

$$\begin{bmatrix} x_0 & -c & & & & \\ -c & x_0 & -1 & & & \\ & -1 & x_A & -1 & & \\ & & & \ddots & & \\ & & & -1 & x_0 & -c \\ & & & & -c & x_0 \end{bmatrix}_{n+4} = 0.$$

This can be written as

$$\left(x_0^2 - c^2\right)^2 B_n - 2x_0\left(x_0^2 - c^2\right) B_{n-1} + x_0^2 B_{n-2} = 0 \qquad n \geqslant 2. \quad (20)$$

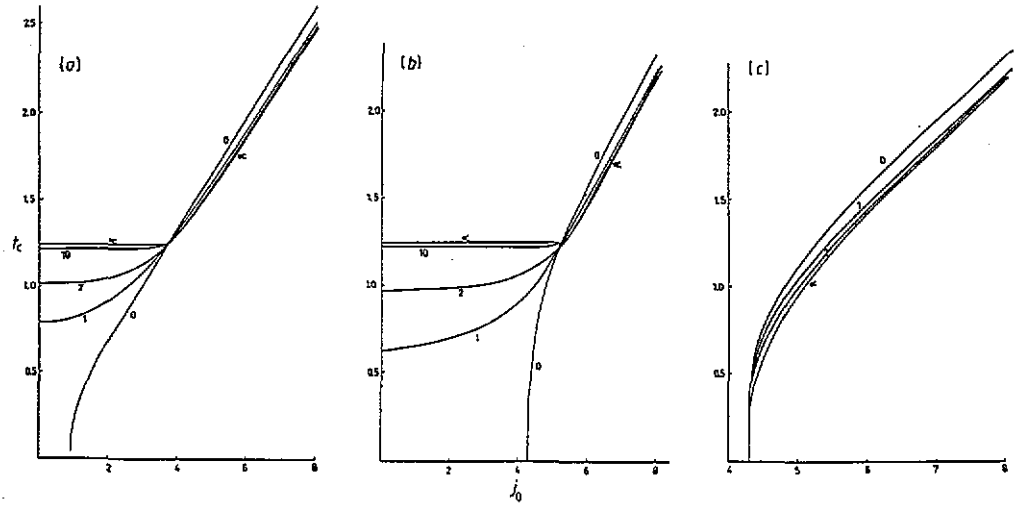

Figure 4. The Curie temperature versus j_0 for the system in figure 1(*d*). The choice of parameters is (*a*) ω 2, $\omega_0 = 1$; (*b*) $\omega = 2$, $\omega_0 = 3$; (*c*) $\omega = 3$, $\omega_0 = 3$.

Again equation (20) can be easily solved numerically for arbitrary n. In figure 4, we have shown our results for the same sets of parameters, namely $\omega = 2$, $\omega_0 = 1$ in figure 4(*a*); $\omega = 2$, $\omega_0 = 3$ in figure 4(*b*) and $\omega = 3$, $\omega_0 = 3$ in figure 4(*c*). We have used $c = j_0/j_A$. The different curves are for different values of n including the $n = \infty$ case. The results are similar to those in figure 3, but the dependence of

t_C on the layer thickness n is smaller above the critical j_0. This is due to the more gradual change in the case with two surface layers. The results for $\omega = 3$, $\omega_0 = 3$ in figure 4(*c*) show the case where no bulk transition is possible. Surface polarizations, however, can occur above the critical j_0.

In conclusion, we have studied the phase transition in finite ferroelectric films in a systematic way by making use of determinants of general order. We have investigated the surface effects due to modification of both exchange constants and transverse fields at the surface. We have seen that surface polarization can occur above the critical curves. This happens even if phase transition is not possible in the bulk. We have found that the Curie temperature for a thin film may be larger or smaller than that in the bulk, depending on the values of J_0 and Ω_0 in the bulk. This is studied in detail for two types of modification to the surface.

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