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# First-order magnetic phase transitions in thin films

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Using the simple Landau model we discuss near-surface magnetic effects for thin films. corresponding to first-order phase transitions. The size effects observed in ultrathin ferroelectric films are in agreement with this theoretical interpretation. The presence of a weak external field is also formulated.

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**1. Introduction.** The theory of Tilley and Zeks[1] provides a reasonable framework fot the analysis of magnetic effects at a second-order transition for films. Based on earlier work by Lubensky and Rubin[2], this theory predicts that, following the sign of the surface coupling, both the order parameter and the critical temperature at the surface, are enhanced or suppressed relative to the bulk parameters. In general, the Curie temperature has been observed to decrease with decreasing film thickness, the magnetization can be enhanced for the ultrathin films, especially for monolayers. Although such highly ordered films seem in contradiction with our intuition and conventional wisdom in ferroelectricity, they agree with current theoretical understanding [1, 2]. On the other hand, the study of ferroelectric thin films has been of growing interest owing to potential applications in the field of microelectronics and dynamic random access memory. Most ferroelectric thin films are first order phase transition ferroelectrics. $KNO_3$ films in the ferroelectric phase [3], have spontaneous polarization values greater than those in bulk single crystals, raised a great hope in the commercialization of such compounds. More recently, numerous experimental studies of thin films and small particles manufactured on the basis of ferroelectric materials, such as $BaTiO_3$ [4], $PbTiO_3$ [5] and $PbZrO_3$ [6] have shown that magnetic properties change noticeably with particle size or film thickness decrease. Obviously, the development of such materials needs the understanding and a careful characterization of their magnetic properties. This necessites the extension of the theory of Tilley and Zeks to first-order phase transitions, as in $KNO_3$. In Section 2 the formulation of the first-order transitions in thin films, including the effect of a weak external field, is presented. The experimental interest of our main results is discussed. Section 3 contains a brief summary of our results.

**2. First-order phase transitions in thin films.** The free-energy in the vicinity of the slightly first-order magnetic transition is given by the following free-energy functional

$$\frac{F}{S} = \int_0^\infty \left[ aM^2 - \frac{b}{2}M^4 + \right.$$
$$\left. + \frac{c}{3}M^6 + \beta\left(\frac{\partial M}{\partial z}\right)^2 + \gamma M^2 \delta(z) \right] dz, \qquad (1)$$

where $S$ is the surface area of the film with plane surfaces at $z = \pm D/2$. Notice that due to geometry chosen, the order parameter depends only on the $z$ coordinate, fluctuations of the order parameter $M$ in a plane perpendicular to the $z$-axis being neglected. The surface coupling $\gamma$ can be positive or negative; the value of $M$ at $z = 0$ is a minimum for $\gamma < 0$ and a maximum for $\gamma > 0$. As usual, we assume that the main temperature dependence is contained in the Landau coefficient $a(T) = a_1(T - T_{c0})/(T_{c1} - T_{c0})$, where $T_{c0}$ is the Curie-Weiss temperature. The remaining coefficients are taken to be temperature independent; they are positive, since we are concerned with a bulk transition of first order at $T_{c1}$. To begin, let us recapitulate some details relevant to our analysis. Instead of working with the parametrization (1), it is better to introduce dimensionless parameters defined at the bulk temperature transition. Defining $a_1 = a(T_{c1}) = 3b^2/16c$, $\xi_1 = \sqrt{\beta/a_1}$, $M_1 = M(T = T_{c1}) = \sqrt{3b/4c}$ we make the scale transformations $z' = z/\xi_1$, $\widetilde{M} = M/M_1$, $\widetilde{\gamma} = \gamma/\sqrt{a_1\beta}$. The Landau free energy functional, including the surface contribution, reads

$$\frac{F}{S} = 2a_1\xi_1 M_1^2 \int_0^{\frac{D}{2}} \left[ \widetilde{a}\widetilde{M}^2 - 2\widetilde{M}^4 + \widetilde{M}^6 + \right.$$
$$\left. + \left(\frac{\partial \widetilde{M}}{\partial z'}\right)^2 + \widetilde{\gamma}\widetilde{M}^2 \delta\left(z' - \frac{D}{2}\right) \right] dz', \qquad (2)$$

where in order to make the equations dimensionless we have defined $D = d/\xi_1$ and where the reduced tempera-

ture is $\widetilde{a} = a/a_1$. We discuss the two signs of $\widetilde{\gamma}$ separately.

**A.** *The extraordinary transition* $\widetilde{\gamma} < 0$. When $\widetilde{\gamma} < 0$ the magnetization at the boundaries is enhanced compared with that in the bulk and $\widetilde{M}(z')$ has the shape of a "hammock" with a minimum at $z' = 0$. The film has two equivalent surfaces at $z' = \pm D/2$. The Euler-Lagrange equations resulting from Eq.(2) including the boundary condition on these surfaces lead to the set of equations

$$D = 2 \int_{\widetilde{M}(0)}^{\widetilde{M}\left(\frac{D}{2}\right)} \frac{d\widetilde{M}}{\sqrt{\left(\widetilde{a} - 2\widetilde{M}^2 - 2\widetilde{M}^2(0) + \widetilde{M}^4 + \widetilde{M}^4(0) + \widetilde{M}^2\widetilde{M}^2(0)\right)\left(\widetilde{M}^2 - \widetilde{M}^2(0)\right)}} \tag{3}$$

$$\widetilde{\gamma}^2\widetilde{M}^2\left(\frac{D}{2}\right) = \widetilde{a}\widetilde{M}^2\left(\frac{D}{2}\right) - 2\widetilde{M}^4\left(\frac{D}{2}\right) + \widetilde{M}^6\left(\frac{D}{2}\right) - \widetilde{a}\widetilde{M}^2(0) + 2\widetilde{M}^4(0) - \widetilde{M}^6(0).$$

The thin film limit

$$\frac{D}{2} \approx \sqrt{\frac{\widetilde{M}\left(\frac{D}{2}\right) - \widetilde{M}(0)}{\left(\widetilde{M}\left(\frac{D}{2}\right) + \widetilde{M}(0)\right)\left(\widetilde{a} - 2\widetilde{M}^2\left(\frac{D}{2}\right) - 2\widetilde{M}^2(0) + \widetilde{M}^4\left(\frac{D}{2}\right) + \widetilde{M}^4(0) + \widetilde{M}^2\left(\frac{D}{2}\right)\widetilde{M}^2(0)\right)}}$$

gives a simple relation between $D$ and the ratio $r = \widetilde{M}(0)/\widetilde{M}(D/2)$:

$$r = 1 - \frac{|\widetilde{\gamma}|\, D}{2}. \tag{4}$$

This limits the validity of this approach to $|\widetilde{\gamma}|\, D \ll 1$. At the approximation considered, the magnetization in the film middle is solution of the quadratic equation

$$\widetilde{a} - \frac{|\widetilde{\gamma}|}{D} - 4\widetilde{M}^2(0) + 3\widetilde{M}^4(0) = 0 \tag{5}$$

giving

$$\widetilde{M}^2(0) = \frac{2 + \sqrt{1 - \frac{3}{\Delta}(T - T_s)}}{3}, \tag{6}$$

where $\Delta = T_{c1} - T_{c0}$. Computing the surface transition temperature necessites the calculation of the free energy. We get

$$F = \frac{2Da_1\xi_1}{|\widetilde{\gamma}|} M_1^2 \widetilde{M}^4\left(\frac{D}{2}\right)(1 - r)\left(1 - \widetilde{M}^2\left(\frac{D}{2}\right)\right). \tag{7}$$

The condition $F = 0$ is satisfied when $\widetilde{M}(D/2) = 1$ and the surface critical temperature reads

$$T_s = T_{c1} + \frac{\Delta\,|\gamma|}{a_1 d}. \tag{8}$$

The latent heat of the transition which results from the discontinuity of the order parameter, can be deduced from the equilibrium free energy (7). At the critical surface temperature, it is given by

$$\frac{\Delta Q_s}{\Delta Q_B} = \frac{d_s T_s}{T_{c1}}. \tag{9}$$

Here $\Delta Q_B = T_{c1}a_1(M_1^2/3\Delta)$ is the latent heat of the bulk in mean-field theory and $d_s$ is the film thickness. The above relation which has the dimension of a length, has to be rearranged in a form convenient to the analysis of experimental data [6]. Indeed, the quantities obtained by integration of the transition peaks are related to our definition by $\Delta Q_s = [\Delta Q_s]_{\text{measured}} S$ and $\Delta Q_B = [\Delta Q_B]_{\text{measured}} V$, where $V$ ($S$) is the volume (surface) of the bulk (film) material. The ratio $V/S$ is given by $d_{\max}$, the film dimension where $T_s/T_{c1} \to 1$, i.e reaches the bulk limit; it is expected that for $d > d_{\max}$, $T_s/T_{c1} = 1$.

Since high Curie temperatures and magnetic moments are desirable for applications, it is worthwhile to analyse experimental data on ferroelectric $KNO_3$ thin films. Indeed, the spontaneous polarization value in the surface is greater than in the bulk for specimens 75 nm thick [7, 8]. Obviously, use of Eq.(6) far from $T_s$ is highly questionable. However, since $T_{c1} = 462\,\text{K}$, is not too high with respect to ambient temperature, we apply

this expression to the evaluation of the spontaneous polarization. The result, $M_s/M_{\rm bulk} = 1.2$ does not coincide with the experimental value (1.5). However, this observation is in total disagreement with earlier measurements [9]. This discrepancy has never been explained, and the existence of an extraordinary transition for $KNO_3$ films is far from being assessed definitely.

**B.** *External magnetic field.* The method is easily extended to the case of an external magnetic field. Now the free energy is

$$F^h = F - h\int_0^\infty M dz.$$

After a convenient redefinition: $\widetilde{h} = h/a_1 M_1$ it is easy to see that the result (5) generalizes to

$$-\frac{\widetilde{h}}{2\widetilde{M}_h(0)} + \widetilde{a} - \frac{\widetilde{\gamma}}{D} - 4\widetilde{M}_h^2(0) + 3\widetilde{M}_h^4(0) = 0.$$

The above equation is easy to handle if we make the assumption of a weak external field ($\widetilde{h} \ll 1$). Now, it is allowed to replace $\widetilde{M}_h(0)$ in the coefficient of $\widetilde{h}$ by its value (6) in the absence of external field. This results in

$$\widetilde{M}_h^2(0) = \frac{2 + \sqrt{4 - 3\widetilde{a} + \dfrac{3|\widetilde{\gamma}|}{D} + \dfrac{3\widetilde{h}}{2\widetilde{M}(0)}}}{3}$$

and

$$\widetilde{a}_s = 1 + \frac{|\widetilde{\gamma}|}{D} + \frac{\widetilde{h}}{2}.$$

The expression above predicts that the critical temperature increases as a linear function of the (weak) applied field and as an increasing function of the surface coupling. Hence, the magnetic enhancement provided by thin plates is strengthened by the presence of an external field.

**C.** *The ordinary transition* $\widetilde{\gamma} > 0$. Now, the order-parameter decreasing at the boundary, the surface transition temperature becomes lower than the bulk transition temperature and we have $\widetilde{a}_s < 1$. Reproducing the calculations of the former subsection with the necessary changes we get

$$T_s = T_{c1} - \frac{\Delta\gamma}{a_1 d}. \qquad (10)$$

Thus the leading contribution drives the surface transition below the bulk transition, as expected. Expression (6) is replaced by

$$\widetilde{M}^2\left(\frac{D}{2}\right) = \frac{2 + \sqrt{1 - \frac{3}{\Delta}(T - T_s)}}{3} \qquad (11)$$

whereas $[\Delta Q_s/\Delta Q_B]_{\rm measured}$ remains given by $d_s T_s/d_{\max} T_{c1}$. Thus we predict the same variation of the surface critical temperature and the latent heat at the transition (modulated by a linear dependence on the thickness) as functions of film thickness. Such finite-size effects have already been measured in antiferroelectric $PbZrO_3$ nanoparticles[6]. In further comparing the data obtained and minimizing the measurement uncertainties, we select the two lowest data for thin films at 32 nm and 34 nm and make a mean value approximation resulting in

$$\langle d\rangle = 34\,\text{nm}, \quad \langle T_s\rangle = 470\,\text{K}, \quad \langle \Delta Q_s\rangle = 1.3\,\text{J/g}.$$

The bulk data are borrowed to the review [10]. This compound exhibits a high transition temperature ($T_{c1} = 505\,\text{K}$) and a Curie-Weiss temperature of the same order ($\Delta = 33\,\text{K}$). the remaining parameters $\Delta Q_B$ and $d_{\max}$ are read on the data curves [6] for large $d$. They are $\Delta Q_B = 6\,\text{J/g}$ and $d_{\max} = 100{-}200\,\text{nm}$. Thus we predict

$$\left[\frac{\Delta Q_s}{\Delta Q_B}\right]_{\rm measured} = 0.22 = \frac{d_s T_s}{d_{\max} T_{c1}} \sim 0.32{-}0.16.$$

For such a rough comparison the agreement is quite satisfying. The decrease of the latent heat with decreasing particle size indicates a decrease in the spontaneous and saturation polarizations, behavior predicted by expressions like (11).

Experimental results for $PbTiO_3$ fine particles (Refs. [5, 11, 12]) show a transition heat which decreases more slowly than the Curie temperature. Indeed, the bulk values of critical temperature and latent heat (766 K, 1750 J/mol) are reached respectively for $d_{\max} = 200, 1000\,\text{nm}$. Taking into account this results by choosing $d_{\max} = 1000\,\text{nm}$ we obtain at $d_s = 31\,\text{nm}$ ($T_s = 488\,\text{K}$)

$$\left[\frac{\Delta Q_s}{\Delta Q_B}\right]_{\rm measured} = 0.3 \approx \frac{d_s T_s}{d_{\max} T_{c1}} \sim 0.2.$$

**3. Conclusion.** Taking into account intrinsic surface effects gives a simple inverse thickness relationship for the critical temperature. A rough analysis shows that the presence of a weak exernal field increases the enhancement for an extraordinary transition. A careful comparison with experimental results on displacive systems ($PbTiO_3$ and $PbZrO_3$) shows a good agreement between theoretical calculations and these results. The law (10) is formally identical to finite-size scaling formulae $(T_{c1} - T_s)/T_{c1} = (d/d_0)^{-\lambda}$ where the microscopic length $d_0$ is a characteristic of the particular system. The critical shift exponent $\lambda$ is the reciprocal of the correlation

length exponent $\nu$ according to the standard finite-size scaling theory (for a recent review see Ref. [13]). The behavior $\lambda \simeq 1$ is predicted by the Ising model in the 2D limit. The Landau model gives $d_0 = (T_{c1} - T_{c0})\,\gamma/a_1$.


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