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SIZE EFFECTS ON THE CURIE TEMPERATURE OF FERROELECTRIC PARTICLES

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Landau–Devonshire theory for ferroelectric phase transition is applied to ferroelectric spherical particles. The extrapolation length is shown to be size dependent. The Curie temperature as a function of size is calculated. Theoretical results are compared with experimental data in the literature and good agreement is obtained.

Keywords: A. ferroelectrics, D. phase transitions

1. INTRODUCTION

SIZE and surface effects on the properties of ferroelectrics is not only of theoretical interest, recent development of ferroelectric films and composite materials has made it a subject of practical importance. In attacking this problem, various approaches including phenomenological Landau–Devonshire theory [1–7], transverse Ising model [7–10] and scaling theory [11] have been taken. Unfortunately, they have been applied so far to ferroelectric films and semi-infinite ferroelectrics. On the other hand, owing to the advanced powder synthesis techniques in recent years, experiments on size effect in ultrafine ferroelectric particles have been accumulating [12–17]. Jaccard *et al.* [12] observed that KDP fine particles embedded in an insulating medium show no ferroelectric phase transition if the size is less than 150 nm. Glass *et al.* [13] investigated the evolution of ferroelectricity in ultrafine-grained $\text{Pb}_5\text{Ge}_3\text{O}_{11}$ in a glass matrix, and showed that when the grain size is smaller than about 10 nm, the polarization is unstable. For PbTiO_3 particles, Ishikawa *et al.* [14] carried out a Raman study. They found that the soft mode frequency decreases with decreasing particle size. An empiric formula for the size dependence of T_c was proposed. From the empiric fitting, the critical size can be obtained to be 13.8 nm. Zhong *et al.* [15] made a specific heat study of PbTiO_3 particles. It was shown both T_c and polarization decrease with decreasing particle size. Empiric fitting of the T_c versus size gave a critical size of 9.1 nm. For BaTiO_3 particles, Uchino *et al.* [16]

measured the particle size dependence of axis ratio c/a . It showed a lowering of T_c with decreasing size. A critical size of 115 nm was obtained from the empiric fitting. However, no theoretical calculation has been reported in this respect except for an empiric fitting [14–16]. It is desirable to extend the above theories to ferroelectric particles. In the present work, we study the size and surface effect of ferroelectric particles using the Landau–Devonshire theory. Size dependence of the phase transition temperature is obtained and compared with available experiments.

2. THEORY

To apply the Landau–Devonshire theory to a finite size and inhomogeneous ferroelectrics, the total free energy instead of the energy density should be used. It can be written

$$F = \int \left[\frac{1}{2} A (T - T_{0\infty}) P^2 + \frac{1}{4} B P^4 + \frac{1}{2} D (\nabla P)^2 \right] dv + \int \frac{1}{2} D \delta^{-1} P^2 dS, \quad (1)$$

where the volume integral and surface integral give the free energy of the interior and surface layer respectively. δ is the extrapolation length that describes the difference between the surface and the interior. $T_{0\infty}$ is the bulk Curie–Weiss temperature and equals the bulk Curie temperature $T_{c\infty}$ in the case of second order phase transition. The gradient term $D(\nabla P)^2$ accounts for the inhomogeneous distribution of polarization.

In the present work, we focus on the static behavior of the ferroelectrics, thus, the effect of external electric field are neglected. The depolarizing field is also ignored. Although depolarization effect is very important in finite and inhomogeneous ferroelectrics, however, if the free carrier density and its velocity is high enough or the medium where the particles are embedded in is conductive at the transition temperature, the depolarizing field can be compensated as discussed by Fensenko *et al.* [18].

To obtain the spatial distribution of polarization, the Euler-Lagrange equation

$$D\nabla^2 P = A(T - T_{0\infty})P + BP^3 \quad (2)$$

must be solved subject to the boundary condition

$$\frac{\partial P}{\partial n} + \delta^{-1}P = 0 \quad \text{at the surface,} \quad (3)$$

where n is the unit normal to the surface.

In the case of ferroelectric films, equations (2) and (3) have been simplified and solved for second order [2] and first order [3] transitions. For a ferroelectric particle of arbitrary shape, however, they are very difficult to solve.

We therefore suppose the particle to be spherical with diameter d . The polarizations are in the same direction, that is, the unique polar direction of the crystal. In the absence of depolarizing field, the distribution of the polarization magnitude depends only on the surface effect, i.e., the extrapolation length δ . The latter can be assumed to be independent of the angle between the surface normal and the polarization [4], the magnitude of the polarization is therefore expected to be a function of only the radius r . Using spherical coordinates, equations (2) and (3) can be written

$$D\left(\frac{d^2 P}{dr^2} + \frac{2}{r} \frac{dP}{dr}\right) = A(T - T_{0\infty})P + BP^3 \quad (4)$$

$$\frac{dP}{dr} + \delta^{-1}P = 0, \quad r = \frac{d}{2}. \quad (5)$$

Near the Curie temperature, T_c , equation (4) can be linearized

$$D\left(\frac{d^2 P}{dr^2} + \frac{2}{r} \frac{dP}{dr}\right) = A(T - T_{0\infty})P. \quad (6)$$

For $\delta > 0$, it is expected that $T_c < T_{c\infty}$, we have the solution for P

$$P = P_0 \frac{J_{1/2}(r/\xi)}{(r/\xi)^{1/2}}, \quad (7)$$

where $\xi = (D/A|T_c - T_{c\infty}|)^{1/2}$ and $J_{1/2}$ is the 1/2 order Bessel function. Using the identity $(J_m(x)/x^m)' = -J_{m+1}(x)$ and the boundary condition we have the equation for T_c

$$\frac{J_{3/2}(d/2\xi)}{J_{1/2}(d/2\xi)} = \frac{\xi}{\delta} \quad (8)$$

For $\delta < 0$, i.e. $T_c > T_{c\infty}$, similarly, we have

$$P = P_0 \frac{I_{1/2}(r/\xi)}{(r/\xi)^{1/2}} \quad (9)$$

and

$$\frac{I_{3/2}(d/2\xi)}{I_{1/2}(d/2\xi)} = -\frac{\xi}{\delta}, \quad (10)$$

where $I_{1/2}$ and $I_{3/2}$ are the 1/2 order and 3/2 order modified Bessel functions (Bessel function with imaginary argument).

A significant modification is to the extrapolation length δ . It is determined by the interaction constants and the coordination number on the surface and in the interior. If the interaction constant between nearest-neighbor pseudo-spins is J_s when both pseudo-spins are on the surface and is J otherwise, and the pseudo-spins form a simple cubic lattice with lattice constant a_0 , then δ can be expressed as [1, 7]

$$\frac{1}{\delta} = \frac{5J - 4J_s}{a_0 J}. \quad (11)$$

In ferroelectric films or semi-infinite ferroelectrics, δ is thickness independent. In a spherical ferroelectric particle of diameter d , the average coordination number n_{av} at the surface will be smaller when d decreases, hence, δ is size dependent. Assuming $d \gg a_0$, then $n_{av} = 4(1 - a_0/d)$, and δ can be written

$$\frac{1}{\delta} = \frac{5J - n_{av}J_s}{a_0 J} = \frac{5}{d} + \frac{1}{\delta_\infty} \left(1 - \frac{a_0}{d}\right), \quad (12)$$

where δ_∞ is the extrapolation length when $d = \infty$. The size dependence of δ results in some interesting characteristics as will be shown latter.

When a first order phase transition is considered, B becomes negative and a term of P^6 with positive coefficient is added. Since the equation parallel to equation (4) cannot be linearized in this case, we solve it numerically using finite difference method by dividing the radius into 1000 sections, and the spatial distribution of P at different temperature and particle size is calculated. Substitute the polarization into the free energy expression, the free energy as a function of temperature is calculated, thus the Curie temperature obtained.

3. RESULTS AND DISCUSSION

Equations (7) and (9) may be compared with the analogues for a film [1]. The function $J_{1/2}(x)/x^{1/2}$ and $J_{3/2}(x)/x^{1/2}$ may be regarded as the spherical equivalents of $\cos(x)$ and $\sin(x)$, and likewise function $I_{1/2}(x)/x^{1/2}$ and $I_{3/2}(x)/x^{1/2}$ are the equivalents of $\cosh(x)$ and $\sinh(x)$ [1]. Thus the analogy is quite close.

The spatial distribution of polarization in the sphere is calculated for ferroelectrics of a second order and a first order phase transition respectively. Similar to the results of ferroelectric films [2, 3], the polarization at the surface is reduced compared with that in the interior when $\delta > 0$ and it is enhanced when $\delta < 0$. In the case of $\delta < 0$, polarization can exist well above the bulk Curie temperature.

Figure 1 shows the reduced Curie temperature $T_c/T_{c\infty}$ as a function of d at different δ_∞ for ferroelectrics with second order phase transition, which is obtained via equations (8) and (10). Numerical calculations similar to those used for a first order transition were also carried out. The results are the same as Fig. 1. The dependence of $T_c/T_{c\infty}$ on d for ferroelectrics with first order phase transition are shown in Fig. 2. $\delta_\infty = \infty$ means that the polarization at the surface is the same as that in the interior when $d = \infty$.

It is seen that when $\delta_\infty > 0$, T_c is always lower than that for $\delta_\infty = \infty$. When $\delta_\infty < 0$, T_c can be much greater than $T_{c\infty}$. These are similar to those in ferroelectric films [2, 3].

No matter the δ_∞ values, T_c will become zero provided the particle is small enough. It is different from ferroelectric films. In films, only when $\delta > 0$, can the T_c be zero at a small thickness. If $\delta < 0$, T_c increases with decreasing thickness and will never become zero [2, 3]. The difference is attributed to the fact that δ is size dependent in ferroelectric particles.

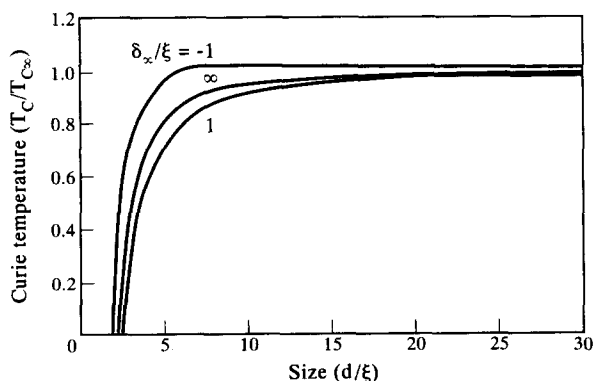


Fig. 1. T_c as a function of size for ferroelectrics with second order phase transition. $A = 1$, $B = 1$, $D = 1$, $T_{c\infty} = 1$, $\xi = 1$.

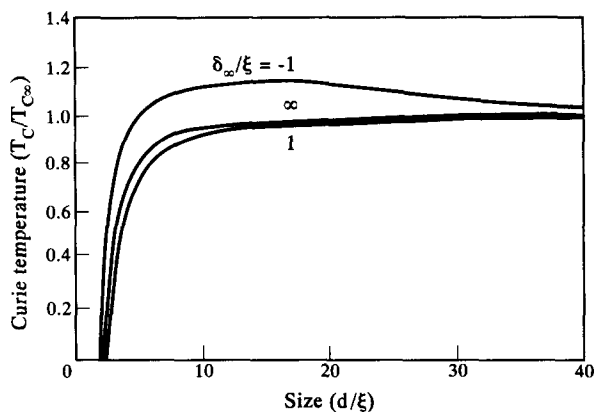


Fig. 2. T_c as a function of size for ferroelectrics with first order phase transition. $A = 1$, $B = -0.12$, $C = 0.09$, $D = 1$, $T_{c\infty} = 1$, $T_{0\infty} = 0.97$.

Even $\delta_\infty < 0$, δ will become positive when $d < 5|\delta_\infty| + a_0$ [equation (11)], so T_c behaves like that for $\delta > 0$.

In the case of $\delta_\infty < 0$, the size dependence of T_c is not monotonic. T_c increases slowly with decreasing particle size when d is large and decreases steeply when d is small. At larger values of d and d decreases, δ hardly changes while the volume fraction of surface layer increases. This layer tends to have a higher T_c , so the T_c increases. At smaller value of d , δ will change into positive, so T_c behaves like that for $\delta_\infty > 0$. Experimentally, Arlt *et al.* [19] measured the Curie temperature of BaTiO_3 with grain size of $6.8 \mu\text{m}$, $0.7 \mu\text{m}$ and $0.28 \mu\text{m}$ to be 128°C , 137°C and 124°C respectively. This might be due to the size dependence of δ .

The size at which $T_c = 0 \text{ K}$ is the ferroelectric critical size. It can be seen from Fig. 1 and 2 that the stronger the surface coupling (smaller δ^{-1}), the smaller the critical size.

To compare with the experiments, the size dependence of T_c of PbTiO_3 and BaTiO_3 are calculated. The bulk value of Curie temperature

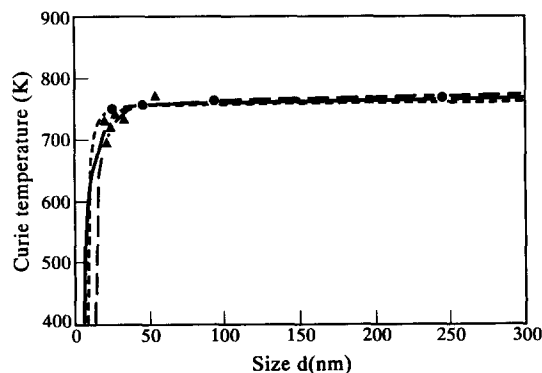


Fig. 3. Size dependence of T_c of PbTiO_3 particles.

Table 1. Parameter values for PbTiO₃ and BaTiO₃ (cgs unit)

	T_{∞} (K)	$T_{0\infty}$ (K)	Curie constant (10 ⁵ K)	A 10 ⁻⁵	B 10 ⁻¹²	C 10 ⁻²¹	D 10 ⁻¹⁶	δ_{∞} nm
PbTiO ₃	765 ^a	722 ^a	4.1 ^a	3.1 ^a	-2.0 ^a	5.8 ^a	5 ^c	3
BaTiO ₃	403 ^b	391 ^b	1.7 ^b	7.4 ^b	-4.4 ^b	3.7 ^b	1263 ^d	43

^a Reference [20]. ^b Reference [21]. ^c Reference [22]. ^d Reference [23].

T_{∞} , Curie-Weiss temperature $T_{0\infty}$, coefficient A , B and C are from [20] and [21] (listed in Table 1). The values of D are determined based on an estimation by Zhirnov [22] and Wemple [23], while δ is taken to be adjustable. Figure 3 shows the size dependence of T_c of PbTiO₃ particles, where solid line is our calculation, solid triangles with long dashed line are Raman scattering results and empiric fitting in [14], solid circles with dashed line are specific heat measurement results and empiric fitting in [15]. Figure 4 shows the size dependence of T_c of BaTiO₃ particles, in which solid line is our calculation, solid circles with dashed line are the axis ratio results and empiric fitting in [16].

It can be seen from the two figures that the agreement between the experimental and our calculation is good. It is also interesting to note that the calculation predicts a smaller critical size than that by the empiric formula. For PbTiO₃ and BaTiO₃, the predicted values are 4.2 nm and 44 nm respectively. Possible mechanism responsible for the difference may be the polarization gradient, the noncrystalline surface layer and depolarization effect. If we ignore the gradient term in equation (1), the size dependence of T_c can be derived

$$T_c = T_{\infty} - \frac{6D}{\delta A d} \quad (13)$$

It is similar in form to the empiric formula used in [14–16]. Besides, if there is a noncrystalline layer at

the surface, it will make the nominal size greater than the effective size, and its influence will increase with decreasing size. In addition, it has been shown that the Curie temperature of ferroelectric films is reduced if depolarization effect is taken into consideration [4], thus the critical size will be larger.

4. CONCLUSION

The Curie temperature of ferroelectric particles as a function of the size is calculated with the extrapolation length being size dependent. The calculation agrees well with the experimental results of PbTiO₃ and BaTiO₃ and predicts a smaller critical size.

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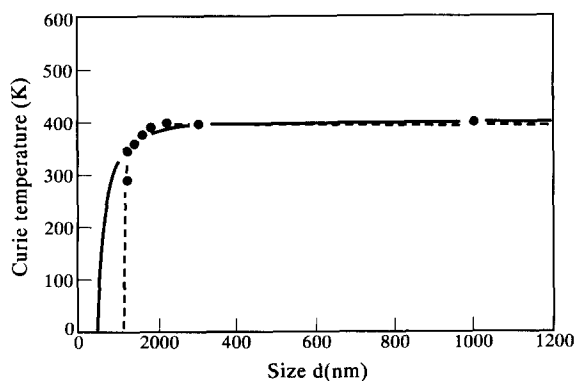


Fig. 4. Size dependence of T_c of BaTiO₃ particles.

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