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Phenomenological theory of size effects in ultrafine ferroelectric particles (PbTiO₃-type)

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ABSTRACT

A new phenomenological model is proposed and discussed to study the size effects on phase transitions in PbTiO₃-type ferroelectric particles. This model, by taking size effects on the phenomenological Landau-Ginzburg-Devonshire coefficients into consideration, can successfully explain the size effects on Curie temperature, c/a ratio, thermal and dielectric properties of lead-titanate-type ferroelectric particles. Theoretical and experimental results for PbTiO₃ fine particles are also compared and discussed. The relationship between the current model and the model of Zhong *et al* (Phys. Rev. B 50, 698 (1994)) is also discussed.

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I Introduction

Size effects on ferroelectric materials have been studied both experimentally ¹⁻⁶ and theoretically ⁷⁻¹³. Experimental results all showed that there are strong size effects on ferroelectric materials. Cottam, Tilley and Zeks ⁷ investigated the occurrence of surface modes in semi-infinite ferroelectric materials. Three different approaches were used: (1) a microscopic pseudo-spin theory based on the Ising model in a transverse field, (2) a macroscopic Landau theory in which surface effects can be introduced phenomenologically and (3) a polariton model appropriate to the very long wavelength region. Existence conditions and dispersion relations were deduced for the localized surface modes, which were predicted by all three methods. The results were illustrated by means of numerical examples. Methods (1) and (2) gave rise to similar results within certain limits and a formal relationship between these two approaches was established. Tilley has discussed phase transitions in ferroelectric thin films using a theoretical model based on the Landau-Devonshire expansion. A surface is characterised by an extrapolation length δ , the negative of the logarithmic derivative of the order parameter at the surface. For negative δ , the critical temperature T_c of a film is increased above the bulk value, while for positive δ it is decreased. It was shown that depolarisation effects further decrease T_c in general (See ref [7] for details).

Using this theory, Tilley and Zeks *et al* ⁸ discussed the thickness effects on the second-order ferroelectric/paraelectric phase transition in ferroelectric thin films. By introducing a sixth-order term, Scott *et al* ¹⁴ discussed the thickness dependence of first-order ferroelectric/paraelectric phase transitions in ferroelectric thin films.

A Landau-type phenomenological theory for a size-driven phase transition in ferroelectric particles of BaTiO_3 and PbTiO_3 was clearly demonstrated by Zhong *et al* ⁹⁻¹³ taking the surface and non-equilibrium energy into consideration and the introduction of a surface extrapolation length δ . The model can be used on some simple particle geometries, such as thin films, spherical and cylindrical particles. It may be solved numerically. For spherical ferroelectric particles, we may assume uniaxial polarisation, the magnitude of which depends only on the radius ($r = d/2$). Contrary to the case of

thin films, the extrapolation length was shown to be size dependent; the spatial distribution of polarization was obtained by numerical solutions of the Euler-Lagrange equations with boundary condition $\frac{dP}{dr} + \frac{P}{\delta} = 0$. The size dependent phase transitions have the same order as the temperature-driven phase transitions. The polarisation decreases with decreasing particle size and eventually disappears (a size driven phase transition); i.e. the Curie temperature decreases with decreasing particle size and reaches zero at the critical size. The calculated size dependence of T_c for PbTiO_3 and BaTiO_3 was said to be in excellent agreement with the experimental results for Sol-Gel (SG) derived powders. Thus the size dependent behaviour of SG BaTiO_3 appears to be “normal” in spite of the calculated critical size (44nm) being somewhat smaller than the experimental value (115nm) ¹. For PbTiO_3 the predicted critical size was 4.2nm, while that obtained from experiment was 8.2—13.8 nm ².

In this paper, the experimental results of size effects on PbTiO_3 ultrafine particles are first summarised. Then, a brief introduction to the theory of Zhong *et al* ⁹ and some results are given in section 3. Calculations by the author based on the model of Zhong *et al* ⁹ are also presented. This shows that this model cannot give a good explanation of the size effect on thermal properties. A new model derived by the author is proposed and explained in section 4 & 5. Some calculations are also given and some discussions based on this new model. In section 6, the relationship between the model of Zhong *et al* ⁹ and the new model proposed by the author is discussed.

II Experimental results

All the experiments done on PbTiO₃, BaTiO₃ and PbZrO₃ particles show that the Curie temperature decreases with decreasing particle size. Experiments on PbTiO₃ showed that the ferroelectric properties decrease with decreasing particle size; including Curie temperature, latent heat, tetragonality (*c/a* ratio) and soft-mode frequency^{2-4, 6}. Dielectric property measurements also showed clearly that there exists a strong size effect¹⁵.

Experiments conducted on PbZrO₃ anti-ferroelectric fine particles also showed that the phase transition temperature, latent heat, *c/a* ratio all decrease with decreasing particle size; the extrapolated critical size is 23±3nm, dielectric measurement also showed that the diffuseness of the phase transition increases with decreasing particle size⁵.

Experiments of BaTiO₃ ferroelectric fine particles showed that the phase transition temperature decreases with particle size; thus, when the particle size is less than 105nm, the structure became cubic^{1, 16}. The transmission electron microscopic results also confirmed this result¹⁷.

In the following two subsections, the experimental results on PbTiO₃ particles are first summarised, then a new model of size effects on ferroelectric particles of PbTiO₃-type is proposed.

A. Size dependence of Curie Temperature of PbTiO₃²

From Zhong *et al*, the size dependence of the Curie temperature can be described by the following formula²:

$$T_c = T_{\infty} - \frac{A}{d - d_0} \quad (1)$$

Where T_{∞} is the Curie temperature of bulk PbTiO₃ crystals, which was taken to be 766K; *A* and d_0 are constants derived from the experimental value, *d* is the particle

diameter. From the experimental data analysis, the values of $A=256\text{nm}\cdot\text{K}$ and $d_0=8.8\text{nm}$ were determined ². This gave us a critical size $d_c=9.1\text{nm}$, where the Curie temperature decreased to 0K.

Ishikawa *et al* ^{3, 4} obtained a similar formula for PbTiO_3 particles by the Raman Scattering method, and later verified this by X-ray diffraction. They obtained a critical size d_c of about 9-11nm.

Experiments on BaTiO_3 ¹ and anti-ferroelectric PbZrO_3 particles ⁵ gave similar formulas.

B. Size dependence of latent heat and entropy change at the phase transition.

Experiments² on PbTiO_3 showed that the latent heat ΔQ of PbTiO_3 particles clearly showed a size dependence; for particle size from $1\mu\text{m}$ down to 23nm, the latent heat decreased by 20 times. The entropy change ΔS at the phase transition is given by

$\Delta S = \frac{\Delta Q}{T_c}$. Fig.1 b shows the size dependence of the entropy change during the phase

transition. It drops rapidly with decreasing particle size. Careful study of this relationship reveals an exponential variation with the inverse size of the particles. From the experiment data analysis, we found the following empirical formula:

$$\Delta S = \text{EXP}\left(-\frac{40\text{nm}}{d}\right) \quad (2)$$

This is shown in Fig.1 b. $\text{Ln}(\Delta S)$ and $1/d$ are linearly related.

III Results on Ferroelectric Particles using theory of Zhong *et al* ⁹

A. Model ²

The model of Zhong *et al* ⁹ for ferroelectric particles was based on the Landau phenomenological theory by taking surface and inhomogeneous effects into consideration. If the ferroelectric has a first-order phase transition, for a finite-size and inhomogeneous ferroelectric, the total free energy should be written:

$$G = \int [\frac{1}{2}\alpha_0(T - T_{0\infty})P^2 + \frac{1}{4}\beta P^4 + \frac{1}{6}\gamma P^6 + \frac{1}{2}K(\nabla P)^2]dv + \int \frac{1}{2}K\frac{P^2}{\delta} dS \quad (3)$$

Where P is the polarisation, $\beta < 0$, and $T_{0\infty}$ is the Curie-Weiss temperature of bulk material. The second integration corresponds to surface effects, and δ is the extrapolation length. It reflects the difference between surface and bulk. It is the length below the surface where the polarisation drops to zero. K is a constant and determines the contribution of inhomogeneity.

For a second-order phase transition, $\beta > 0$, and $T_{0\infty}$ equals the Curie temperature $T_{c\infty}$.

B. Results for ferroelectric particles with a first-order phase transition ²

For fine particles with a first order phase transition such as PbTiO_3 , the Euler-Lagrange free energy function is:

$$K\nabla^2 P - \alpha_0(T - T_{0\infty})P - \beta P^3 - \gamma P^5 = 0 \quad (4)$$

with boundary condition:

$$\frac{\partial P}{\partial n} = -\frac{P}{\delta} \quad (\text{on surface of the particles}) \quad (5)$$

Where n is the unit normal to the surface.

For a ferroelectric particle of arbitrary shape, Eqs. (4 and 5) are very difficult to solve. Two simplifications may be made. First, the particles are assumed to be spherical with diameter d . Second, let the polarisation lie unidirectional, depending only on the radius r . Then, equations (2) and (3) in spherical coordinates become:

$$D \left[\frac{d^2 P}{dr^2} + \frac{2}{r} \frac{dP}{dr} \right] = \alpha_0 (T - T_{0\infty}) P + \beta P^3 + \gamma P^5, \quad (6)$$

$$\frac{dP}{dr} + \frac{P}{\delta} = 0, \quad r = \frac{d}{2}. \quad (7)$$

For a spherical particle, δ will depend on size because the coordination number on the surface will be smaller for a smaller particle. The average coordination number can be written:

$$n_{av} = 4 \left[1 - \frac{a_0}{d} \right] \quad (8)$$

Thus:

$$\frac{1}{\delta} = \frac{5}{d} + \frac{1}{\delta_{\infty}} \left[1 - \frac{a_0}{d} \right] \quad (9)$$

Where δ_{∞} is the extrapolation length for $d=\infty$.

Calculations⁹ based on this model showed that it could successfully explain the size effect on phase transition temperatures such as BaTiO₃, PbTiO₃ and PbZrO₃. Calculations showed that the Curie temperature and polarisation would decrease with decreasing particle size. The model predicted that there exists size driven phase transitions for which, below a critical size, polarisation cannot be established in the crystal and the particles will transform into a cubic para-electric phase. Readers should refer to reference⁹ for details.

C. Size effect on latent heat and entropy change at phase transition based on the model of Zhong *et al*

The model of Zhong *et al* ⁹ successfully explains the size effects on ferroelectricity and phase transition temperature. From the experimental results of PbTiO₃ and PbZrO₃ particles, the phase transition decreases with decreasing particle size. On the other hand, the latent heat decreases much faster with decreasing particle size than does the Curie temperature. In this section, the thermal properties are calculated using this model which shows that it cannot explain the latent heat properties very well. Thus, some modification needed to be done on this model. This will be discussed in the next section.

Fig.2 shows the calculated latent heat and entropy jump across the phase transition. The entropy jump does not agree very well with the experimental results. All the experimental results on PbTiO₃ ^{2, 6} and PbZrO₃ ⁵ phase transitions showed that the entropy jump dropped sharply with decreasing particle size, but the calculated value showed a small increase with decreasing particle size based on the model of Zhong *et al*. This forces the calculated latent heat to decrease more slowly than the Curie temperature, which contradicts the experimental results. Results for PbTiO₃ ultrafine particles showed that as the particle size decreases from 1 μ m to 23nm, the Curie temperature decreases from 493°C to 477°C, a drop of only 16°C, but the latent heat decreases from 1740J/mol to 61J/mol, which is a much larger percentage decrease. Curve fitting showed that the relationship between the size and latent heat was very close to exponential (Fig.1).

This model failed because the phenomenological coefficients were assumed to be size independent. Careful comparison with experimental results implies that, in order to explain the size effect on latent heat and entropy jump of phase transition, the size effect on the phenomenological coefficients have to be taken into consideration.

IV Size dependence of phenomenological coefficients

The size dependence of phenomenological coefficients was already observed in experiment. Cem Basceri *et al* ¹⁸ has reported that the first-term coefficient of LGD power series was thickness dependence for barium strontium titanate (BST) ferroelectric thin films. From the experiment they obtained the following relationship:

$$\alpha(t) = \alpha_0(T - T_{0\infty}) + \frac{A}{t}, \quad (10)$$

where t is the thickness of the thin film.

For ferroelectric particles such as PbTiO_3 , which have a first-order phase transition, it was necessary to take a size dependent second-term coefficient for the LGD power series in order to explain the experimental results and make a change to the size dependence of the first-term coefficient.

After careful study of the experimental data for PbTiO_3 , it was found that if the phenomenological coefficients are assumed to be size dependent and have the following relation, good agreement with experimental results was obtained:

$$\alpha(T, d) = \alpha_0(T - T_{0\infty}) + \frac{A}{d - D_s} \quad (11)$$

$$\beta(d) = \beta_\infty \exp\left(-\frac{B}{d}\right) \quad (12)$$

assuming γ (eq. 6) is size independent.

Here β_∞ is the value of β for bulk crystals, A and B are constants derived from the experimental values. For PbTiO_3 , $A=0.04 \text{ J}\cdot\text{m}^2\cdot\text{C}^{-2}$ and $B=80 \text{ nm}$. D_s is a special particle size very close to the critical size and obtained from experiment. $D_s=8.8 \text{ nm}$ for PbTiO_3 . $T_{0\infty}$ is the Curie-Weiss temperature of bulk materials and d is the particle size.

A. Microscopic explanation

Following Devonshire ¹⁹, we assume that the vibration of each ion can be written in the form:

$$E = au^2 + bu^4 \quad (13)$$

where a and b are the force constants of the vibration, u is the displacement distance. Only even orders lower than four are included in the energy expression.

The displaced ion is equivalent to a dipole moment which we assume to have components of $(\gamma_x x, \gamma_y y, \gamma_z z)$ where the γ 's are constants of the order of the ionic charge. Now if the substance is polarised along z there will be a force acting on the ion having component (ζP_z) , where ζ is Lorenz factor, and hence an additional term in the potential energy of magnitude: $-\zeta(\gamma_z z P_z)$.

Then the partition function f for a single ion is given by:

$$f = \int_{-\infty}^{+\infty} \exp\left(\frac{\zeta\gamma_z z P_z - az^2 + bz^4}{kT}\right) dz \quad (14)$$

The free energy per unit volume is given by:

$$G = -NkT \sum Lnf + \frac{1}{2} \zeta P_z^2 \quad (15)$$

where N is the number of unit cells per unit volume and the summation is over the different ions in the unit cell. Simplifying this formula and comparing it with the LGD form:

$$G = \frac{1}{2} \alpha P_z^2 + \frac{1}{4} \beta P_z^4 + \frac{1}{6} \gamma P_z^6 \quad (16)$$

We have:

$$\alpha = \zeta - \frac{1}{2} N \zeta^2 \left[\frac{\gamma_z}{a} - \frac{kT \gamma_z^2}{a^2} \left(\frac{3b}{a} \right) \right] \quad (17)$$

$$\beta = \frac{N \zeta^2}{4} \frac{b \gamma_z^4}{a^2} \quad (18)$$

For detailed deduction of the above formula, refer to Devonshire *et al* ¹⁹.

From the experimental results for BaTiO₃, PbTiO₃, PbZrO₃ fine particles^{2, 5, 6, 16} the measured c/a ratio decreases with decreasing particle size. This will change the force the ion feels. The dependence of force constants on particle size was also shown by the soft-mode measurement. Raman scattering on PbTiO₃ showed the soft mode decreasing sharply with decreasing particle size. So, the force constants a and b will change with particle size, therefore the phenomenological constants α and β should be size dependent.

B. Macroscopic explanation

According to Tilley *et al*⁸ and Zhong *et al*⁹, the surfaces of ferroelectric thin films and particles are different from that of the inner part of the particle. The surface region has different polarisation and dielectric constant. The free energy of the whole system can be expressed into surface and bulk terms.

$$\begin{aligned}
 G &= G_{surface} + G_{bulk} = \left(\frac{1}{2} \alpha_{surface} P_{surface}^2 + \frac{1}{4} \beta_{surface} P_{surface}^4 + \frac{1}{6} \gamma_{surface} P_{surface}^6 \right) \\
 &+ \left(\frac{1}{2} \alpha_{bulk} P_{bulk}^2 + \frac{1}{4} \beta_{bulk} P_{bulk}^4 + \frac{1}{6} \gamma_{bulk} P_{bulk}^6 \right) \quad (19) \\
 &= \frac{1}{2} \alpha_{effective} P_{effective}^2 + \frac{1}{4} \beta_{effective} P_{effective}^4 + \frac{1}{6} \gamma_{effective} P_{effective}^6
 \end{aligned}$$

The ions near the surface will feel a different force than those at the inner part of the crystal. The phenomenological coefficient for the surface will be different from that for the bulk material. When the particle is very large, the surface effects can be neglected and the $\alpha_{effective}$, $\beta_{effective}$ and $\gamma_{effective}$ will equal their bulk values. On the other hand, they will approach the surface values when the particle size is very small.

V Size effect on ferroelectric properties based on a new model

Based on the assumption of size dependence of the phenomenological coefficients, a new model is now proposed to predict the size effects on ferroelectricity of spherical particles. All the calculations are based on PbTiO_3 to allow the theoretical calculations to be compared with the experimental results.

From the former discussions, the new model can be written as:

$$G = \frac{1}{2}\alpha(T, d)P^2 + \frac{1}{4}\beta(d)P^4 + \frac{1}{6}\gamma P^6 \quad (20)$$

$$\alpha(T, d) = \alpha_0(T - T_{0\infty}) + \frac{A}{d - D_s} \quad (21)$$

$$\beta(d) = \beta_\infty \exp\left(-\frac{B}{d}\right) \quad (22)$$

where $A=0.04 \text{ J}\cdot\text{m}^2\cdot\text{C}^{-2}$, $B=80 \text{ nm}$ and $D_s=8.8 \text{ nm}$ for lead titanate particles. Other parameters for lead titanate are as follows: $\alpha_0=2.79\times 10^5 \text{ J}\cdot\text{m}\cdot\text{C}^{-2}\cdot\text{K}$, $\beta_\infty=-1.62\times 10^9 \text{ J}\cdot\text{m}^5\cdot\text{C}^{-2}$, $\gamma=4.23\times 10^{11} \text{ J}\cdot\text{m}^9\cdot\text{C}^{-6}$.

A. Size driven phase transition

From eq. (20), the spontaneous polarisation P_s , phase transition temperature T_c and the spontaneous polarisation at T_c (P_{sc}) can be written:

$$P_s = \frac{-\beta(d) + \sqrt{\beta(d)^2 - 4 \times \alpha(T, d) \times \gamma}}{2\gamma} \quad (23)$$

$$T_c = T_{0\infty} - \frac{A}{(d - D_s) \times \alpha_0} + \frac{3\beta(d)^2}{16\alpha_0\gamma} \quad (24)$$

$$P_{sc} = -\frac{3\beta(d)}{4\gamma} \quad (25)$$

Substituting (23) into (20) and taking $T=0K$, the free energy as a function of d can be obtained. Fig.3a shows the theoretical results. Clearly, there exists a size driven ferro/para-electric phase transition and a critical size d_c , below which the polarisation cannot be established in the particle.

The spontaneous polarisation P_s at $T=0K$, as a function of particle size, is shown in Fig.3b. It has the characteristic of a first-order phase transition, the spontaneous polarisation jumps to zero where the particle size reaches the critical size d_c .

The size dependence of the phase transition temperature is calculated according to eq.(21), and compared with experimental values in Fig.4. Note the calculated temperature is renormalized to 766K when $d=\infty$. The agreement is very good and the Curie temperature has a significant drop only near the critical size.

B. Size effect on latent heat and entropy change

The discontinuous change in polarisation causes a discontinuous change in entropy. The entropy jump ΔS at T_c can be written:

$$\Delta S(d) = \frac{1}{2} \alpha_0 P_{sc}^2 = \frac{3\alpha_0 \beta(d)}{8\gamma} \quad (26)$$

The resulting latent heat is:

$$\Delta Q(d) = T_c \times \Delta S = \left(T_0 - \frac{A}{(d - D_s) \times \alpha_0} + \frac{3\beta(d)^2}{16\alpha_0 \gamma} \right) \times \frac{3\alpha_0 \beta(d)}{8\gamma} \quad (27)$$

Fig.5 shows the size effect on entropy and latent heat. Note the calculated value of $\Delta S(d=\infty)$ is renormalized into $2.3 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$ and $\Delta Q(d=\infty)$ is renormalized to $1750 \text{ J} \cdot \text{mol}^{-1}$ to compare with the experimental results. It can be seen from these figures that the agreement between experimental data and theoretical calculation is excellent.

Substituting (23) into (26), we have:

$$\Delta S = \frac{3\alpha_0 \beta_\infty}{8\gamma} \times \text{EXP} \left(-\frac{B}{d} \right) \quad (28)$$

$$\text{So } \quad \text{Ln}(\Delta S) = -\left(\frac{B}{d}\right) + \text{Ln}\left(\frac{3\alpha_0\beta_\infty}{8\gamma}\right) \quad (29)$$

This formula gives the linear relationship between $\text{Ln}(\Delta S)$ and $\frac{1}{d}$. The gradient of the line is $-B$. From the experimental values, the measured gradient (Fig.1b) is -80 nm . Thus, $B=80 \text{ nm}$.

C. Size effect on crystal structure (c/a ratio)

According to Devonshire's¹⁹ calculation, $\left(\frac{c}{a} - 1\right)$ is proportional to P_s^2 . Therefore, we have:

$$\eta(d) \equiv \frac{c}{a} - 1 = K \times P_s^2(d) \quad (30)$$

where K is a constant.

Substituting (20) into (30), and choosing the appropriate value for K , and putting $\eta(d=\infty)=0.0652$, which is the bulk value of PbTiO_3 , we have:

$$R(d) \equiv \eta(d=\infty) - \eta(d) \equiv \left(\frac{c}{a}\right)_{d=\infty} - \left(\frac{c}{a}\right)_d = K(P_s^2(d=\infty) - P_s^2(d)) \quad (31)$$

Fig.6a shows the size dependence of $\eta(d)$ of PbTiO_3 particles; the solid line is the theoretical calculation and solid and open circles are experimental data measured by X-ray diffraction. $\text{Ln}\{R(d)\}$ versus reduced particle size $(d-D_c)$ is shown in Fig.6b. Clearly this is a linear relationship when the particle size is larger than 25 nm . So, the relationship between $R(d)$ and $(d-D_c)$ can be written approximately in the exponential form:

$$R(d) \equiv \left(\frac{c}{a}\right)_{d=\infty} - \left(\frac{c}{a}\right)_d \approx K \times \text{EXP}[-C(d - D_c)] \quad (32)$$

where D_c is the critical particle size and C and K are constant. When d is equal to D_c , the particle changes to the paraelectric phase and $\left(\frac{c}{a}\right)_{d=D_c} = 1$. Substituting into (32), we

obtain:

$$K = \left(\frac{c}{a} \right)_{\infty} - 1 \quad (33)$$

Formula (31) can be rewritten as:

$$\left(\frac{c}{a} \right)_d = \left(\frac{c}{a} \right)_{\infty} - \left[\left(\frac{c}{a} \right)_{\infty} - 1 \right] \text{EXP}[-C(d - D_c)] \quad (34)$$

This is the empirical formula obtained by S. Chattopadhyay from experimental values of PbZrO₃ and PbTiO₃ particles^{5, 6}. This formula is a very good approximation for relatively larger particles. For example, it applies above 25nm for PbTiO₃ fine particles very well.

D. Size effect on dielectric property

From (eq. 20), the susceptibility below the Curie temperature $T_c(d)$ can be obtained as:

$$\begin{aligned} \chi_1(T, d) &= \frac{\partial^2 A}{\partial D^2} \Big|_{E=0} = \alpha(T, d) + 3\beta(d)D^2 + 5\gamma D^4 \\ &= -4\alpha(T, d) + \frac{3\beta^2(d)}{\gamma} \left[1 + \sqrt{1 - \frac{4\alpha(T, d)\gamma}{\beta^2(d)}} \right] \end{aligned} \quad (35)$$

Above the Curie temperature, the susceptibility is:

$$\chi_2(T, d) = \frac{1}{\alpha(T, d)} \quad (36)$$

For ultra-fine particles, it is assumed that the particle size d is distributed about an average size d_0 according to a Gaussian distribution function of the form:

$$f(d) = f_0 \times \exp \left[-\frac{(d - d_0)^2}{2\sigma^2} \right] \quad (37)$$

where σ is the standard deviation and f_0 is the normalization factor. Defining a deviation factor $\xi = \frac{\sigma}{d_0}$ to represent the spreading of particle size, the effective susceptibility is

then:

$$\chi_{effect}(T, d_0) = \frac{\int_0^{d_c(T)} \chi_2(T, d) f(d) dd + \int_{d_c(T)}^{\infty} \chi_1(T, d) f(d) dd}{\int_0^{\infty} f(d) dd} \quad (38)$$

where $d_c(T)$ is the critical size at temperature T . If the temperature is higher than T , all the particles size less than $d_c(T)$ will be in the paraelectric phase.

In this model the real integration is taken from the critical size d_c to ∞ because the model is invalid when the crystal size below d_c (see section 5.5). The above equation becomes:

$$\chi_{effect}(T, d_0) = \frac{\int_{d_c}^{d_c(T)} \chi_2(T, d) f(d) dd + \int_{d_c(T)}^{\infty} \chi_1(T, d) f(d) dd}{\int_{d_c}^{\infty} f(d) dd} \quad (39)$$

Fig.7 shows the susceptibility versus temperature for different particle sizes and deviation factor ξ . The dielectric peak decreases and moves to lower temperatures when the particle size decreases. Also with larger deviation factor ξ , the dielectric peak becomes smaller and diffuse, in agreement with the experimental measured results for BaTiO₃, PbTiO₃ and PbZrO₃ ferroelectric particles ^{1, 5, 6, 15}.

Note that we do not try to explain the size effect on the dielectric constant measured at room temperature for BaTiO₃ ²¹ and PbTiO₃ ²² ultrafine particles by this theory. That behavior has been explained successfully by *Shaikh et al* ²¹ by taking the effects of strain and domain walls into consideration.

E. Validity of the new model

The inverse relationship between the LGD coefficient $\alpha(d)$ and the particle size d makes the model invalid when the particle size is less than d_c . The inverse relationship forces the $\alpha(d)$ to diverge at d_c and gives invalid results below d_c . Therefore, the new model can not be used when the particle size is less than d_c .

This problem for this model stems from the simple assumption of $\alpha(d)$. The relationship was obtained from experimental empirical formulae and it is a good approximation for

relatively larger particles. When the particle size become very small, the inverse relationship is invalid and another kind of formula should be proposed to discuss the physical properties of smaller particles. At present, there are not enough experimental data to realize an approximate formula for $\alpha(d)$ of particle size near and below d_c .

VI Relationship with the Model of Zhong *et al*⁹

In that model, only the surface effects and non-equilibrium effects were taking into consideration in the free energy formula. They assumed the LGD coefficients were size independent.

The new model takes the size effect on LGD coefficients into consideration. Furthermore, the surface effect and non-equilibrium terms are considered and re-introduced into the size dependence of the LGD coefficients. So, the LGD coefficients α , β , γ should be the effective coefficients of the particle. By this modification, the thermal properties of ferroelectric particles can be explained successfully.

Another advantage of this new model is the simpler free energy expression. It can be solved easily and the physical properties can be discussed analytically.

VII Summary

An improved phenomenological theory is proposed by taking the size effects on LGD coefficients into account.

By assuming the size dependence of the LGD coefficients α and β , one can successfully explain the size effects on physical properties of PbTiO₃-type ferroelectric particles, including thermal property, *c/a* ratio, dielectric property and Curie temperature.

The new model also predicts a size driven phase transition for which the ferroelectricity disappears when the particle size reaches a critical particle size.

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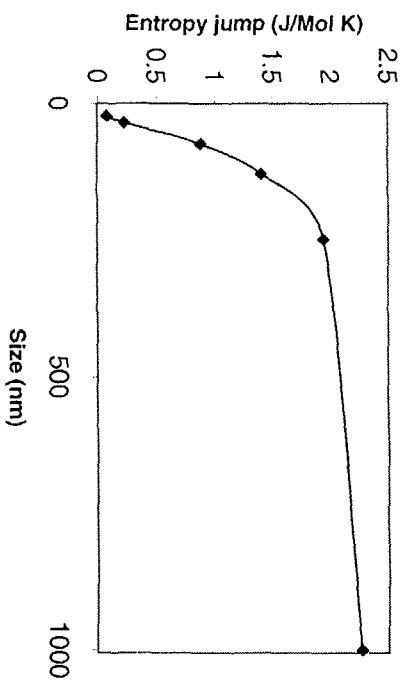
Figure Caption:

- Fig.1** Size dependence of entropy change at phase transition of PbTiO_3 particles.
- (a) shows the relationship between size and ΔS .
- (b) shows the relationship between ΔS and $\ln(\Delta S)$ versus $\frac{1}{d}$. It is clear that $\ln(\Delta S)$ has a linear relationship with $\frac{1}{d}$.
- Fig.2** Entropy jump at phase transition according to the model of Zhong *et al.* All the LGD coefficients are taking from ref. [9] ($\alpha_0=1$, $\beta=0.12$, $\gamma=0.09$, $K=25$, $\delta_\infty=3\text{nm}$)
- Fig.3** Size dependence of free energy and spontaneous polarisation
- Fig.4** Size dependence of Curie temperature.
- Fig.5** Size dependence of latent heat and entropy jump at Curie temperature.
- Fig.6** (a) Size dependence of c/a ratio.
(b) Relationship between $\ln\{R(d)\}$ and $(d-D_c)$
In figure (a) • From Zhong *et al* [2]
* From Ishikawa *et al* [4]
- Fig.7** Dielectric susceptibility of different particle size and deviation factor.

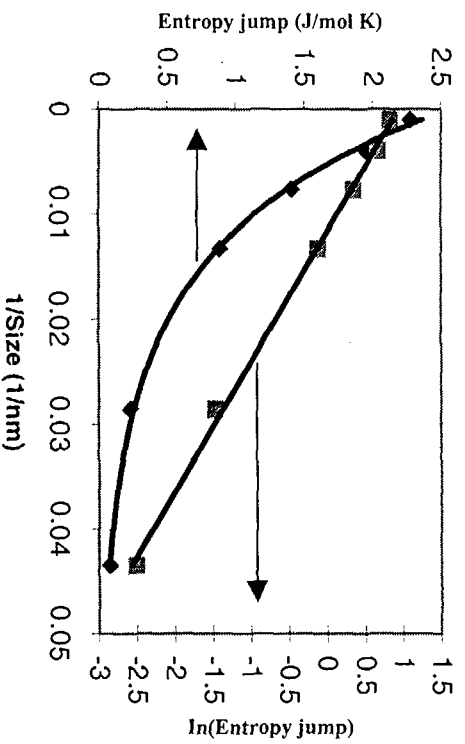
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(a)



(b)

Figure 1

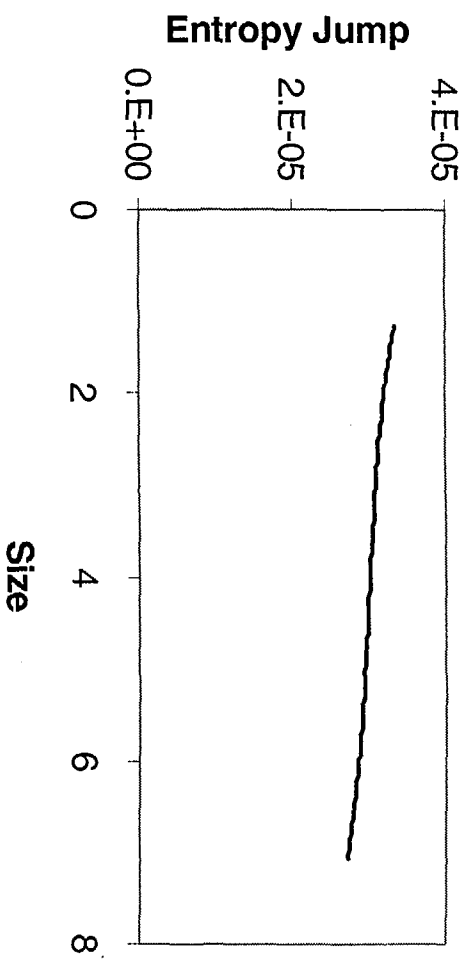
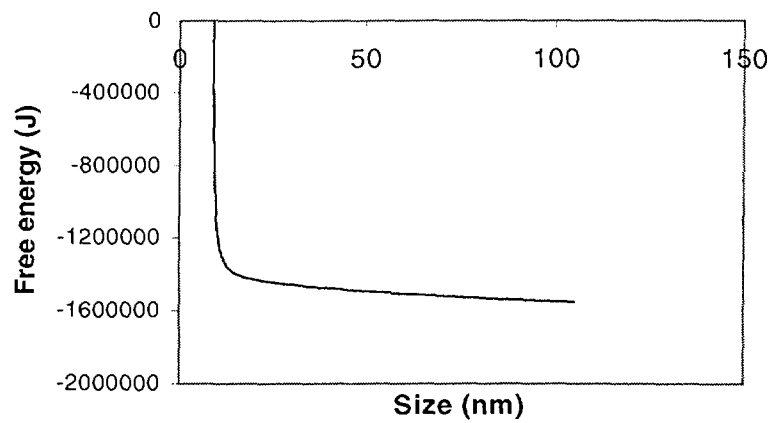
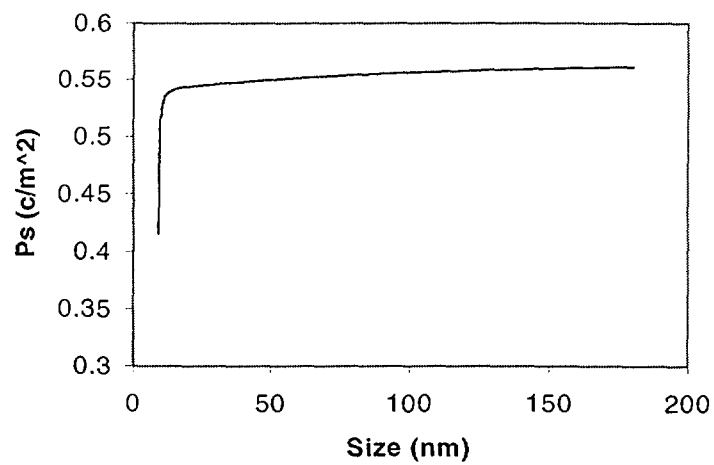


Figure 2



(a)



(b)

Figure 3

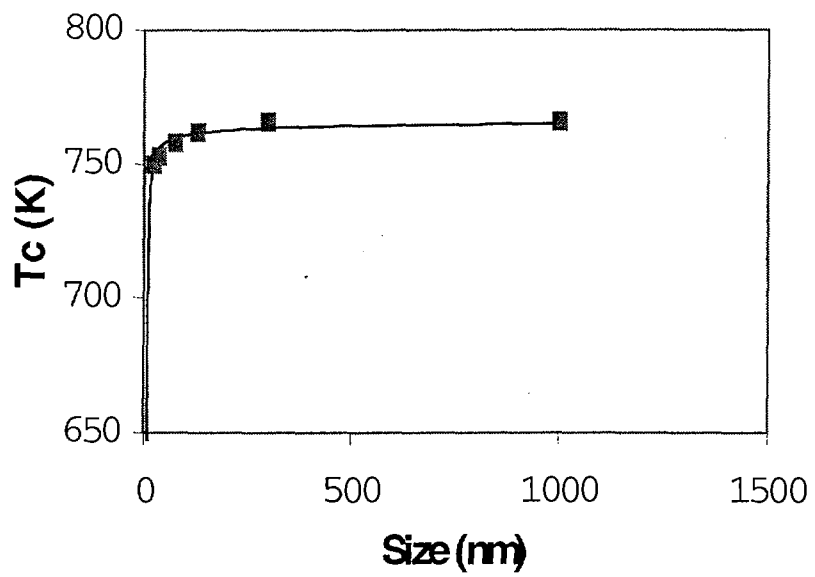
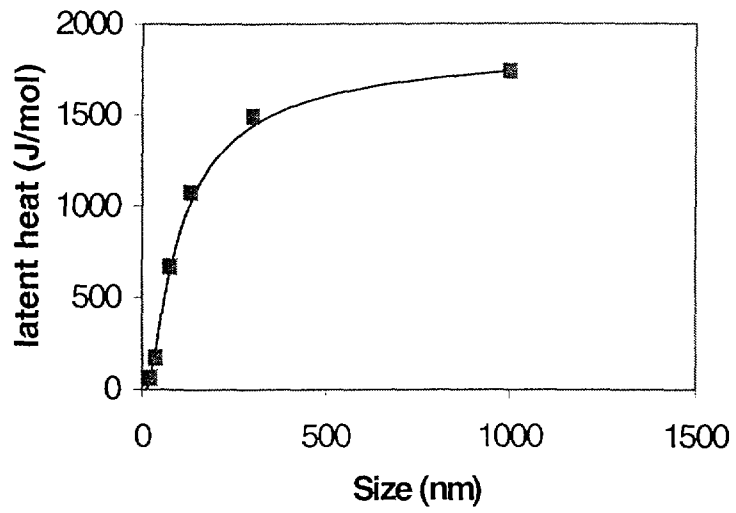
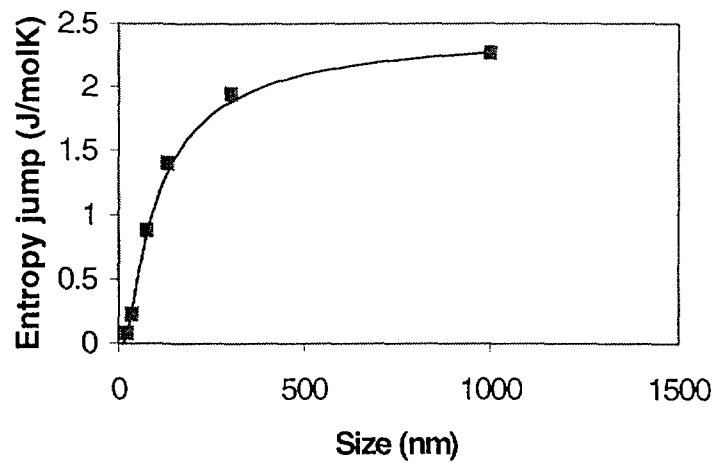


Figure 4

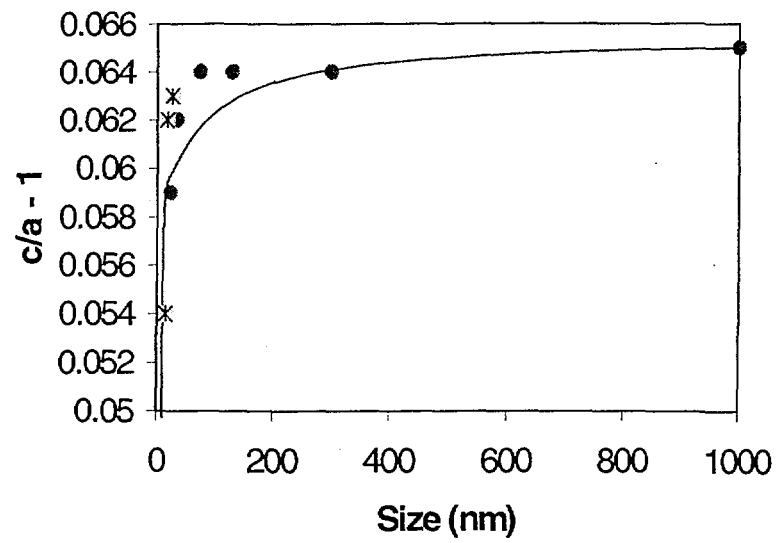


(a)

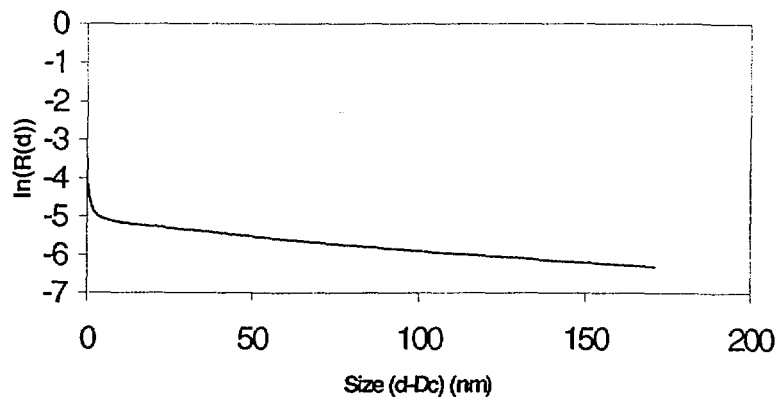


(b)

Figure 5



(a)



(b)

Figure 6

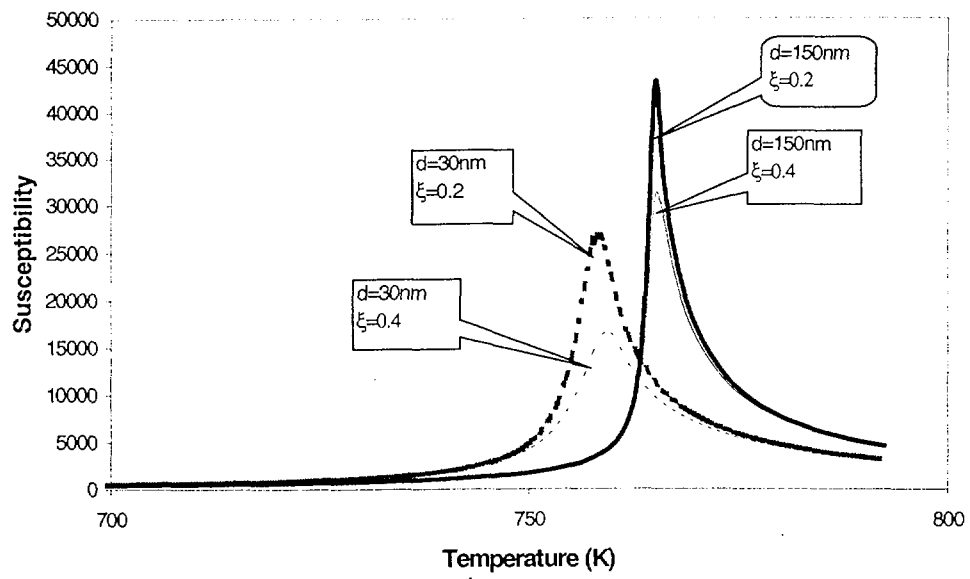


Figure 7