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Theory of size-driven transitions in displacive and order–disorder ferroelectrics

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Abstract. We present a simple theory for structural transitions in displacive ferroelectrics of the perovskite (ABO_3) type. As in earlier approaches, our model is based on the competition between the elastic energy cost for the displacement of the B-ion from the centrosymmetric position, and the energy gain due to ferroelectric ordering of the dipoles. We use an effective single-site approximation which leads naturally to a first-order transition. This transition takes place at a certain temperature $T_c(L)$ as the temperature is varied, and at a certain size $L_c(T)$ as the size of the system is varied. The transition temperature $T_c(L)$ is suppressed as the sample size is reduced, and vanishes for samples below a certain size. This is in accordance with recent observations on nanocrystalline perovskites. For systems with a *continuous* bulk transition, which can also be treated within our theory, we show that size effects are highly suppressed, a result that is also borne out by experiments on order–disorder ferroelectrics with a continuous transition.

1. Introduction

Though the experimental study of finite size effects in ferroelectric materials has a long history [1, 2], the development of advanced synthetic techniques has now made it possible to study compounds in the form of phase-pure, ultrafine particles with a narrow size distribution. There is also a strong motivation for studying size-limited, ferroelectric systems in view of their current and potential applications as sensors, memory elements, nano-robotic and micro-electromechanical devices [3].

A ferroelectric is termed ‘displacive’ when the elementary dipoles strictly vanish in the paraelectric phase, and ‘order–disorder’ when they are non-vanishing but thermally average out to zero in the paraelectric phase [4]. A similar distinction may also be made in terms of the dynamics of the phase transition. However, it is now apparent that quite a few ferroelectrics fall somewhere in between the two ideal limits of ‘displacive’ and ‘order–disorder’. In recent years, the displacive ferroelectric transitions in $PbTiO_3$ and $BaTiO_3$ nanoparticles have been studied in detail. The natures of the size effect observed in the two systems are essentially similar. A decrease in the particle size causes monotonic reductions in (i) the transition temperature T_c and (ii) the tetragonal distortion of the unit cell which characterizes the ferroelectric phase. So, at a low enough particle size, the lattice tends to assume the high temperature, high symmetry, cubic paraelectric structure.

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Uchino *et al* [5] have found that T_c (in °C) falls with particle size L following the relation

$$T_c(L) = T_c(\infty) - \frac{B}{(L - L_c)} \quad (1)$$

where $T_c(\infty) = 128$ (500) °C, $B = 700$ (588.5) °C nm and $L_c = 110$ (12.6) nm for BaTiO₃ (PbTiO₃).

In a recent study of nanocrystalline PbTiO₃ using dielectric, thermal and structural measurements, [6], it was established that with decreasing particle size (i) there is a monotonic decrease in the T_c , (ii) the value of the peak dielectric constant (ϵ_{max}) decreases, (iii) the ferroelectric transition becomes increasingly diffuse and (iv) the crystallographic unit cell tends towards higher symmetry ($c/a \rightarrow 1$). Qualitatively similar results were also obtained for PbZrO₃, a displacive *antiferroelectric* [7]. A decrease in T_c with size was also indirectly suggested [8] from a study of the temperature dependence of the Raman soft mode frequency [9], while a size dependence of the soft mode was observed later [10].

It is also instructive to compare finite size effects in displacive and order–disorder ferroelectrics. In electrically insulated samples of sub-micrometre KH₂PO₄, the depolarization field appeared to prevent the stabilization of ferroelectric ordering below a critical size [11]. However, a later study of NaNO₂, a typical order–disorder system, showed clearly that there was no suppression of T_c down to 5 nm in samples suspended in either electrically insulated or conducting media [12]. It is clear that size effects are much weaker for order–disorder ferroelectrics. This feature is also predicted by our theory (section 5).

In recent years, there have been a few attempts to understand theoretically the nature of size effects in ferroelectrics. Using the phenomenological Landau–Devonshire theory, Zhong *et al* [13] have shown that the ferroelectric T_c should decrease with decreasing size, ultimately leading to a size-driven phase transition from the ferroelectric to the paraelectric phase. Shih *et al* [14] have considered the effect of incorporating the depolarization energy in the Landau free energy density.

In this paper, we restrict ourselves mainly to the description of quasi-free ferroelectric nanoparticles. The system is assumed to consist of loosely aggregated, unclamped particles which are not electrically isolated. Under such circumstances, we can ignore the effects of both external strain and depolarization. This approximates the experimental situation considered by Chattopadhyay *et al* [6]. Specifically, we have selected PbTiO₃ as the model system, but the results should apply to other displacive-type systems with first-order transitions as well.

PbTiO₃ is a classical displacive ferroelectric with a tetragonal perovskite structure ($a = 0.3899$ nm, $c = 0.4153$ nm at room temperature). In its paraelectric phase, PbTiO₃ has a cubic perovskite structure ($a = c = 0.396$ nm just above T_c) consisting of TiO₆ octahedra arranged in a simple cubic pattern, with the Pb ions occupying the spaces in between. It undergoes a first-order transition to a tetragonal ferroelectric phase at $T_c = 768$ K. At room temperature, the Ti and O ions are displaced with respect to the Pb ions, parallel to the polar axis with displacements $d_{Ti} = 0.018$ nm and $d_O = 0.047$ nm [15].

The paper is organized as follows. In section 2 we present our model and discuss the qualitative physics of the phase transition. Section 3 gives the details of the calculation, and our results are presented in section 4. In the model adopted in the present paper, the transition takes place as a result of competition between an ordering tendency of dipoles in adjacent cells and the elastic energy cost associated with the displacement of the atoms. Our main results are the following. We offer a simple physical explanation for the first-order transition in displacive systems driven by temperature and system size. We calculate the strain in the unit cell and make comparison with experiments. While the temperature dependence of the strain does not agree very well with experiments, the size dependence is in excellent agreement. We show that for ferroelectrics with a second-order bulk transition, size effects are highly suppressed (section 5).

We present the phase diagram for both kinds of ferroelectric in the temperature–size plane. The paper ends with a brief discussion of the advantages and limitations of our theory, and prospects for future work (section 6).

2. The model and its physical basis

A dipole moment is created in each unit cell (ABO_3) by the displacement of the B-ion from the centre of the unit cell to an off-centre position. This is accompanied by a distortion of the cubic unit cell to a tetragonal one with sides $a \times a \times c$. The order parameter, $\sigma = c/a - 1$, obtained from powder x-ray diffraction studies [6], is a measure of the strain or distortion of the unit cell.

Clearly, there is an energy cost at each site associated with the displacement [17] ξ_i of the ‘central’ B-ion. In spite of this cost, the system may find it profitable to undergo a distortion accompanied by an off-centre shift of the B-ion if there is a sufficiently large negative contribution from the interaction energy of dipoles when they are aligned. We describe this energy phenomenologically by an interaction $-J\xi_i\xi_j$ between nearest neighbours and refer to this term as the ‘Ising’ term (see below). J is positive for ferroelectrics, whereas a negative J will describe antiferroelectrics. In the present work we focus mainly on ferroelectrics (see however section 6).

The effective Hamiltonian for the problem is thus the sum of an elastic part and an Ising part. In the single-site approximation employed by us, the long-range dipole–dipole interaction is taken care of by an effective field. The form of the elastic part may be deduced from simple symmetry considerations. The cost of a displacement ξ_i of the central atom at the i th unit cell and an associated strain σ_i ($\equiv c/a - 1$) of the unit cell can be written as a power-series expansion in ξ_i and σ_i , at each site. Only even powers of ξ_i are allowed in the expansion since the energy cannot depend on which way the atom moves. There is no such restriction for the strain σ , which is a scalar. We thus arrive at the Hamiltonian

$$H(\xi, \sigma) = \sum_i \left(\frac{1}{2}k_2\xi_i^2 + \frac{1}{4}k_4\xi_i^4 + a\sigma_i^2 - b\sigma_i\xi_i^2 \right) - J \sum_{i,j} \xi_i\xi_j. \quad (2)$$

There is no term proportional to σ_i alone since, when all $\xi_i = 0$, the system should be in equilibrium with $\sigma_i = 0$.

An additional consideration has gone into the truncation of the power series. It is expected on symmetry grounds that the thermally averaged value, $\langle\sigma\rangle$, of the strain will be an even function of the thermally averaged displacement $\langle\xi\rangle$, and, for small distortions, $\langle\sigma\rangle \sim \langle\xi^2\rangle$. This is borne out extremely well from experimental data on PbTiO_3 (figure 1). From the data we find the empirical relation

$$\langle\sigma\rangle \simeq A \frac{\langle|\xi|^2\rangle}{a^2} \quad (3)$$

where $A = 3.24$ for PbTiO_3 . The quadratic relation holds good for other oxides as well [18], with different values of A .

We may therefore conclude that ξ^2 and σ are of the same order of smallness. The power series expansion in (2) thus retains all terms up to $\mathcal{O}(\sigma^2)$ or $\mathcal{O}(\xi^4)$.

Starting with the Hamiltonian (2), we can easily integrate out the strain field σ , to arrive at an effective free energy in terms of the displacements,

$$F(\xi_i) = \frac{1}{2}\lambda_2 \sum_i \xi_i^2 + \frac{1}{4}\lambda_4 \sum_i \xi_i^4 - J \sum_{(ij)} \xi_i\xi_j \quad (4)$$

where $\lambda_2 = k_2$ and $\lambda_4 = k_4 - b^2/4a$.

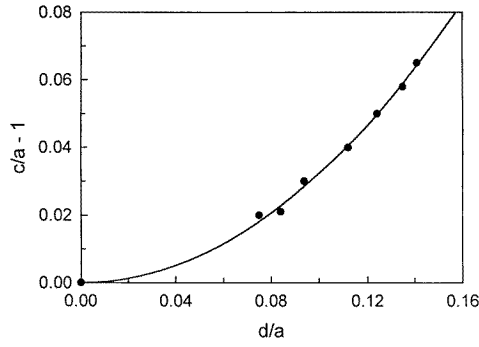


Figure 1. The tetragonal strain, $\sigma (= c/a - 1)$ of the PbTiO_3 unit cell plotted as a function of d/a (the displacement $|\xi|$ of the homopolar atom in units of lattice spacing) [18]. The filled circles correspond to measurements [16] at different temperatures below T_c , and the line is the best fit to equation (3).

To obtain a physical picture of the temperature driven transition in bulk samples, we introduce variables α_i and d_i corresponding to the direction and magnitude of the displacement,

$$\xi_i = d_i \alpha_i \quad (5)$$

where $\alpha_i (= \pm 1)$ is an Ising variable. With this change of variables, the ferroelectric part of the Hamiltonian (see equation (10)) becomes a compressible Ising term [19], since the coupling ($\sim Jd^2$) is proportional to the displacement. At a temperature T , the Ising part cannot be ordered (and hence the system cannot be a ferroelectric) if the coupling is less than T (we set k_B , the Boltzmann constant, equal to unity in this paper). This means that the system can be a ferroelectric *only if* d^2 is greater than $\sim T/J$. Even when $d^2 > T/J$, whether it actually is a ferroelectric or a paraelectric depends on energetic considerations. This explains why we expect a first-order transition driven by temperature.

To treat this quantitatively, we may perform a partial trace over the α degree of freedom and evaluate a free energy functional of the distortions d_i alone, given by

$$e^{-F(d)} = \text{Tr}_{\alpha_i} e^{-H(\alpha, d)}. \quad (6)$$

The global minimum of $F(d)$ determines the thermodynamic phase. We shall see in the following section that this procedure automatically leads to a first-order transition.

The size induced transition can also be easily understood within this picture. For a system with $N = (L + 1)^3$ sites, the elastic energy $\sim N$ and the Ising energy is $\sim Nz(L)$ where $z(L)$ is the average coordination number of the cubic lattice of linear size L (we hereafter measure L in units of lattice spacing a) given by

$$z(L) = \frac{1}{(L + 1)^3} [6(L - 1)^3 + 30(L - 1)^2 + 48(L - 1) + 24]. \quad (7)$$

For very large L , $z \rightarrow 6$ and the system, let us say, is ferroelectric ($T < T_c$). If we reduce L , this reduces $z(L)$, and the Ising part decreases as a result. This makes the ferroelectric phase unstable at small size and the system becomes a paraelectric below a critical size.

In particular, at zero temperature, when there are no thermal fluctuations, α_i is the same at all sites, and the free energy is simply

$$f(d) = \frac{1}{2}[\lambda_2 - Jz(L)]d^2 + \frac{1}{4}\lambda_4 d^4 \quad (8)$$

which describes a *second-order* transition driven by size when

$$\lambda_2 = Jz(L_c) \quad (9)$$

at a certain critical size L_c .

3. Calculations

In this section we present a mean-field theory for our model. We first perform an integration over the strain variable as explained in the previous section. The effective Hamiltonian (4) expressed in terms of d_i and α_i is

$$F(d, \alpha) = \frac{1}{2}\lambda_2 \sum_i d_i^2 + \frac{1}{4}\lambda_4 \sum_i d_i^4 - J \sum_{\langle ij \rangle} d_i d_j \alpha_i \alpha_j. \quad (10)$$

Recall that d_i is the magnitude of the displacement of the central ion in the i th unit cell and α_i is its sign. We now perform a trace over the α variables at the mean-field level, to obtain

$$F(d_i) = \frac{1}{2}\lambda_2 \sum_i d_i^2 + \frac{1}{4}\lambda_4 \sum_i d_i^4 + \frac{1}{2}J \sum_{\langle ij \rangle} m_i m_j d_i d_j - T \sum_i \ln 2 \cosh \left(\frac{J d_i \sum_j m_j d_j}{T} \right). \quad (11)$$

The thermal average $m_i = \langle \alpha_i \rangle$ is determined by the self-consistency equation

$$m_i = \tanh \left(\frac{J d_i \sum_j m_j d_j}{T} \right). \quad (12)$$

In this paper, we resort to the approximation $d_i = d$, i.e., we assume that the central atom displaces by the *same amount in all the unit cells*. Therefore, the free energy per unit cell $f(d_i) = F(d_i)/N$ is given by (see equation (11))

$$f(d) = e(d) + I(d) \quad (13)$$

where we have separated the elastic part

$$e(d) = \frac{1}{2}\lambda_2 d^2 + \frac{1}{4}\lambda_4 d^4 \quad (14)$$

and the Ising part

$$I(d) = J d^2 \frac{1}{N} \sum_{\langle ij \rangle} m_i m_j - \frac{1}{N} \sum_i T \ln 2 \cosh \left(\frac{J d^2 \sum_j m_j}{T} \right). \quad (15)$$

For the bulk case, equation (12) gives a uniform solution $m_i = m$. We thus have

$$I(d) = \frac{1}{2}Jz m^2 d^2 - T \ln 2 \cosh \left(\frac{Jz m d^2}{T} \right) \quad (16)$$

where z is the coordination number of the cubic lattice.

The schematic plots of $e(d)$, $I(d)$ and $f(d)$ are shown in figure 2. It can be seen that the elastic part is an increasing function of the displacement with a minimum at $d = 0$, whereas the Ising part is constant, equal to $-T \ln 2$, for $d < d_c = \sqrt{T/Jz}$ and decreases (i.e. increases in magnitude, being negative always) for larger d . Indeed, for $d < d_c$, $m = 0$ (see equation (12)) and therefore $I(d) = -T \ln 2$. For large d , $I(d) \sim -d^2$, so that the quartic term in $e(d)$ dominates for large d , resulting in a stable free energy function, as shown in figure 2. As a result, the free energy develops a second minimum at d_0 , which is found by solving the equation $\partial f / \partial d = 0$. It is this two-minimum structure of the free energy that leads to a first-order transition between the ferroelectric ($d = d_0$) and paraelectric ($d = 0$) phases.

Minimizing the free energy in equation (13) with respect to d , we obtain

$$\lambda_2 d + \lambda_4 d^3 - Jz m^2 d = 0 \quad (17)$$

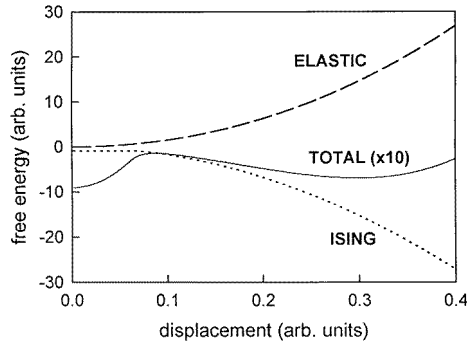


Figure 2. Schematic plots of the different contributions to the free energy (equation (4)). The elastic part (dashed line) has a minimum at the origin. The second minimum is produced by the Ising part (short dashes) which is constant up to a certain displacement and begins to decrease after that. This results in the full free energy with two minima (continuous line).

corresponding to the two minima, one at $d = 0$ and the other at

$$d_0 = \sqrt{\frac{Jzm^2 - \lambda_2}{\lambda_4}}. \quad (18)$$

At the first-order transition, the two minima coexist, i.e., $f(0) = f(d_0)$, or

$$\frac{1}{2}\lambda_2 d_0^2 + \frac{1}{4}\lambda_4 d_0^4 + \frac{1}{2}Jzm^2 d_0^2 - T_c \ln \cosh\left(\frac{Jzm^2 d_0^2}{T_c}\right) = 0. \quad (19)$$

We need three independent conditions to fix the three parameters of our theory λ_2 , λ_4 and J . The last two equations supply two of these conditions, in which we insert the experimental values of T_c and d_0 . The third condition is the equation $\lambda_2 = Jz(L_c)$, derived at the end of the last section.

From experiments on PbTiO_3 , we have $d_0 = 0.299 \text{ \AA}$ and $T_c \simeq 768 \text{ K}$. We find that $L_c \simeq 10$ (lattice units) leads to good agreement with experimental data for the size dependence of the strain [6]. We note that Zhong *et al* [13] also obtain $L_c \simeq 10$. Using these values in the three equations above, we obtain $J = 4.345909 \times 10^4 \text{ K \AA}^{-2}$, $\lambda_2 = 2.3718 \times 10^5 \text{ K \AA}^{-2}$ and $\lambda_4 = 2.6529 \times 10^5 \text{ K \AA}^{-4}$.

Not surprisingly, since $Jzd_0^2/T_c \simeq 30.27$, we obtain $m \simeq 1$ for all the sites (see equation (12)). This, in fact, also turns out to be the case for a finite lattice, as we find by numerically solving equation (12) explicitly for a finite lattice with *open* boundary conditions.

The discussion in this section so far assumes that λ_2 is positive. When λ_2 is negative, it is easy to see that $d = 0$ is no longer a minimum, but a maximum, since the second derivative at $d = 0$ is simply equal to the spring constant: $f''(d = 0) = \lambda_2$. As a result, one no longer has a first-order transition, but a continuous one. All the equations in this section except equation (19) are valid in this case, which is discussed in detail in section 5.

4. Results

Figure 3 shows our result for the strain as a function of temperature for the bulk case (solid line), while the experimental data [18] are shown by solid circles. The lack of quantitative agreement is ascribed to the fact that in our mean-field theory, the ferroelectric is completely saturated, i.e., $m \simeq 1$ at all $T < T_c$.

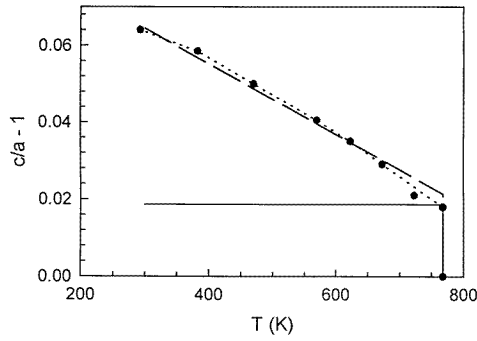


Figure 3. The strain plotted as a function of temperature for bulk PbTiO_3 . The filled circles are the experimental points and the solid line is from the theory. The dashed line is obtained by assuming a weak linear temperature dependence for λ_2 , and the dotted line by assuming a temperature dependent λ_4 (see figure 4).

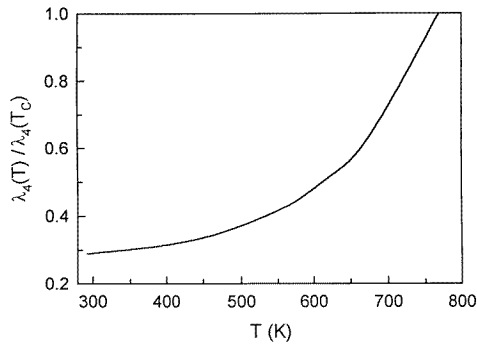


Figure 4. The ratio $\lambda_4(T)/\lambda_4(T_c)$ plotted as a function of temperature. This dependence leads to the dotted line shown in figure 3.

We can correct for this disagreement in two ways. The first possibility is to assume a weak temperature dependence for λ_2 , of the form $AT + B$. For $B = 5.45 J$, $A = 5.5 \times 10^{-4} J K^{-1}$, we obtain $\lambda_4 = 1.23 J \text{ \AA}^{-2}$ and $J = 1.65 \times 10^5 K \text{ \AA}^{-2}$ (T is in kelvin), which leads to the dashed line shown in figure 3. We find that while this makes the order parameter temperature dependent, it also makes it J independent and therefore size independent, though the size-driven transition still remains.

Alternatively, we can assume a temperature dependence for λ_4 which can be assigned by requiring that the order parameter agree with experiment. This turns out to be a rather strong temperature dependence for λ_4 which we show in figure 4. For simplicity, however, our subsequent results are obtained by assuming that both λ_2 and λ_4 are independent of temperature.

We have shown in figure 5 a plot of the strain calculated as a function of system size at a temperature of 300 K, along with the corresponding experimental data [6]. In this graph, we have normalized the calculated strain by demanding that it agrees with the experimental value for the bulk system at this temperature. The agreement with experiment is clearly quite good.

Figure 6 shows the size–temperature phase diagram, obtained by calculating the strain. The phase boundary for systems with $\lambda_2 > 0$ (solid line) is a line of first-order transitions for all $T > 0$, but the size-driven transition at $T = 0$ is continuous, as noted above. It can be seen from the phase diagram that for systems with $\lambda_2 > 0$ our theory predicts a suppression

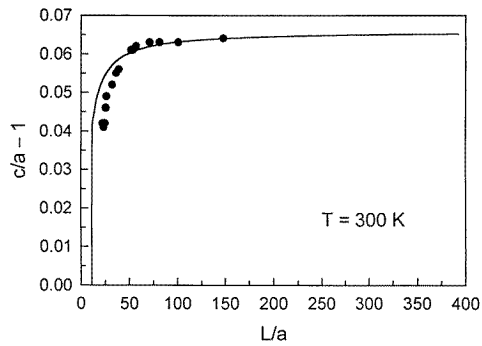


Figure 5. The strain in the tetragonal phase ($c/a - 1$) as a function of reduced system size at 300 K. The solid line shows the strain calculated from our theory (see the text), while the filled circles are experimental points [6].

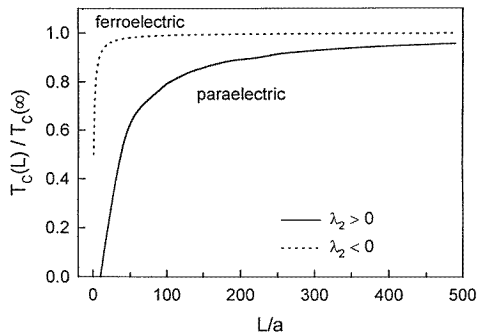


Figure 6. The phase diagram of ferroelectrics in the temperature–size plane obtained within our theory. We have plotted the reduced temperature $T_c(L)/T_c(\infty)$ against the reduced particle size. The solid line is for systems with $\lambda_2 > 0$ and is a first-order line separating the tetragonal ferroelectric phase from the cubic paraelectric phase. Note that there is an appreciable suppression of T_c as the system size is reduced, and T_c is zero below a critical size. The dotted line is for the systems with $\lambda_2 < 0$ and is a line of second-order transitions separating the low-temperature ferroelectric phase from the high-temperature paraelectric phase. The transition temperature T_c in this case remains practically equal to its bulk value down to very small sizes. In particular, there is no size-induced transition and the system remains in the ordered phase below $T_c/2$ for all sizes. The $\lambda_2 < 0$ case usually corresponds to order–disorder ferroelectrics.

of T_c as the system size is reduced. This is in agreement with experimental results and other theoretical studies on displacive systems. To our knowledge, all typical displacive systems are found to exhibit first-order transitions ($\lambda_2 > 0$) at T_c . This correlation was not thought to be theoretically necessary prior to the present work.

5. Ferroelectrics with $\lambda_2 < 0$

For systems with $\lambda_2 < 0$, the local potential experienced by the central B-ion has a double well structure, i.e., there is a local maximum at $d = 0$ and two minima at $d = \pm d_0$.

In this case, it is easy to see that size effects are highly suppressed. Firstly, we note that the Ising term can never lead to a minimum at $d = 0$ for any finite temperature. Therefore, an increase in temperature can destroy the ferroelectric order via a continuous transition.

The distortion continues to have the value given by equation (18), but $m = \langle \alpha \rangle$ vanishes when $Jz(L)d_0^2/T = 1$. The last condition can be met by changing T or by changing system size. For the bulk system ($z(L) = 6$), this condition is satisfied for $T = T_c$. We can therefore write $z(L)/6 \simeq T/T_c$, where L is the size at which there is a size-driven transition at temperature T . Note that when expressed in terms of the reduced transition temperature, $t = T_c(L)/T_c(\infty)$, the above equation (which describes the boundary between the ferroelectric and paraelectric phases) is independent of our model parameters. If T/T_c is about 0.9 (say), then we have to go to systems as small as $L \sim 10$ (see equation (7)) to observe size effects.

Most systems of the order–disorder type, e.g., triglycine sulphate and sodium nitrite, exhibit second-order ($\lambda_2 < 0$) paraelectric transitions. Typically, the lattice spacings in these systems are $\sim 4 \text{ \AA}$, so we have to obtain samples of size $\sim 40 \text{ \AA}$ to have observable size effects, even at so high a temperature as $0.9 T_c$. At lower temperatures the corresponding critical sizes are even smaller. In particular, for $T \leq 0.5 T_c$, we do not expect any size-driven transition, since $z(L)$ must be larger than 3. Such a suppression of size effects in order–disorder ferroelectrics has actually been observed in experiments [12].

We also show the phase diagram for ferroelectrics with $\lambda_2 < 0$ in figure 6, and it is instructive to study the difference between the two kinds of ferroelectric ($\lambda_2 < 0$ and $\lambda_2 > 0$). We attribute the suppression of size effects in the case of ferroelectrics with $\lambda_2 < 0$ to the absence of a structural transition accompanying the ferroelectric transition. Indeed, at any temperature, one has to go to much smaller samples to meet the requirement $Jz(L)d_0^2/T = 1$ (which is the transition condition for $\lambda_2 < 0$ systems) than the co-existence condition given by equation (19) (which is the transition condition for $\lambda_2 > 0$ systems).

6. Discussion

An important qualitative merit of our theory is that it can be easily extended to include antiferroelectric oxides, simply by making J negative. The ordered phase will have a nonzero value for an antiferroelectric order parameter such as sublattice polarization α_S . The molecular field at any site i , due to the nearest neighbours, will be opposite in sign to the order parameter at that site, so that the product of the molecular field and J will have the same sign as for the ferroelectric case. The theory as worked out above in terms of displacements will go through without any further change, and the results will be identical to that for ferroelectrics, with J replaced by $|J|$. Recent experimental studies of size-driven transitions in antiferroelectric materials [7] report results very similar to those in ferroelectrics, confirming our expectation.

We can explain the form of the empirical equation (1) for size-driven transitions very easily in our theory. For size-driven transitions, we obtain from equation (19), upon replacing λ_2, λ_4 and J by their values determined from bulk data, an equation of the form $\ln \cosh(A_1 z(L)/T_c) = A_2 z(L)/T_c - A_3$, for some A_1, A_2 (measured in K) and A_3 , a dimensionless number. It is clear that this equation will have a solution of the form (1) for large L since $z(L)$ is given by equation (7). The numbers A_1, A_2 and A_3 can be related to the parameters $T_c(\infty), B$ and L_c appearing in equation (1). The actual numbers appearing in equation (1) will of course depend on material parameters.

Our theory has only three fitting parameters, whereas the phenomenological Landau theories [13, 14] have about twice as many. This is clearly so because our theory is based on a microscopic model which identifies the different contributions to the system free energy as being due to the elastic and ferroelectric parts. As a result, we are also able to describe the *structural* transition in displacive systems in addition to the ferroelectric transition, to which it is related. Earlier, we have pointed out that all known displacive ferroelectrics exhibit first-order transitions, and a qualitative merit of our theory is that the first-order transition

appears in a very natural way for displacive ferroelectrics, with minimal assumptions about the form of the elastic part of the Hamiltonian. With the lowest-order nonlinear elastic term, i.e., the fourth-order term, we are able to describe the first-order transition. This is an essential difference from earlier approaches based on a Landau expansion of the free energy.

We have also shown that our theory can describe size-driven transitions in ferroelectrics with continuous as well as discontinuous transitions. For systems with continuous transitions in the bulk (such as certain order–disorder ferroelectrics), i.e., $\lambda_2 < 0$, our model correctly predicts a suppression of size effects relative to ferroelectrics with discontinuous transitions. Our simple estimate for the critical size at which size effects become important in these systems is in agreement with data on NaNO_2 [12]. The current approach is superior to the Landau theory for size-driven transitions [13] since size effects in order–disorder systems can also be addressed in it.

Although our model gives a useful physical picture for both temperature- and size-driven transitions, it is rather too simple to provide perfect quantitative agreement. We have made several simplifying assumptions, the first being that the displacement has the same magnitude throughout the sample. This is not necessarily true, especially for small systems where the displacement at the surface could be different from that in the bulk. This, and the subsequent neglect of thermal fluctuations, turn out to be rather drastic approximations. The strongly first-order character of the transition (i.e. the very weak, almost nonexistent, temperature dependence of the order parameter) is probably an artifact of our mean-field approximation. We have also performed calculations based on the Bethe–Peierls approximation [20], which takes into account short-range correlations between dipoles. However, this does not lead to a more realistic temperature dependence for the order parameter [21].

An interesting question, which cannot be answered within the framework of our theory, is whether the transition remains first order beyond mean-field theory. Further, since our theory is an effective single-site theory, it cannot capture the phenomenon of the lattice mode softening that is observed in these systems [22].

We do not consider the effect of depolarization field in our theory. The depolarization field, under certain circumstances, can lead to better quantitative agreement with experiment [14]. However, in the experimental situation that we have described [6], the effect of the depolarization field should be negligible as explained in section 1. We have not explicitly considered the role of long-range interactions between dipoles, since this will simply lead to a reparametrization of J in the type of theory presented in this paper.

In conclusion, we have presented a simple unified mean-field theory for ferroelectrics with continuous as well as discontinuous structural transitions, which captures the physics of both temperature-induced transitions in the bulk and size-induced transitions in nanoparticles. The size effects are understood in a simple way as being a result of the smaller coordination number near the surface of the particle. Very generally, we have shown that ferroelectrics with continuous bulk transition have suppressed size effects, while ferroelectrics with first-order bulk transition have appreciable size effects. We emphasize that, in our theory, it is the sign of λ_2 (i.e., the order of the transition) that is important, and not the displacive or order–disorder nature of the ferroelectric. The further identification of $\lambda_2 > 0$ ($\lambda_2 < 0$) systems with displacive (or order–disorder) ferroelectrics can only be justified empirically. Future work will centre around incorporating the effect of thermal fluctuations and obtaining closer agreement with experiments.

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References

- [1] Anliker M, Brugger H R and Känzig W 1954 *Helv. Phys. Acta.* **27** 99
- [2] Känzig W 1955 *Phys. Rev.* **98** 549
- [3] Francombe M H 1993 *Physics of Thin Films: Mechanic and Dielectric Properties* ed M H Francombe and J L Vossen (San Diego: Academic) pp 225–300
- [4] Lines M E and Glass A M 1977 *Principles and Applications of Ferroelectrics and Related Materials* (Oxford: Clarendon)
- [5] Uchino K, Sadanaga E and Hirose T 1989 *J. Am. Ceram. Soc.* **72** 1555
- [6] Chattopadhyay S, Ayyub P, Palkar V R and Multani M 1995 *Phys. Rev. B* **52** 13 177
- [7] Chattopadhyay S, Ayyub P, Palkar V R, Gurjar A V, Wankar R M and Multani M S 1997 *J. Phys.: Condens. Matter* **9** 8135
- [8] Ishikawa K, Yoshikawa K and Okada N 1988 *Phys. Rev. B* **37** 5852 The trends in the experiments of Chattopadhyay *et al* [6] agree with those in the earlier experiments described above. In this paper, for concreteness, we shall refer to the experimental results of Chattopadhyay *et al*
- [9] Burns G and Scott B A 1970 *Phys. Rev. Lett.* **25** 167
Burns G and Scott B A 1973 *Phys. Rev. B* **7** 3088
- [10] Zhong W L, Jiang B, Zhang P L, Ma J M, Cheng H M, Yang Z H and Li L X 1993 *J. Phys.: Condens. Matter* **5** 2619
- [11] Jacard C, Känzig W and Peter M 1953 *Helv. Phys. Acta* **26** 521
- [12] Marquardt P and Gleiter H 1982 *Phys. Rev. Lett.* **48** 1423
- [13] Zhong W L, Wang Y B, Zhang P L and Qu B D 1994 *Phys. Rev. B* **50** 698
- [14] Shih W Y, Shih W-H and Aksay I A 1994 *Phys. Rev. B* **50** 15 575
- [15] Shirane G, Pepinsky R and Frazer B C 1956 *Acta Crystallogr.* **9** 131
- [16] Gavrilachenko V G, Spinko R I, Martynenko M A and Fesenko E G 1970 *Sov. Phys.–Solid State* **12** 1203
- [17] We have assumed above that the distortion of the unit cell takes place along the same axis all through the sample, i.e., all the unit cells have their *c* axis along, say, the *z* direction. This is reasonable, since there would be enormous elastic costs involved in having adjacent unit cells distended along different directions. Accordingly, the displacement can only be along the *z* axis, but it can be either up or down.
- [18] We calculate d_0 from the experimental polarization data using the equation $d_0(T) = P(T)(d_0(T_c)/P(T_c))$; at T_c , both d_0 and P are known from experiments, and $P(T)$ is known over a wide range of temperatures, so we can obtain $d_0(T)$. The $P(T)$ data have been taken from reference [16]
- [19] Domb C 1956 *J. Chem. Phys.* **25** 783
Bergman D J and Halperin B I 1976 *Phys. Rev. B* **13** 2145
Mattis D C and Schultz T D 1963 *Phys. Rev.* **129** 175
- [20] Huang K 1963 *Statistical Mechanics* (New York: Wiley)
- [21] Sheshadri K and Lahiri R unpublished
- [22] Cochran W 1960 *Adv. Phys.* **9** 387