Ferroelectric Phase Transitions in Small Particles and Local Regions

A. P. Levanyuk[*]

Departamento de Fisica de la Materia Condensada, Universidad Autonoma de Madrid, Madrid 28049, Spain and Jozef Stefan Institute, P.O. Box 3000, 1001 Ljubljana, Slovenia

R. Blinc[†]

Jozef Stefan Institute, P.O. Box 3000, 1001 Ljubljana, Slovenia

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Phase transitions in spherical particles of a cubic ferroelectric are considered within Landau-Ginzburg-Devonshire theory. Concentrating on effects of the depolarizing field, we study competition between states with homogeneous polarization and vortex structures. For large radii of the sphere ($R > R_c$), the phase transition is into a vortex state while for $R < R_c$ it might be into an homogeneous state. R_c is proportional to the square root of the dielectric constant of the environment. If this constant is of the order of unity, a transition into homogeneous state is practically impossible. The obtained results are applied to a discussion of the formation of "polar nanoclusters" in relaxors.

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Discussion of ferrolectric phase transitions (PTs) in small particles has a long tradition starting with papers from Kanzig and co-workers in the 1950s [1–3]. This topic has become especially popular over the past two decades because of growing interest in ferroelectric phenomena at small scales. Surprisingly, the analytical phenomenological theory of such PTs remains poorly developed even in its most basic points. We discuss this situation in some detail below, principally intending to account for effects of depolarizing fields, which were the main focus of Kanzig and co-workers. They designed experiments in which processes of compensation of the depolarizing field were hampered [1], and only recently similar experiments were performed by Li and Shih [4] without adequate theoretical support. As a result, the problem of finding the PT temperature in a particle of a ferroelectric which is cubic in the paraelectric phase has not been solved in analytical phenomenological theory until now, to the best of our knowledge. The solution of this problem for a spherical particle of such a ferroelectric embedded in a dielectric medium is the main result of the present work. We solve this problem not for a general case but supposing that the particle surface is neither hampering nor favoring the ferroelectric phase transition (free surface). Even in this case we need further simplifications to get an analytical solution, and a more complete solution is far beyond the present work. We shall discuss modifications of our idealized solution, which are expected when moving to more realistic cases.

This problem of a ferroelectric PT in a spherical particle is related to the problem of formation of so-called polar nanoregions or precursor polar clusters in regions with a high local Curie temperature, which are expected in materials with disorder. Let us emphasize that the question about the creation and nature of the polar precursor regions or polar nanoclusters is at the heart of the interpretation of properties of the so-called relaxors [5–7]. That is why the present work is directly related to the understanding of the properties of these materials. Let us emphasize that we consider only part of the problem of the local transition in a ferroelectric region with a locally elevated Curie temperature. Indeed, even in a nonferroelectric the local condensation occurs not at a temperature equal to the local value of the PT temperature but at a lower temperature because the environment of the region in question "is not ready" to transform and hampers the transformation in the region. We do not take this effect into account, concentrating on the effects of the depolarizing field, which are, to our understanding, the most important.

In what follows we consider first an academic case of a 2D or infinite cylindrical particle of a ferroelectric with two polar axes in the plane and in an isotropic dielectric environment. This case is mathematically simpler than the 3D case of a spherical particle, but both the qualitative results and the mathematical difficulties are already there. Then we consider the ferroelectric PT in a spherical particle of a material, which is cubic in the paraelectric phase, with the same assumptions and approximations as before. Finally, we discuss the relevance of the results in this Letter to the question of the nature and properties of polar nanoclusters in relaxors.

To find the PT temperature and the profile of polarization appearing at the PT we study the stability of a paraelectric phase with respect to different polarization distributions. The loss of stability is signaled by the appearance of nontrivial solutions of a system of equations consisting of linearized governing equations for polarization, the electrostatic equations, and the boundary conditions. Among the infinite number of ways to lose stability, only the earliest one, i.e., that which occurs at the highest temperature, is that which happens at the PT. The problem reduces to finding this temperature and the form of the polarization distribution that brings about this stability loss. This method has been repeatedly used by many authors; see Refs. [8–12].

We obtain the linearized equations of state using the harmonic part of the Landau-Ginzburg-Devonshire (LGD) free energy which for the 2D case has the form

$$F = \int \rho d\rho d\varphi \left(\frac{A}{2}\mathbf{P}^2 + \frac{g}{2}\left\{ \left(\frac{\partial P_\rho}{\partial \rho}\right)^2 + \left(\frac{\partial P_\varphi}{\partial \rho}\right)^2 + \frac{1}{\rho^2}\left[\left(\frac{\partial P_\rho}{\partial \varphi} - P_\varphi\right)^2 + \left(\frac{\partial P_\varphi}{\partial \varphi} + P_\rho\right)^2 \right]\right\}\right), \qquad (1)$$

where ρ, φ are polar coordinates, $A = A'(T - T_c)$, T_c is the PT temperature in bulk, $g = \text{const}$, and the gradient term can be found in Ref. [13]. There are two governing equations for the ferroelectric polarization:

$$\left(A + \frac{g}{\rho^2}\right)P_\rho - g\left[\frac{1}{\rho}\frac{\partial}{\partial \rho}\left(\rho \frac{\partial P_\rho}{\partial \rho}\right) + \frac{\partial^2 P_\rho}{\rho^2 \partial \varphi^2}\right] + \frac{2g}{\rho^2}\frac{\partial P_\varphi}{\partial \varphi} = E_\rho, \qquad (2)$$

$$\left(A + \frac{g}{\rho^2}\right)P_\varphi - g\left[\frac{1}{\rho}\frac{\partial}{\partial \rho}\left(\rho \frac{\partial P_\varphi}{\partial \rho}\right) + \frac{\partial^2 P_\varphi}{\rho^2 \partial \varphi^2}\right] - \frac{2g}{\rho^2}\frac{\partial P_\rho}{\partial \varphi} = E_\varphi. \qquad (3)$$

Adding the equation for electrostatic potential we obtain, for the interior of circle, a system of three coupled equations in partial derivatives. The solutions also have to satisfy boundary conditions at the surface relating electric fields in internal and external regions. The problem becomes too complicated and it is reasonable to make use of physical ideas.

Physically, one can expect competition between the closed flux solutions, i.e., that of a vortex, and the solutions corresponding to homogeneous polarization in the circle. In the first case, where the electric field is zero and the external medium plays no role, one can put $P_\rho = 0$ and consider P_φ depending on ρ only. Then the equation for P_φ reads

$$\frac{1}{\rho}\frac{d}{d\rho}\left(\rho \frac{dP_\varphi}{d\rho}\right) - \left(\frac{A}{g} + \frac{1}{\rho^2}\right)P_\varphi = 0, \qquad (4)$$

with the boundary condition of a free surface: $dP_\varphi/d\rho = 0$ at $\rho = R$. Solutions of this equation regular at $\rho = 0$ have for $A > 0$ and $A < 0$, correspondingly, the forms $P_\varphi = CI_1[\sqrt{(A/g)}\rho]$ and $P_\varphi = CJ_1[\sqrt{(-A/g)}\rho]$, where $J_\nu(x)$ and $I_\nu(x)$ are Bessel and modified Bessel functions, respectively. The first solution does not satisfy the boundary condition if $C \neq 0$, i.e., only a trivial solution is possible if $A > 0$; that is, the paraelectric is stable with respect to vortex formation. For the second solution the boundary condition is satisfied if $A = -g(\mu_n/R)^2$, where μ_n is the nth root of the equation $J_1'(x) = 0$. The earliest loss of stability corresponds to the smallest value of μ_n: $\mu_1 \simeq 1.8$. The vector field and the form of $P_\varphi(\rho)$ arising at the stability loss are shown in Figs. 1(a) and 1(b). Vortexlike distributions have been obtained computationally in several papers; see, e.g., Refs. [14,15]. However, the radial dependence of the polarization value just after PT [Fig. 1(b)] has not been singled out to the best of our knowledge.

To define the PT temperature we have to compare the loss of stability with respect to vortex formation with other possibilities of stability loss. We mean specifically the loss of stability with respect to the homogeneously polarized circle. Calculation of the electric field in this case is a standard problem with the dielectric displacement inside the circle taken as $\mathbf{D} = \varepsilon_0\varepsilon_b\mathbf{E} + \mathbf{P}$, where ε_b is the so-called base dielectric constant [16]. The field inside the circle is $\mathbf{E} = -[\varepsilon_0(\varepsilon_b + \varepsilon_p)]^{-1}\mathbf{P}$, where ε_p is the dielectric constant of the environment. One finds that the loss of stability occurs at $A = -[\varepsilon_0(\varepsilon_b + \varepsilon_p)]^{-1}$. Since the temperature of this type of stability loss does not

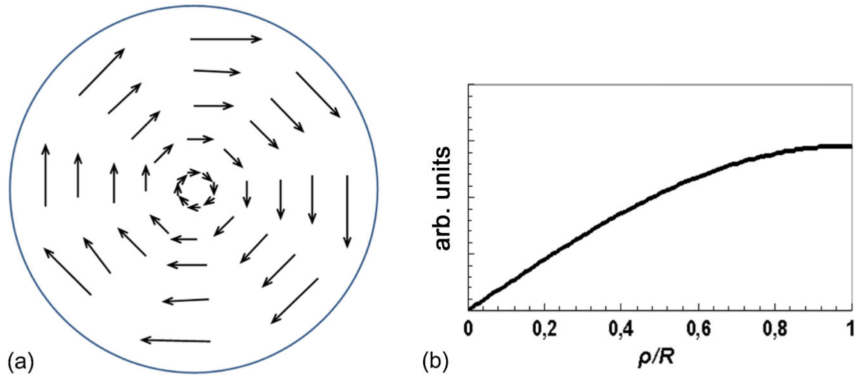

FIG. 1 (color online). Polarization distribution just after the paraelectric-ferroelectric phase transition in an infinite cylinder. (a) Vector plot and (b) radial dependence of the polarization value.

depend on R, the earliest stability loss for large R is with respect to vortex formation and the PT temperature is given by the earlier result. However, for small R it is possible that the PT into a homogeneous state occurs before and instead of vortex formation. The character of the PT changes at $R = R_c = \mu_1 (g\varepsilon_0)^{1/2}(\varepsilon_b + \varepsilon_p)^{1/2}$. Since $(g\varepsilon_0)^{1/2}$ is, normally, about interatomic distances, this critical radius is also about interatomic distances in an environment with small ε_p; i.e., the PT via vortex formation occurs for all values of R. However, in a medium with high ε_p, the critical radius can be considerably larger than atomic distances. We shall not discuss the above results here because they are not very different from the 3D case which is our focus of interest.

For this case the harmonic part of LGD free energy is

$$F = \int r^2 \sin\theta dr d\theta d\varphi f(\mathbf{P}), \tag{5}$$

where

$$f(P) = \frac{A}{2}P^2 + \frac{g}{2}\left\{\left(\frac{\partial P_r}{\partial r}\right)^2 + \left(\frac{\partial P_\theta}{\partial r}\right)^2 + \left(\frac{\partial P_\varphi}{\partial r}\right)^2 + \frac{1}{r^2}\left[\left(\frac{\partial P_\varphi}{\partial \theta}\right)^2 + \left(\frac{\partial P_r}{\partial \theta} - P_\theta\right)^2 + \left(\frac{\partial P_\theta}{\partial \theta} + P_r\right)^2\right] + \frac{1}{r^2\sin^2\theta}\left[\left(\frac{\partial P_r}{\partial \varphi} - \sin\theta P_\varphi\right)^2 + \left(\frac{\partial P_\theta}{\partial \varphi} - \cos\theta P_\varphi\right)^2 + \left(\frac{\partial P_\varphi}{\partial \varphi} + P_r \sin\theta + P_\theta \cos\theta\right)^2\right]\right\}. \tag{6}$$

The full scale mathematical study is even less feasible here than in the 2D case, and once more we make use of physical arguments. To study the conditions for the appearance of a vortex in a sphere, one can put $\mathbf{E} = 0$, $P_r = P_\theta = 0$ and suppose that P_φ does not depend on φ. Then for P_φ, we obtain

$$AP_\varphi - g\left[\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial P_\varphi}{\partial r}\right) + \frac{\partial}{r^2 \sin\theta\partial\theta}\left(\sin\theta\frac{\partial P_\varphi}{\partial\theta}\right) - \frac{P_\varphi}{r^2\sin^2\theta}\right] = 0. \tag{7}$$

It is helpful to formulate a Sturm-Liouville problem,

$$\frac{d}{\sin\theta d\theta}\left(\sin\theta\frac{dy}{d\theta}\right) - \frac{y}{\sin^2\theta} = -\lambda y, \tag{8}$$

with the condition of finiteness for $y(\theta)$. One obtains associated Legendre functions, $P_l^1(\cos\theta) = y_l(\theta)$, as the eigenfunctions and $\lambda_l = l(l+1)$, $l \geq 1$. Presenting $P_\varphi(r, \theta)$ as

$$P_\varphi(r, \theta) = \sum P_{\varphi l}(r) y_l(\theta), \tag{9}$$

we decompose the problem of finding solutions for Eq. (7) into a set of problems for different l,

$$\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{dP_{\varphi l}}{dr}\right) - \left(\frac{A}{g} + \frac{l(l+1)}{r^2}\right)P_{\varphi l} = 0, \tag{10}$$

with the boundary condition $dP_{\varphi l}/dr = 0$ at $r = R$. Solutions of Eq. (10) which are regular at $r = 0$ are spherical Bessel functions of order l,

$$P_{\varphi l} = C j_l\left(\sqrt{\frac{-A}{g}}r\right) = C\sqrt{\frac{\pi}{2r}}J_{l+1/2}\left(\sqrt{\frac{-A}{g}}r\right). \tag{11}$$

For $A > 0$ the argument is imaginary, i.e. the solutions do not satisfy the boundary condition, while for $A < 0$ this is possible for

$$A = -g\left(\frac{\mu_n^l}{R}\right)^2, \tag{12}$$

where μ_n^l is the nth root of the equation $j_l'(x) = 0$. The real loss of stability with respect to vortex formation corresponds to the minimum value of $\mu_n^l = \mu_1^1 \simeq 2.1$.

Since $y_1(\theta) = \sin\theta$, the form of the polarization distribution arising at the stability loss with respect to vortex formation is (see also Fig. 2)

$$P_r = P_\theta = 0, \qquad P_\varphi \propto j_l\left(\frac{\mu_1^1 r}{R}\right)\sin\theta. \tag{13}$$

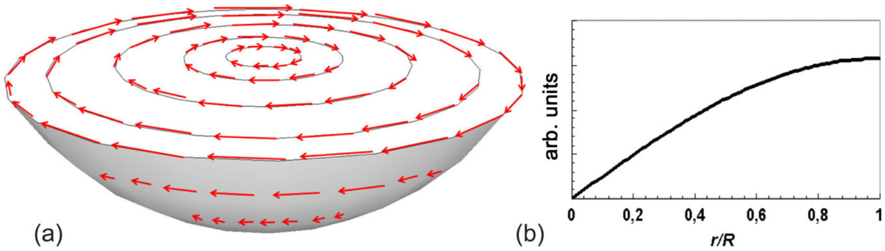

FIG. 2 (color online). Polarization distribution just after the paraelectric-ferroelectric phase transition in a sphere. (a) Vector plot and (b) radial dependence of the polarization value.

As we also do for the case of a circle, we compare the loss of stability given by Eq. (12) and the loss of stability with respect to homogeneous polarization. Analogously to the 2D case, we find $\mathbf{E} = -[\varepsilon_0(\varepsilon_b + 2\varepsilon_p)]^{-1}\mathbf{P}$, and the stability is lost at

$$A = -[\varepsilon_0(\varepsilon_b + 2\varepsilon_p)]^{-1}. \tag{14}$$

For the critical radius we, therefore, have $R_c = \mu_1^1(g\varepsilon_0)^{1/2}(\varepsilon_b + 2\varepsilon_p)^{1/2}$. The PT into a homogeneously polarized state would occur at $T = T_{th} = T_c - [\varepsilon_0 A'(\varepsilon_b + 2\varepsilon_p)]^{-1}$. For $BaTiO_3$, $A' = 6.6 \times 10^5\ \mathrm{J\,m\,C^{-2}\,K^{-1}}$, $T_c = 383$ K, $\varepsilon_b = 7$ (see, e.g., Ref. [17]), and for the sphere in vacuum, i.e., for $\varepsilon_p = 1$, we find $T_{th} = -1.7 \times 10^4$ K; i.e., such a PT is impossible. The normal situation is that the phase transition proceeds into the vortex state at $T = T_{tv}$; for example, for $R = 100$ nm, we find from Eq. (12) that $T_c - T_{tv} = 0.7 \times 10^{-3}$ K, given that $g = 2 \times 10^{-11}\ \mathrm{J\,m^{-3}\,C^{-2}}$ (Ref. [17]). It becomes natural that Kanzig and co-workers [2] found no suppression of the PT in small particles of $BaTiO_3$ with diameters of about 200 nm, while in uniaxial KH_2PO_4, where vortex states are impossible, there was no PT for particles with diameters less than 150 nm [1].

The above results emphasize that the depolarizing field plays an extremely important role for a ferroelectric PT in a particle or in a local region. A PT into a homogeneously polarized state is only possible in an environment with a high dielectric constant. The latter situation occurs in relaxors and it is worthwhile to discuss this in more detail. Originally, the idea of formation of polar regions in a nonpolar matrix due to the locally elevated temperature of a ferroelectric PT was put forward by Smolenskii and Isupov [18,19], where fluctuations of a number of impurities in some (artificially chosen) regions were considered as the reason for the local elevation of T_c. The same reason has been postulated by Burns and Dacol [20] who, unlike Isupov, believed these regions consisted of a small number of the unit cells. Both groups virtually supposed that the temperature of the local PT was approximately equal to the local value of T_c (T_{cl}). This is not evident even if the depolarizing field were absent [8,9], but the most important fact is that both Isupov and Burns overlooked the effects of the depolarizing field. These effects are extremely important for ferroelectric PT in small isolated particles, as we have shown above, so it is natural to suspect that they might be important for local ferroelectric PT as well. One might expect that the effects of the depolarizing field are not as dramatic in local PT as they are for small particles because these local transitions occur in regions surrounded by a medium with a high dielectric constant, which is characteristic of a ferroelectric not too far from the PT. In the case of relaxors, we should take the temperature dependence of this dielectric constant into account.

We suppose that the regions of locally elevated PT temperature expected in relaxors are spherical and have the same radius R. As before, we consider the effects of the depolarizing field only, neglecting the nonelectrostatic effects. To begin with, consider the possibility that the local PT in these regions is into a uniformly polarized state ($T = T_{th}$). The temperature of this PT we calculate using Eq. (14), but taking into account the fact that the dielectric constant of the medium [ε_p in Eq. (14)] now depends on temperature. We are interested in the case of the matrix having a large dielectric constant (ε):

$$\varepsilon_p = \varepsilon \simeq [\varepsilon_0 A'(T - T_c)]^{-1}, \tag{15}$$

where T_c now has a different meaning from the previous sections, denoting the Curie temperature of the matrix, not that of the inclusion (particle). The latter is denoted as T_{cl}. Neglecting ε_b in Eq. (14), we find that

$$T_{th} = \frac{T_c + 2T_{cl}}{3}. \tag{16}$$

The possibility of a PT into a homogeneously polarized state is realized if $R < R_c$. Using the above formula for R_c and Eq. (15), we can rewrite this condition as

$$R < \mu_1^1(g\varepsilon_0)^{1/2}[2\varepsilon(T_{th})]^{1/2} \simeq 3\sqrt{\frac{g}{A'(T_{th} - T_c)}} = 3r_c(T_{th}), \tag{17}$$

where $r_c(T_{th})$ is the correlation length for the order parameter (polarization) at $T = T_{th}$. Two comments should be made on this formula. Firstly, the value of $r_c(T_{th})$ is usually very small. Indeed, identifying the Burns temperature with T_{th} and using, for example, data from Ref. [20] (see Table 1) and Eq. (16), and then assuming the same values for g and A' as above for $BaTiO_3$, we find that, for a phase transition into a homogeneous state, R should be less than 1 nm. Secondly, since the dimension of the region of locally elevated PT temperature is comparable to the correlation length of the environment at the temperature of the expected local PT, our approximation of considering only electrostatic effects and neglecting the nonelectrostatic coupling becomes questionable and one can expect that the real temperature of the local PT is considerably less than that given by Eq. (16). Unfortunately, an account for both electrostatic and nonelectrostatic effects is fairly tricky and is well beyond the present work.

It makes sense to consider another possibility: a phase transition into a vortex state, given by Eq. (12). The temperature of this PT does not depend on the dielectric constant of the environment and, therefore, on T_c. This correlates with an observation made in Ref. [20]. When studying $(Pb_{1-3x/2}La_x)(Zr_{1-y}Ti_y)O_3$ with $y = 0.65$ and different values of x, it has been mentioned that the Burns temperature stays approximately the same for different x while T_c changes substantially. Of course, this correlation cannot be taken too seriously given the artificial character of our model of a relaxor, where all the regions with an elevated temperature are spherical with the same radius R. According to Eq. (12), the temperature of the PT with vortex formation strongly depends on R so that even a moderate spread of values of the radii would smear the evidence of a local PT in the sample. The vortex state formed just after the PT evolves with a further lowering of temperature: it becomes a closed flux domain structure and perhaps transforms into a homogeneous state with a further lowering of temperature because of the increase in the dielectric constant of the medium. Recently, several authors have speculated about transformations in the polar nanoregions, e.g., Refs. [21,22], and the possibility of a local PT with vortex formation provides some room for such speculations.

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*levanyuk@uam.es

†Deceased.

[1] C. Jaccard, W. Kanzig, and M. Peter, Helv. Phys. Acta **26**, 521 (1953).

[2] M. Anliker, H. R. Bruger, and W. Kanzig, Helv. Phys. Acta **27**, 99 (1954).

[3] F. Jona and G. Shirane, *Ferroelectric Crystals* (Dover, New York, 1993).

[4] X. Li and W. H. Shih, J. Am. Ceram. Soc. **80**, 2781 (1997).

[5] L. E. Cross, Ferroelectrics **76**, 241 (1987).

[6] R. Blinc, V. V. Laguta, B. Zalar, and J. Banys, J. Mater. Sci. **41**, 27 (2006).

[7] R. A. Cowley, S. N. Gvasaliya, S. G. Lushnikov, B. Roessli, and G. M. Rotaru, Adv. Phys. **60**, 229 (2011).

[8] H. Suhl, Appl. Phys. **8**, 217 (1975).

[9] H. Schmidt and F. Schwabl, Phys. Lett. **61A**, 476 (1977).

[10] E. V. Chensky and V. V. Tarasenko, Sov. Phys. JETP **56**, 618 (1982).

[11] D. R. Tilley and B. Zeks, Solid State Commun. **49**, 823 (1984).

[12] A. M. Bratkovsky and A. P. Levanyuk, J. Comput. Theor. Nanosci. **6**, 465 (2009).

[13] A. Hubert and R. Schafer, *Magnetic Domains* (Springer, Berlin, 1998).

[14] I. I. Naumov, L. Bellaiche, and H. Fu, Nature (London) **432**, 737 (2004).

[15] I. I. Naumov and H. Fu, Phys. Rev. Lett. **98**, 077603 (2007).

[16] A. Tagantsev, Ferroelectrics **375**, 19 (2008).

[17] J. Hlinka and P. Marton, Phys. Rev. B **74**, 104104 (2006).

[18] G. A. Smolenskii and V. A. Isupov, Zh. Tekh. Fiz. **24**, 8 (1954).

[19] V. A. Isupov, Sov. Phys. Tech. Phys. **1**, 1846 (1956); Phys. Solid State **45**, 1107 (2003).

[20] G. Burns and F. H. Dacol, Phys. Rev. B **28**, 2527 (1983).

[21] J. Toulouse, Ferroelectrics **369**, 203 (2008).

[22] B. Dkhil, P. Gemeiner, A. Al-Barakaty, L. Bellaiche, E. Dul'kin, E. Mojaev, and M. Roth, Phys. Rev. B **80**, 064103 (2009).