Pseudo-proper ferroelectricity in thin films

A. Cano\textsuperscript{1,}\textsuperscript{1} and A.P. Levanyuk\textsuperscript{1,}\textsuperscript{2}

\textsuperscript{1} European Synchrotron Radiation Facility, 6 rue Jules Horowitz, BP 220, 38043 Grenoble, France
\textsuperscript{2} Departamento de Física de la Materia Condensada, C-III, Universidad Autónoma de Madrid, E-28049 Madrid, Spain

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We study ferroelectricity in thin films of pseudo-proper ferroelectrics such as the so-called spiral multiferroics. We find that this type of ferroelectricity stands better against depolarizing fields than conventional one. Its single-domain state can be easily preserved by metallic electrodes even in ultrathin films. In fact, single-domain ferroelectricity can be generated as a metastable state in the absence of electrodes. We also find a new regime of small thickness where unscreened films develop unusual multi-domain states with properties determined by non-electrostatic boundary conditions.

Introduction.– The discovery of a new type of ferroelectricity caused by a cycloidal ordering of magnetic moments \cite{1} is one of the key events that has triggered the current interest in multiferroics. This type of multiferroicity is realized in the rare-earth manganites RMnO\textsubscript{3} (R = Gd, Tb, Dy), and has been successfully explained on the basis of the inverse Dzyaloshinskii-Moriya interaction \cite{2}. From the phenomenological point of view, these systems can be considered as new examples of pseudo-proper ferroelectrics \cite{3} in which the electric polarization is (bi-)linearly coupled with the primary order parameter of the transition \cite{4}.

Much of the interest in ferroelectrics concerns their thin-film properties since they are at the root of a large number of applications (in memory devices, field-effect transistors, etc.). For conventional proper ferroelectrics this has been addressed theoretically by means of both first-principles calculations \cite{5} and Landau-like approaches \cite{6}. One of the main outcomes is that single-domain (uniform) ferroelectricity is very difficult to retain below certain sizes. Instead, there appears multi-domain structures which are largely the result of the depolarizing fields that inevitably persist in real devices \cite{7}. As regards pseudo-proper ferroelectrics, the thin film properties of these systems have not yet been addressed in the same detail.

In this paper we show that pseudo-proper ferroelectricity proves more robust against depolarizing field effects. We illustrate this robustness in different experimental situations. When the film is sandwiched between metallic short-circuited electrodes, for example, the critical screening length necessary to keep single-domain ferroelectricity is much larger than in conventional ferroelectrics. In TbMnO\textsubscript{3}, for example, it is expected $\sim 150\text{Å}$, which largely exceeds the screening length of many metals. The physics behind this result has nothing to do with any eventual smallness in the induced polarization. This can be noted in a conventional ferroelectric, where no increase of the critical screening length is obtained by the mere reduction of its spontaneous polarization. The reason is that the aforementioned linear coupling sets a new length scale $\lambda$ in the problem, and this quantity overwhelms the typical length scale for the gradients of polarization in determining the above critical screening. On the other hand, in the absence of electrodes single-domain ferroelectricity can be generated as a metastable state in striking contrast to conventional ferroelectrics. This is possible because the pseudo-proper mechanism does not require the vanishing of the polarization stiffness. Therefore, despite the depolarizing field increases this stiffness, the virtual single-domain ferroelectric instability remains sufficiently close in temperature. In addition, the new length scale $\lambda$ opens a small-thickness regime in which non-electrostatic boundary conditions become important for multi-domain ferroelectricity. This is evidenced in the period of the states that cause the instability of the paraelectric phase in a film without electrodes. For film thicknesses $l \gg \lambda$ the period decrease by reducing $l$ as in conventional ferroelectrics. When $l$ reaches $\lambda$, however, it becomes comparable to the film thickness, and therefore the average out of the corresponding depolarizing field ceases to be efficient. A further reduction of $l$ then produces an increase of such a period whose precise form depends on the non-electrostatic boundary conditions. This latter behavior, unlike in the magnetic case \cite{8}, is rather unusual for a ferroelectric and, to the best of our knowledge, has been unnoticed so far.

Equations of state.– The instability towards ferroelectricity in the pseudo-proper case can be analyzed from the (linearized) equations of state:

\begin{equation}
AP - f\eta = -\partial_z V, \quad (1a)
\end{equation}
\begin{equation}
(a - c_\parallel \partial_y^2 - c_\perp \partial_z^2)\eta - fP = 0, \quad (1b)
\end{equation}
\begin{equation}
(\varepsilon_\parallel \partial_y^2 + \partial_z^2)V - 4\pi \partial_z P = 0. \quad (1c)
\end{equation}

Here $P$ is the electric polarization (assumed to be perpendicular to the film), $V$ is the electrostatic potential and $\eta$ is the primary order parameter. The coefficient $a$ is therefore the control parameter, $a = a'(T - T_0)$, whereas $A$ represents the bare polarization stiffness, $f$ is the coupling constant that allows for ferroelectricity, $c_\parallel$ and $c_\perp$ account for the extra stiffness of non-uniform distributions of $\eta$, and $\varepsilon_\parallel$ is the in-plane dielectric constant. Eq. (1c) results from Maxwell’s equations and Eqs. (1a) and
structures produce the minimal electric field in the ferroelectric, and therefore have the lowest stiffness. Consequently these structures are the most natural suspects of being responsible for the instability of the paraelectric phase as they are in conventional ferroelectrics. To move on we have to check whether this is actually compatible with the corresponding boundary conditions.

**Real electrodes.**—Consider first the case of a film sandwiched between short-circuited electrodes. We model the imperfect screening in the metal with insulating dead layers of thickness $d$ [10] and assume that the film thickness is $l \gg d$ in the following. Then, to satisfy the electrostatic boundary conditions, the above solutions have to be such that

$$k_z \tan \frac{k_z l}{2} = \varepsilon_y k_y \left( \frac{k_y d}{2} \right)$$

if $k_y d \ll 1$ as we expect. The maximum $a$ will be obtained for $k_z l \ll 1$, which is clearly compatible with $k_z \ll k_y$ if $d \ll l$. We then have

$$k_y^2 = \left( 1 + \frac{1}{3} \left( \frac{a}{k_z} \right)^2 + \ldots \right) \frac{1}{\pi^2} k_z^2.$$  

Substituting in (2) we can see that, below the critical dead-layer thickness

$$d_c = \sqrt{\frac{3A}{\pi \varepsilon_y} \lambda},$$

where $\lambda = (Ac)^{1/2} / |f|$, the single-domain state appears before these multi-domain structures for the value $a_c = f^2 / \left( A + 4\pi^4 f^2 \right)$ of the control parameter.

As we see, $d_c$ is inversely proportional to the strength of the linear coupling between $P$ and $\eta$ which, “by definition,” has to be relatively small in pseudo-proper ferroelectrics. In TbMnO$_3$, for example, the estimates of the spin-phonon coupling given in [10] indicate that $\lambda \sim 150 \text{A}$. On the other hand $A, \varepsilon_y \sim 20 - 30$ in accordance with [1]. Thus, in contrast to the conventional case [6], the screening of practically any electrode will prevent the splitting of a pseudo-proper ferroelectric into different domains at the transition point.

**No electrodes.**—The hampering of multi-domain states in pseudo-proper ferroelectrics is also manifested for dead layers thicker than $d_c$. Consider the extreme case in which there are no electrodes, i.e., there is no screening of the depolarizing field. In this case, the electrostatic boundary conditions are such that

$$k_z \tan \frac{k_z l}{2} = \varepsilon_y k_y.$$  

for the multi-domain structures considered before. $k_z$ then has to be $\sim \pi / l$ to satisfy the condition $k_z \ll k_y$. Accordingly $k_y \approx \varepsilon_y \left( \frac{2k_y}{\pi k_z l} \right)$, and, substituting into Eq. (2), we can see that these states do not appear before the single-domain solution if the thickness of the film is smaller than $\lambda$. One may then naively conclude that, below this thickness, the loss of stability takes place without

$k_z \tan \frac{k_z l}{2} = \varepsilon_y k_y.$
the formation of domains since the multi-domain states that normally appear in conventional ferroelectrics get suppressed. However this is not the end of the story, since less conventional structures may come into play. We have so far ruled out structures with $k_z \gtrsim k_y$ because they seem unfavorable from the point of view of the depolarizing field. This option, however, has to be reconsidered for $l < \lambda$. It corresponds to solutions with $k_z l \ll 1$, for which $k_y = \left(\frac{k_z l}{2\pi}\right) \left(1 + \frac{1}{3} \left(\frac{k_z l}{2}\right)^2 + \ldots\right) k_z$ in accordance with (5). One can see that, in fact, these solutions appear before the single-domain state for $l < \lambda$, thus causing the instability of the paraelectric phase.

We note that the period of the conventional structures that appear for $l \gg \lambda$ varies $\sim (\lambda l)^{1/2}$ with the film thickness (see Fig. 1). This period becomes larger than the film thickness if $l < \lambda$, which explains the further tendency of the system to get rid of these structures: they are no longer effective in reducing locally the depolarizing field. Once this efficiency is lost, the factors that determine the subsequent behavior for $l < \lambda$ are no longer effective in reducing locally the depolarization. This option, however, has to be reconsidered for $l < \lambda$. It corresponds to solutions with $k_z l \ll 1$, for which $k_y = \left(\frac{k_z l}{2\pi}\right) \left(1 + \frac{1}{3} \left(\frac{k_z l}{2}\right)^2 + \ldots\right) k_z$ in accordance with (5). One can see that, in fact, these solutions appear before the single-domain state for $l < \lambda$, thus causing the instability of the paraelectric phase.

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This scenario, in which natural boundary conditions for $\eta$ are implicit, holds for $c_\perp \neq 0$. The only changes are the following. The relation obtained instead of Eq. (2) has two $k_z$ roots for a given $k_y$. Accordingly the general solution of the linearized equations of state is the linear combination of the corresponding functions. For $l > \lambda$ the second $k_z$ is associated with a surface contribution that gives exponentially small corrections to the structures described before. The paraelectric instability is therefore practically insensitive to the non-electrostatic boundary conditions as in conventional ferroelectrics. For $l < \lambda$, however, the second $k_z$ becomes relevant to describe the $z$-dependence of the structure that appears at the transition point. But this changes neither the period of the structures obtained above nor the fact that these solutions appear before the single-domain state. These latter results, however, are sensitive to the precise form of the non-electrostatic boundary conditions.

We also note that pseudo-proper ferroelectrics have the following remarkable property. We have seen that, without electrodes, the instability of the paraelectric phase implies the appearance of multi-domain ferroelectricity. But the single-domain state is relatively close in energy in spite of its depolarizing field ($A+4\pi \simeq A$). Thus, by lowering the temperature, it is possible to have the situation in which the free energy develops at least a local minimum about the single-domain solution. That is, a situation in which single-domain ferroelectricity is metastable. This can be revealed by considering the tentative state of local equilibrium $\eta_0 = -\frac{1}{2} (a - \frac{f^2}{1+a^2})$, where $b$ is the coefficient of the nonlinear term $b\eta^3$ omitted so far in (1), and computing the stiffness associated with the perturbations $\eta_0 \rightarrow \eta_0 + \eta'$ that could drive the system out of that state. It is clear that, among all possible perturbations, those associated with the multi-domain structures considered before are the best candidates to do this job. But if the control parameter is $a \leq \sqrt{\frac{\lambda}{1-\frac{\lambda}{A}}}$ the resulting stiffnesses are positive. The single-domain state is then robust against its splitting into different domains, even though the corresponding depolarizing field is not screened (which is unthinkable in a conventional ferroelectric).

Conclusions.– We have studied the specific features of the instability towards ferroelectricity in thin films of pseudo-proper ferroelectrics. Single-domain (uniform) ferroelectricity can be kept in films sandwiched between short-circuited electrodes without requiring any exceptional screening in the metal. In fact, this state can be generated as a metastable state even without electrodes. In addition, the properties of multi-domain states reveal new fundamental physics related to non-electrostatic boundary conditions.

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* Electronic address: cano@esrf.fr
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[6] See, e.g., A.M. Bratkovsky and A.P. Levanyuk, J. Comput. Theor. Nanosci. 6, 465 (2009); arXiv:0801.1669 and the references therein.
[7] Real electrodes have finite screening lengths and/or there can be insulating “dead layers” in between the ferroelectric-metal interfaces which, mathematically, are equivalent situations [6].
[8] See, e.g., Eq. (6) in T. Garel and S. Doniach, Phys. Rev. B 26, 325 (1982).
[9] In spiral multiferroics demagnetizing field effects are expected to be very small since the magnetization already oscillates in bulk samples. In TbMnO$_3$, for example, the period of these oscillations is $\sim 2.1$ nm [Kenzelmann et al., Phys. Rev. Lett. 95, 087206 (2005)], which is in fact much smaller than size of domains that are potentially relevant.
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First of all, we have to consider the possibility of having \( M \) magnetoelectric effect [1], which can be taken in its simplest form [2]: in the sense that, whithout the coupling to \( \eta \) the “primary” order parameter of the transition of our interest, while the concomitant polarization \( P \) is “secondary” in the sense that, whithout the coupling to \( \eta \), it would remain zero. The relevant coupling is due to the inhomogeneous magnetoelectric effect [1], which can be taken in its simplest form [2]:

\[
F_{ME} = f_0 P \cdot \left[ (\mathbf{M} \cdot \nabla)\mathbf{M} - \mathbf{M}(\nabla \cdot \mathbf{M}) \right],
\]

since we are interested in distributions of polarization that vary only at relatively large scales.

To our purposes, it suffices to consider space variations along the \( y \) and \( z \) directions and the \( z \)-component of the polarization only [3]. Thus, neglecting for a while the depolarizing field, the free energy of the paramagnetic phase can be taken as

\[
F = \frac{A}{2} P^2 + \frac{C}{2} \left[ (\partial_y P)^2 + (\partial_z P)^2 \right] + f_0 P \left[ M_z(\partial_y M_y) - M_y(\partial_y M_z) \right] + \frac{a_y}{2} M_y^2 + \frac{a_z}{2} M_z^2 + \frac{b}{4} |\mathbf{M}|^4
\]

\[
- \frac{c_{||}}{2} (\partial_y M_y)^2 + \frac{g}{4} (\partial_y^2 M_y)^2 + c_{\perp} (\partial_z M_z)^2.
\]

The appearance of the longitudinal magnetization wave \( \mathbf{M} = (0, \xi \cos Qy, 0) \) can be described by assuming that \( c_{||} > 0 \). Thus, the wavevector of this modulation is \( Q = \sqrt{c_{||}/g} \). Putting \( P = 0 \) this structure transforms into the cycloid \( \mathbf{M} = (0, \xi \cos Qy, \eta \sin Qy) \) when \( a_y + bM_z^2/4 - c_{||}^2/(2g) = 2a = 0 \). Without clamping \( P \) this changes as follows. First of all, we have to consider the possibility of having \( M_z = M_z(y, z) \neq 0 \) and \( P = P(y, z) \neq 0 \) simultaneously. Then, in accordance with free energy [7], these quantities must satisfy the constituent equations

\[
[A - C(\partial_y^2 + \partial_z^2)] P + f_0 \left[ M_z(\partial_y M_y) - M_y(\partial_y M_z) \right] = -\partial_y V,
\]

\[
(a_y + bM_z^2 + c_{||} \partial_y^2 + \frac{g}{2} \partial_y^4 - 2c_{\perp} \partial_z^2)M_z + f_0 \left[ 2P(\partial_y M_y) + M_y(\partial_y P) \right] = 0,
\]

where \( V \) is the electrostatic potential in the system (due to space variations of \( P \)). Putting \( M_z = \eta(y, z) \sin Qy + \theta(y, z) \cos Qy \) and linearizing the above equations we get

\[
[A - C(\partial^2_y + \partial_z^2)] P - f \left( \eta + \frac{1}{2Q}(\partial_y \theta) \right) = -\partial_y V,
\]

\[
(a - c_{||} \partial_y^2 - c_{\perp} \partial_z^2)\eta - fP = 0,
\]

\[
2(a - c_{||} \partial_y^2 - c_{\perp} \partial_z^2)\theta + fQ^{-1}(\partial_y P) = 0.
\]

where \( f = f_0 Q \) and \( a = [a_y + bM_z^2/4 - c_{||}^2/(2g)]/2 \). Since \( \eta, \theta \) and \( P \) are expected to be smoother functions than \( \sin Qy \) and \( \cos Qy \), higher harmonics have been neglected.

We note that the function \( \theta(y, z) \) describes local changes in the phase of the magnetic cycloid which, in accordance that [9c], are associated with the non-uniformity of the distribution of polarization. In our problem, this distribution is expected to vary at distances much larger than the period of the cycloid \( 2\pi/Q \). Therefore, the phase of the cycloid remains practically unaltered and actually can be neglected for our purposes (\( \theta/\eta \sim k_y/Q \ll 1 \), where \( k_y \) is the wavevector for the space variations of \( P \). Eq. (9c) then can be omitted, and Eqs. (9a) and (9b) reduce to Eqs. (1a) and (1b).

* Electronic address: cano@esrf.fr

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