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Strain-induced diffuse dielectric anomaly and critical point in perovskite ferroelectric thin films

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It is shown that a strong but diffuse dielectric anomaly, commonly expected only in disordered ferroelectrics, may be inherent in strained and defect-free perovskite ferroelectric thin films. The origin of this unusual anomaly, which was never predicted for a defect-free system, is the overcritical trace of a critical point in the film phase diagram. This possibility is illustrated by the mean-field thermodynamic calculations performed for (111)-oriented $PbTiO_3$ films epitaxially grown on dissimilar cubic substrates. It is shown that clear symmetry reasons exist for the unusual behavior of the system. The essential prediction of the theory is that the type of the dielectric anomaly can be tailored by the sign of the misfit strain imposed on the film in paraelectric state: compressive strain leads to a standard Curie-Weiss anomaly, whereas the tensile one results in a diffuse anomaly.

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Anomalies in the temperature dependence $\varepsilon(T)$ of the dielectric permittivity are known to be a typical feature of ferroelectric materials. Up to now, the thermodynamic treatment of various systems has revealed only three types of these anomalies in a defect-free single-domain crystal: singularity, discontinuity, and discontinuity in the slope of the $\varepsilon(T)$ curve (e.g., cusp).[1] These ideal types of anomalies are often experimentally detected in bulk single-crystalline materials, with a certain degree of smearing of the singularities, which can be attributed to such extrinsic factors as finite frequency of the measuring field or the influence of defects. On the other hand, in ferroelectric thin films, as a rule, the dielectric anomalies are substantially diffuse (see, e.g., Ref. 2). Usually, this smearing cannot be attributed to the effect of frequency dispersion so that defect-related arguments are called on.

The goal of this paper is to demonstrate that, in strained perovskite thin films, a regular reason appears for the existence of a strong but diffuse dielectric anomaly. Namely, such an anomaly can be induced by the presence of the *overcritical trace* of a critical point in the film phase diagram. We will show that this phenomenon, which is rare in the case of transitions in bulk crystals,[3] may occur naturally in strained (111)-oriented perovskite films. This possibility will be illustrated by calculations performed for single-domain states of (111)-oriented $PbTiO_3$ films epitaxially grown on dissimilar cubic substrates.

We will start with a thermodynamic analysis of phase transitions occurring in (111)-oriented epitaxial $PbTiO_3$ (PT) films. Due to the mechanical coupling between the film and substrate, the lattice parameters of the ferroelectric in the film plane are usually different from those in the (111) cut of a mechanically free crystal. When the film is in the paraelectric state, this difference can be described by the so-called misfit-strain-tensor $\mathbf{u}^{(m)}$. In the discussed case, this tensor, obviously, has only two nonzero components $u_1 = u_2 \equiv u_m$. [We use the Voigt matrix notation and the rectangular Cartesian reference frame (X_1, X_2, X_3) with the X_3 axis perpendicular to the film/substrate interface.] The misfit strain u_m is generally a function of temperature T (mainly due to the difference in thermal expansion coefficients between the film and substrate) and may also depend on the film thickness and deposition temperature because of the generation of misfit dislocations at the film/substrate interface.[4,5] We shall consider u_m as a given parameter at any temperature T, including the temperature range, where the film is in a ferroelectric state. In this range, $-u_m$ will be defined as a deformation needed to transform the actual in-plane lattice parameter of the epitaxial film into the corresponding lattice parameter of the stress-free paraelectric phase extrapolated to a given temperature T. As demonstrated in the case of (001)-oriented perovskite films,[6,7] the introduction of two external parameters T and u_m is sufficient for the determination of single-domain states of an epitaxial film, if it is thick enough so that the so-called microscopic size effects can be neglected (see Refs. 4 and 8 from Ref. 6). Using the approach developed in Refs. 6 and 7, we shall derive now the misfit strain-temperature phase diagram for single-domain (111)-oriented PT films.

For PT, the thermodynamic analysis may be based on the following expansion of the elastic Gibbs function G (Ref. 8):

$$
\begin{aligned}
G = {} & a_1(\tilde{P}_1^2+\tilde{P}_2^2+\tilde{P}_3^2)+a_{11}(\tilde{P}_1^4+\tilde{P}_2^4+\tilde{P}_3^4)+a_{12}(\tilde{P}_1^2\tilde{P}_2^2+\tilde{P}_1^2\tilde{P}_3^2+\tilde{P}_2^2\tilde{P}_3^2)+a_{111}(\tilde{P}_1^6+\tilde{P}_2^6+\tilde{P}_3^6)+a_{112}[\tilde{P}_1^4(\tilde{P}_2^2+\tilde{P}_3^2) \\
& +\tilde{P}_3^4(\tilde{P}_1^2+\tilde{P}_2^2)+\tilde{P}_2^4(\tilde{P}_1^2+\tilde{P}_3^2)]+a_{123}\tilde{P}_1^2\tilde{P}_2^2\tilde{P}_3^2-\tfrac{1}{2}s_{11}(\tilde{\sigma}_1^2+\tilde{\sigma}_2^2+\tilde{\sigma}_3^2)-s_{12}(\tilde{\sigma}_1\tilde{\sigma}_2+\tilde{\sigma}_1\tilde{\sigma}_3+\tilde{\sigma}_3\tilde{\sigma}_2)-\tfrac{1}{2}s_{44}(\tilde{\sigma}_4^2+\tilde{\sigma}_5^2+\tilde{\sigma}_6^2) \\
& -Q_{11}(\tilde{\sigma}_1\tilde{P}_1^2+\tilde{\sigma}_2\tilde{P}_2^2+\tilde{\sigma}_3\tilde{P}_3^2)-Q_{12}[\sigma_1(\tilde{P}_2^2+\tilde{P}_3^2)+\tilde{\sigma}_3(\tilde{P}_1^2+\tilde{P}_2^2)+\tilde{\sigma}_2(\tilde{P}_1^2+\tilde{P}_3^2)]-Q_{44}(\tilde{P}_2\tilde{P}_3\tilde{\sigma}_4+\tilde{P}_1\tilde{P}_3\tilde{\sigma}_5+\tilde{P}_2\tilde{P}_1\tilde{\sigma}_6),
\end{aligned}
\tag{1}
$$

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where $\tilde{P}_i$ and $\tilde{\sigma}_i$ are the polarization and stress components defined in the crystallographic reference frame $(\tilde{X}_1,\tilde{X}_2,\tilde{X}_3)$. Equation (1) may be rewritten in the film frame (X_1,X_2,X_3) by using the frame transformation $\tilde{X}_i=A_{ij}X_j$ with the matrix **A** given by (the X_1 axis is taken to be parallel to the $[1\ \bar{1}\ 0]$ two fold axis of the cubic parent phase)

$$\mathbf{A}=\begin{pmatrix} 1/\sqrt{2} & -1/\sqrt{2} & 0 \\ 1/\sqrt{6} & 1/\sqrt{6} & -2/\sqrt{6} \\ 1/\sqrt{3} & 1/\sqrt{3} & 1/\sqrt{3} \end{pmatrix}. \tag{2}$$

The most straightforward way to describe the thermodynamics of thin films is, first, to pass from the elastic Gibbs function G to the thermodynamic potential corresponding to the mixed mechanical boundary conditions $u_1=u_2=u_m$, $u_6=0$, and $\sigma_3=\sigma_4=\sigma_5=0$ imposed on an epitaxial film and, second, to eliminate rest of mechanical variables using the same conditions.[6,7] This leads us to an effective thermodynamic potential G_{eff}, which is a function of the temperature, polarization, and misfit strain u_m, only. Applying this procedure to the elastic Gibbs function (1) rewritten in the film frame (X_1,X_2,X_3), we obtain the effective potential

$$\begin{aligned} G_{\mathrm{eff}}=&a_1^*(P_1^2+P_2^2)+a_3^*P_3^2+a_{11}^*(P_1^2+P_2^2)^2+a_{33}^*P_3^4\\ &+a_{13}^*P_3^2(P_1^2+P_2^2)+a_{2223}P_2P_3(P_2^2-3P_1^2)+G^{(6)},\end{aligned}$$

$$a_3^*=a_1-\frac{2(2Q_{11}+4Q_{12}-Q_{44})}{4s_{11}+8s_{12}+s_{44}}u_m, \tag{3}$$

$$a_1^*=a_1-\frac{2(2Q_{11}+4Q_{12}+Q_{44}/2)}{4s_{11}+8s_{12}+s_{44}}u_m,$$

where $G^{(6)}$ represents the P^6 terms of Eq. (1) transformed to the film frame and the contributions independent of the polarization **P** are omitted. In Eq. (3), the explicit expressions are given only for the renormalized second-order coefficients. For the fourth-order coefficients, explicit expressions are very cumbersome so that we list here only their numerical values for PT films. Using the parameters[9] of the Gibbs function G taken from Ref. 8, we found that $a_{11}^*=3.9\times10^8$, $a_{33}^*=2.3\times10^8$, $a_{13}^*=0.92\times10^8$, and $a_{2223}=0.63\times10^8$ (all in SI units).

As expected from general considerations, the thermodynamic potential (3) corresponds to a system of the $\bar{3}m$ symmetry, instead of the $m\bar{3}m$ symmetry inherent in bulk PT crystals. Performing the minimization of $G_{\mathrm{eff}}(P_i,u_m,T)$ with respect to the polarization components P_i, we developed the phase diagram shown in Fig. 1. It can be seen that, depending on the misfit strain, the paraelectric-to-ferroelectric transformation in (111) PT films results in the appearance of phases having the $3m$ or m symmetry. Similar to the case of single-domain (001)-oriented PT films, due to the substrate effect, this phase transition changes its order from the first to second one and leads to the formation of new ferroelectric phases, which do not exist in bulk PT. In particular, when the substrate imposes biaxial compression on the film prototypic state $(u_m<0)$, the *rhombohedral* single-domain ferroelectric state is expected to form in (111)-oriented PT films.

However, completely new features can be also seen in Fig. 1. First, a line of *isomorphic phase transitions* between the phases of m symmetry appears, ending up with a critical point (like in liquid-vapor systems). Second, a special line exists in the phase diagram of (111)-oriented films, shown with the dashed line in Fig. 1. On crossing this line, the dielectric response ε_{33} along the normal to the film plane exhibits a sharp, but nonsingular maximum [see Fig. 2(a)]. Figure 3 shows the misfit-strain dependence of the maximum permittivity ε_{33} observed on crossing this line. The aforementioned features are very unusual for bulk ferroelectrics. Nevertheless, the analysis reveals that, in (111) perovskite thin films, a regular reason exists for their appearance.

The possibility to have an (isolated) critical point in the phase diagram can be derived from the analysis of the origin of ferroelectric single-domain states in the system. Evidently, the biaxial stress in the film lifts the degeneracy of some of the domain states and changes their symmetry. Figure 4 contains a diagram that shows the possible ferroelectric phases and their domain states allowed by the thermodynamic potential given by Eq. (1) (Ref. 10) and the relation between these and the possible phases of the strained system. This relation is a result a straightforward symmetry analysis. It can be seen from this diagram that three generically different phases of the m symmetry are possible. Transitions between these phases, if any, will be isomorphic. Thus there is a symmetry reason for the existence of a line of isomorphic phase transitions (with a critical point at the end of it) in the phase diagram of (111)-oriented PT films.

The line of a sharp peak of the permittivity ε_{33}, shown by the dashed line in the phase diagram (see Fig. 1), can be regarded as a special type of the *overcritical trace* of an isolated critical point. However, the fact that even far from this point this trace is associated with a very strong anomaly of ε_{33} is related to another fascinating feature of the system. This feature can be revealed by inspecting the expansion (3) of the effective potential G_{eff}. It can be seen that two polar-

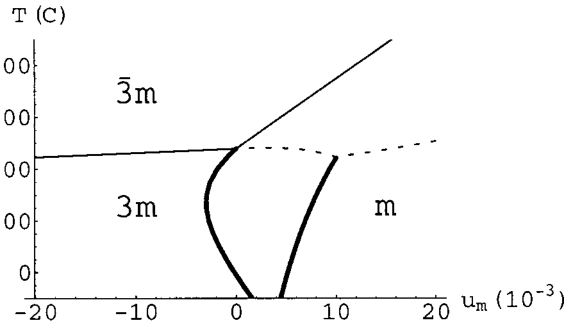

FIG. 1. Misfit strain vs temperature phase diagram for (III) single-domain $PbTiO_3$ thin film epitaxially grown on a dissimilar cubic substrate. The biaxial misfit strain u_m is counted from the paraelectric state of mechanically free $PbTiO_3$. The second- and first-order phase transitions are shown by thin and thick lines, respectively. The overcritical trace of the critical point is shown by the dashed line. The point group symmetry of the phases is indicated.

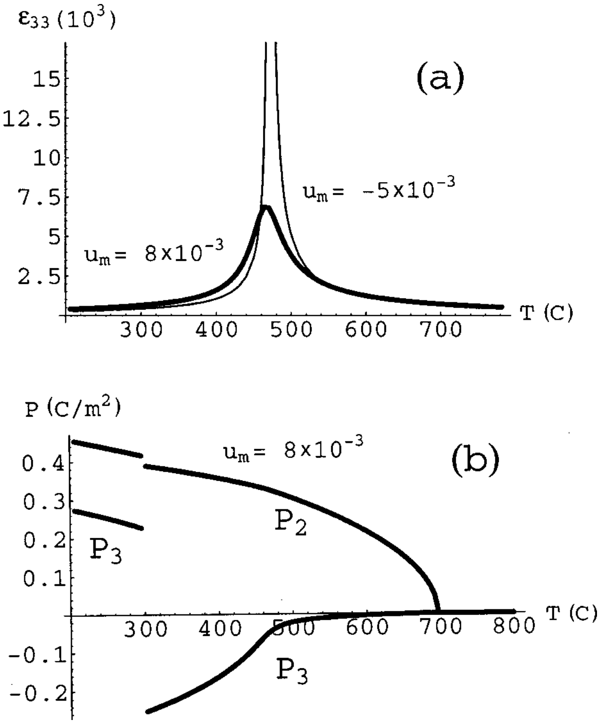

FIG. 2. The out-of-plane component of the relative dielectric permittivity ε_{33} (a) and the spontaneous polarization (b), out-of-plane (P_3) and in-plane (P_2) components, calculated as functions of temperature for a (III) single-domain PbTiO$_3$ thin film. The curves correspond to the vertical cross section of the diagram shown in Fig. 1 for the values of the misfit strain indicated. The change of the slope of $P_3(T)$ corresponds to crossing the overcritical trace shown in Fig. 1 by the dashed line.

ization instabilities are inherent in the paraelectric film, which correspond to the appearance of the in-plane (at $a_1^*=0$) and out-of-plane (at $a_3^*=0$) polarization components. Since in PT (and in many other perovskites) the unit cell is elongated along the polar axis and contracts in the transverse directions, the compressive misfit strain ($u_m<0$) facilitates the out-of-plane direction of the spontaneous polarization, resulting in the rhombohedral ferroelectric phase. On the contrary, the tensile misfit strain ($u_m>0$) favors the in-plane ferroelectric instability. In this case, according to the scheme shown in Fig. 4, the resulting phase can be either of the 2 symmetry or of the *m* symmetry. If the 2 phase forms $(P_1\neq 0, P_2=0, P_3=0)$, the behavior of the system would be mainly controlled by a weak[11] biquadratic coupling between P_1 and P_3 (a comprehensive analysis of the effect of the biquadratic coupling is offered in Ref. 12). This situation is similar to that found in the thermodynamics of (001)-oriented BaTiO$_3$ films,[6,7] where a quadruple point of the second-order phase transitions appears in the phase diagram at $u_m=0$. When the transition to a phase of the *m* symmetry takes place, a pseudoquadruple point should appear formed by two lines of the second-order phase transitions, a line of the first-order transformation, and an overcritical trace. This type of behavior, which is actually found in our system (see Fig. 1), can be readily explained in terms of the energy expansion (3).

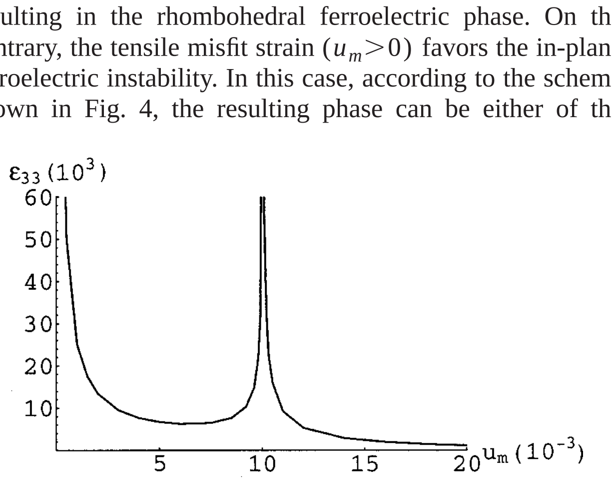

FIG. 3. Misfit-strain dependence of the out-of-plane component of the relative dielectric permittivity ε_{33} calculated along the overcritical trace shown in Fig. 1 by the dashed line.

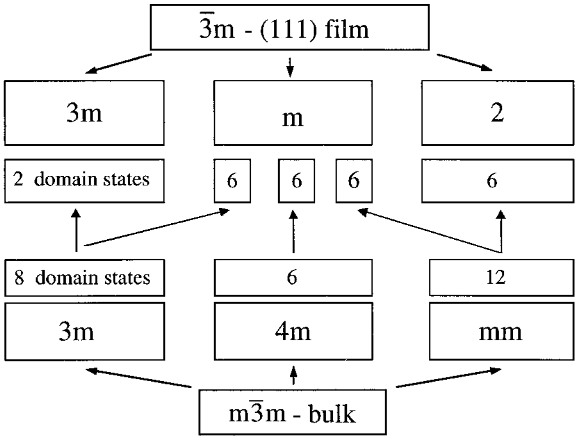

FIG. 4. Diagram illustrating relation between the possible phases of a ferroelectric perovskite when it is (III) strained and the possible domain states of the same ferroelectric when it is mechanically free. Point group symmetry and the number of the domain states of the phases are indicated. It is seen that, in the strained state, three different phases of the same *m* symmetry are possible.

The pseudoquadruple point and a strong dielectric anomaly along the overcritical trace are caused by the presence of the $P_2P_3(P_2^2-3P_1^2)$ coupling term in Eq. (3), which is allowed by the $\bar{3}m$ symmetry of the paraelectric film. Once the in-plane component P_2 of the polarization has appeared, via this term its out-of-plane component becomes a secondary order parameter $P_3\propto P_2^3$ [see Fig. 2(b)]. One can say that, due to this term, the in-plane polarization component P_2 induces a weak *fictive* out-of-plane electric field acting on P_3. Therefore, when on cooling the film crosses the line of the out-of-plane polarization instability,[13] the situation becomes similar to that at the second-order phase transition in the presence of a weak electric field. This explains the smearing out of the singularity in the dependence of ε_{33} on temperature. However, since the fictive field is weak, the anomaly remains strong. The physical meaning of the line of this anomaly is the overcritical trace, which passes through the critical point and ends up at the pseudoquadruple point.

Another feature of the pseudoquadruple point—namely, the first-order phase transition between the "3*m*" and "*m*" phases, is also symmetry determined. Considering the instability of the 3*m* phase with respect to the appearance of the polarization component P_2, it is seen that here the $P_2P_3(P_2^2-3P_1^2)$ term induces a cubic invariant for P_2, which is proportional to $P_{30}P_2^3$ (P_{30} is the spontaneous value of P_3). The cubic order-parameter invariant in the Landau expansion is known to exclude the possibility of the second-order phase transition in the system.[10]

Thus we have shown that, in (111) perovskite ferroelectric films, a regular symmetry reason exists for the appearance of smeared but still strong and sharp dielectric anomaly if the substrate imposes tensile strains ($u_m>0$) on the film prototypic cubic state. On the other hand, when the substrate imposes compressive strains on this state ($u_m<0$), there is no reason for the smearing of dielectric anomaly. As shown in Fig. 2, the standard Curie-Weiss singularity for ε_{33} is expected in (111) PT films at $u_m<0$. We would like to stress that, in the case of (111)-oriented PT films, the theoretical predictions could be checked experimentally. The tensile conditions in the paraelectric phase can be achieved by using Si as a substrate, because its thermal expansion coefficient (TEC) of about $2\times10^{-6}\,\mathrm{K}^{-1}$ is well below the TEC of PT ($\approx 8\times10^{-6}\,\mathrm{K}^{-1}$). The compressive conditions could be provided by MgO substrate, which has a TEC of about $14\times10^{-6}\,\mathrm{K}^{-1}$.

The presented analysis has explicitly addressed the single-domain case. The application of the obtained results to the multidomain situation may be impeded by the impact of the domain-assisted stress release.[14] However, to certain multidomain cases, our results are applicable. First, they are *quantitatively* applicable to the situation (typical for very thin films[14]) where the domain period is larger than the film thickness so that the stress in the ''bulk'' of the domains is virtually equal to that in the corresponding single-domain state. Second, the results can be *qualitatively* applicable to the case of partial domain-assisted stress release. In this case, the ferroelectric film will be still strained in the (111) plane, thus representing a system with the $\bar{3}m$ parent-phase symmetry and with close temperatures of the in-plane and out-of-plane polarization instabilities. As follows from the above analysis, it is these features that are crucial for the specific behavior of the system.

Concerning the approach used in the paper the following remark should be made. Our calculations are based on the Gibbs energy expansion that is available for bulk PT at the moment. The information contained in this expansion might actually not be enough for a correct quantitative description of the problem. The point is that, at present, we do not possess any information on the σP^4-type terms. It can be shown that, after the elimination of elastic variables, these terms will result in a modification of the P^6 terms in the effective thermodynamic potential. This modification will affect the quantitative results of the calculations. As for our main qualitative result, i.e., the appearance of the smeared anomaly of ε_{33}, it holds as long as the in-plane instability results in a phase with the m symmetry. However, if the modification of the P^6 terms leads to the preference of the 2 phase, the prediction of the smeared anomaly is not valid anymore.

In summary, we have shown that a diffuse static dielectric anomaly in ferroelectrics can arise not only due to the presence of imperfections, as customary believed, but also because of the strain effect. The origin of the smeared anomaly lies in an overcritical trace existing in the misfit strain versus temperature phase diagram. We have demonstrated that in (111)-oriented perovskite films these phenomena have regular symmetry reasons for existence. A quantitative description of the above phenomena has been presented for (111) $\mathrm{PbTiO_3}$ films grown on cubic substrates. For this epitaxial system, it is predicted that, depending on the type of strain conditions imposed on the film in the paraelectric state (tensile or compressive), either a smeared or a singular temperature anomaly of ε_{33} is expected.

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