Extrinsic contributions in a nonuniform ferroic sample:

Dielectric, piezoelectric and elastic

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(Dated: 8. September 2000)

Abstract

The contribution $\Delta \varepsilon$ of extremely small motions of domain walls to small-signal permittivity of a multidomain ferroelectric sample has been a research issue for many years. In ferroelastic ferroelectrics such motions contribute also to their piezoelectric (by $\Delta d$) and elastic (by $\Delta s$) properties. Data about their simultaneous existence are scarce but those available point to mutual proportionality of $\Delta \varepsilon$, $\Delta d$ and $\Delta s$, as expected. To understand the magnitude of extrinsic contributions, the origin of the restoring force acting on domain walls must be understood. In the present contribution the theory has been developed based on the model of a plate-like sample in which the ferroelectric-ferroelastic bulk is provided with a nonferroic surface layer. Motion of domain walls in the bulk results in a change of electric and elastic energy both in the bulk and in the layer, which provides the source of restoring force. This makes it possible to determine all mentioned extrinsic contributions. We discuss the applicability of the model to available data for single crystals and also for ceramic grains.

PACS numbers:

Keywords: Extrinsic permittivity, extrinsic piezoelectricity, extrinsic elastic moduli, surface layer

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I. INTRODUCTION

The problem of extrinsic (domain wall) contributions has been addressed by many authors, both experimentally and theoretically. In the prevailing number of cases, only extrinsic permittivity has been studied. For piezoelectric ceramics, Arlt et al.\cite{1} were the first to address the problem of wall contributions to all involved properties: permittivity $\varepsilon$, elastic compliances $s$ and piezoelectric coefficients $d$. In this and related papers, the existence of the restoring force is assumed and its origin was not specified. Later, Arlt and Pertsev\cite{2} offered a more involved approach: when domain wall in a ceramic grain is shifted, uncompensated bound charge appears on the grain boundary, producing electric field. Simultaneously, if the involved domains are ferroelastic, a wall shift results in mechanical stress in surrounding grains. Thus the shift is accompanied by the increase of both electric and elastic energies, leading to restoring forces. Results of these theories have been successfully related to experimental data on all three mentioned contributions: $\Delta \varepsilon$, $\Delta s$ and $\Delta d$.\cite{1, 2}

While there exist a number of such data for ceramic materials\cite{1, 3, 4}, information for single crystals is rather scarce. Understandably, for nonferroelastic ferroelectrics such as TGS only data on $\Delta \varepsilon$ are available;\cite{5} on the other hand for crystals which are both ferroelectric and ferroelastic with more than two domain states, dense domain systems are rather chaotic, difficult to approach theoretically. In the present paper, we have in mind ferroelectric and ferroelastic crystals with only two domain states. In particular, crystals belonging to the KH$_2$PO$_4$ family belong to this category and have been intensively studied. Nakamura et al.\cite{6, 7} determined $\Delta \varepsilon_{33}$ for KH$_2$PO$_4$, CsH$_2$PO$_4$ and CsH$_2$AsO$_4$. For KH$_2$PO$_4$, Nakamura and Kuramoto\cite{8} proved the existence of both $\Delta \varepsilon_{33}$ and $\Delta s_{66}$ while $\Delta d_{36}$ was measured for RbH$_2$PO$_4$\cite{9}. For the same material, all quantities $\Delta \varepsilon_{33}$, $\Delta d_{36}$ and $\Delta s_{66}$ have been measured by Štula et al.\cite{10}. It was found that all these contributions are mutually proportional when measured as a function of temperature, in the temperature interval between $T_C$ and $T_{C-35}$ K. Several other ferroics for which our approach may be applicable will be mentioned at the end of this paper.

In single crystals, the origin of the restoring force is usually connected to domain wall pinning on crystal lattice defects. In our recent papers\cite{11, 12} we introduced the model of a passive surface layer to calculate the restoring force for domain walls and the resulting extrinsic permittivity and piezoelectric coefficient. In fact, the influence of a surface layer
on the properties of a ferroelectric sample was discussed repeatedly several decades ago. In particular, in connection with the sidewise motion of domain walls in BaTiO$_3$, thickness dependence of the coercive field, asymmetry of a hysteresis loop or the problem of energies of critical nuclei, theoretically impossibly high.

In the present paper, we return to this approach. However, in contrast to previous calculations, we offer a more involved model. The shift of a domain wall induced by the application of electric field or elastic stress results in the increase of both electric and elastic energies. In the following, these are explicitly calculated which makes it possible to determine all extrinsic coefficients $\Delta \varepsilon_{33}$, $\Delta s_{66}$ and $\Delta d_{36}$. Their dependence on the sample properties will be discussed.

II. DESCRIPTION OF THE MODEL

We consider a plate-like sample elecroded sample of infinite area with major surfaces perpendicular to the ferroelectric axis $z$. The material is both ferroelectric and feroelastic; domains with antiparallel polarisation differ in the sign of spontaneous shear. However, we
shall approximate the material in the ferroelectric phase by the equation of state

\[ D_x = \varepsilon_0 \varepsilon_a E_x, \]
\[ D_z = \varepsilon_0 \varepsilon_c E_z + P_0, \]

neglecting the intrinsic piezoelectricity. As we shall see, this does not supress the existence the extrinsic piezoelectricity, which is one of the aims of our calculations. In the preceding equation, we also neglect nonlinear terms; for 2nd order phase transitions this limits the validity of our calculations to the temperature region not very close bellow the temperature \( T_C \). Domain walls are assumed to have surface energy density \( \sigma_w \) and zero thickness.

For simplicity, we approximate elastically anisotropic material of the sample by the elastically isotropic one. Neglecting again the intrinsic piezoelectricity, its mechanical properties are described by equations for stress tensor components

\[ \tau_{ij}^{(1)} = 2\mu_d e_{ij}^{(1)}, \]
\[ \tau_{ij}^{(2)} = 2\mu_f \left( e_{ij}^{(2)} - e_{0,ij} \right), \]

where \( \mu_d \) and \( \mu_f \) are Lame coefficients of the passive layers and the bulk respectively; \( e_{ij} \) is the strain tensor, \( e_{0,ij} \) is the spontaneous strain tensor of the central ferroelastic part. We suppose that the only nonzero components of the spontaneous strain tensor are \( e_{0,12} = \)
\( e_{0,21} = \pm e_0 \) in the \( a_+ \) resp. \( a_- \) domain, see Fig. 2. We introduce the asymmetry factor

\[
A = \frac{a_+ - a_-}{a_+ + a_-}.
\]

We neglect thermal interactions and suppose that the sample is thermally isolated. To keep the constant voltage \( V \) on the sample, the electrodes should be connected to external electrical source. In the same way, to keep constant external stress \( \tau_{\text{ext},12} = \tau_{\text{ext}} \), the sample should be deformed by external mechanical force. The infinitesimal work of these external sources should be taken into consideration when discussing the variations of the energy of the isolated system sample + sources.

**III. HELMHOLTZ FREE ENERGY**

In what follows we consider three contributions to Helmholtz free energy, calculated per unit area of the plate-like sample (in the \( x-y \) plane):

- The energy of domain walls per unit area of the sample

\[
U_w = \sigma_w \frac{h}{a} \quad \text{[J \cdot m^{-2}]},
\]

- the electric field energy per unit area of the sample

\[
U_{el}(V, A) = \frac{1}{2} \int_V E_i (D_i - P_{0,i}) \, dV,
\]

where the integration is taken over parallelepiped \( x \in (0, 2a), \; z \in (-t/2, t/2), \; y \in (0, 1 \text{ m}^2/2a) \), and energy of elastic deformations per unit area of the sample:

\[
U_{\text{def}}(\tau_{\text{ext}}, A) = \frac{1}{2} \int_V \tau_{ij} (e_{ij} - e_{0,ij}) \, dV, \quad \text{resp.}
\]

\[
U_{\text{def}}(u, A) = \frac{1}{2} \int_V \tau_{ij} (e_{ij} - e_{0,ij}) \, dV,
\]

where the integration is taken over the same region, in the first case for constant external stress \( \tau_{\text{ext}} \) in the plane \( x = 2a \), in the second one for constant displacement \( u \) in the plane \( x = 2a \). In both cases, the displacement for \( x = 0 \) is chosen to be zero and the boundaries of the sample in \( x-y \) plane are free of stress.

To find the \( U_{el} \) and \( U_{\text{def}} \), we have calculated electric potential and mechanical displacement inside the sample by Fourier method. We present here only the relative simple results for a
“dense pattern approximation”, that is for \( d, h \gg a \):

\[
U_{\text{el}}(V, A) = \frac{dh A^2 P_0^2}{2 \varepsilon_0 (\varepsilon_d h + \varepsilon_c d)} + \frac{V^2 \varepsilon_0^2 \varepsilon_d \varepsilon_c}{2},
\]

\[
U_{\text{def}}(\tau_{\text{ext}}, A) = \frac{h t^2 \mu_f \tau_{\text{ext}}^2}{2 (\mu_d d + \mu_f h)^2} + \frac{d \mu_d}{2} \left( \frac{2 A e_0 + \frac{t \tau_{\text{ext}}}{\mu_d d + \mu_f h}}{2} \right)^2,
\]

\[
U_{\text{def}}(u, A) = \frac{\mu_d du^2 + \mu_f h (2u - 8A e_0 a)^2}{8a^2}.
\]

Infinitesimal work of the electric source at constant voltage \( V \) per unit area of the sample plate is

\[
\delta W_{\text{el}} = V \delta \sigma_0 \quad [\text{J} \cdot \text{m}^{-2}],
\]

where \( \sigma_0 \) is constant Fourier component of the free charge density on the positive electrode, calculated as

\[
\sigma_0(V, A) = \frac{P_0 A + \varepsilon_0 \varepsilon_c V/h}{1 + \varepsilon_d d/(\varepsilon_d h)}.
\]

(1)

Infinitesimal work of the mechanical source, deforming the parallelepiped is

\[
\delta W_{\text{def}} = \tau_{\text{ext}} t/(2a) \delta u \quad [\text{J} \cdot \text{m}^{-2}],
\]

It is easy to prove that the equilibrium domain structure for \( V = 0 \), \( \tau_{\text{ext}} = 0 \) resp. \( u(x = 2a) = 0 \) is symmetric (i.e. \( A=0 \)), with domain width

\[
a_{\text{eq}} = \sqrt{\frac{3.68 \ h \sigma_w}{4 \varepsilon_0^2 \mu_d \mu_f + \frac{P_0^2}{\varepsilon_0 (\varepsilon_d + \varepsilon_c)}}} \left[ 1 + \varepsilon_d d/(\varepsilon_d h) \right]^{-\frac{1}{2}}.
\]

(2)

It can be shown (see e.g. [11]) that within a large interval of the applied voltage the average width

\[
a = (a_+ + a_-)/2
\]

remains constant. This is why \( U_w \) can be also considered as constant.

IV. EXTRINSIC CONTRIBUTIONS \( \Delta \varepsilon_{33}, \Delta s_{66} \) AND \( \Delta d_{36} \)

We calculate the equilibrium effective \( \varepsilon_{33}^{\text{eff}} \) of the sample from the relations

\[
D_{33}^{\text{eff}} = \sigma_0(V, A) = \varepsilon_{33}^{\text{eff}} E_{33}^{\text{ext}} = \varepsilon_{33}^{\text{eff}} \frac{V}{t},
\]

(3)
We keep $\tau_{\text{ext}} = 0$, $V=\text{constant}$ and we take into account that variation of “Helmholtz free energy of the sample + the work of electric source” is zero in equilibrium:

$$\frac{\partial U_{\text{el}}(V, A)}{\partial A} \delta A + \frac{\partial U_{\text{def}}(\tau_{\text{ext}} = 0, A)}{\partial A} \delta A - \delta W_{\text{el}} = 0.$$  \hspace{1cm} \text{(1)}

Solving this standard problem, we get $A = A(V)$ and from the Eqs. (1), (3) the effective $\varepsilon_{33}^{\text{eff}}$. For $\mu_d = \mu_f = \mu$, $\varepsilon_d = \varepsilon_c = \varepsilon_z$ we obtain the relatively simple result:

$$\varepsilon_{33}^{\text{eff}} = \varepsilon_z + \varepsilon_z \frac{h}{d} \cdot \left[ \frac{P_0^2 h}{P_0^2 h + 4 e_0^2 \varepsilon_0 \varepsilon_z \mu} \right]. \hspace{1cm} \text{(4)}$$

The effective elastic compliance of the sample is

$$s_{66}^{\text{eff}} = 4 s_{1212}^{\text{eff}} = \frac{2 e_{12}^{\text{eff}}}{\tau_{\text{ext}}} = \frac{u}{2 a \tau_{\text{ext}}}.$$  \hspace{1cm} \text{(5)}

We put $V = 0$ (shorted sample), apply constant external shear stress $\tau_{\text{ext}}$ and postulate, that variation of “Helmholtz free energy of the sample + the work of mechanical source” is zero in equilibrium

$$\frac{\partial U_{\text{el}}(0, A)}{\partial A} \delta A + \frac{\partial U_{\text{def}}(u, A)}{\partial A} \delta A - \delta W_{\text{def}} = 0.$$  \hspace{1cm} \text{(2)}

Solving this problem, we get $u = u(\tau_{\text{ext}})$ and we get for $\mu_d = \mu_f = \mu$, $\varepsilon_d = \varepsilon_c = \varepsilon_z$:

$$s_{66}^{\text{eff}} = \frac{1}{\mu} + \frac{1}{\mu} \cdot \frac{h}{d} \left[ \frac{4 e_0^2 \varepsilon_0 \varepsilon_z}{(P_0^2 / \mu) + 4 e_0^2 \varepsilon_0 \varepsilon_z} \right]. \hspace{1cm} \text{(6)}$$

To find the effective piezoelectric coefficient of the sample

$$e_{36}^{\text{eff}} = \frac{D_{36}^{\text{eff}}}{\tau_{\text{ext}, 6}} = \frac{\sigma_0}{\tau_{\text{ext}, 6}},$$

we put $V = 0$, apply $\tau_{\text{ext}}$ and solve the problem

$$\frac{\partial U_{\text{el}}(0, A)}{\partial A} \delta A + \frac{\partial U_{\text{def}}(u, A)}{\partial A} \delta A + \frac{\partial U_{\text{def}}(u, A)}{\partial u} \delta u - \delta W_{\text{def}} = 0.$$  \hspace{1cm} \text{(3)}

From here we obtain $A = A(\tau_{\text{ext}})$. Inserting this result into Eq. (1) we obtain $\sigma_0 = \sigma_0(\tau_{\text{ext}})$.

For $\mu_d = \mu_f = \mu$, $\varepsilon_d = \varepsilon_c = \varepsilon_z$ we get finally for the effective piezoelectric coefficient

$$e_{36}^{\text{eff}} = \frac{h}{d} \cdot \left[ \frac{2 e_0 P_0 \varepsilon_0 \varepsilon_z}{P_0^2 + 4 e_0^2 \varepsilon_0 \varepsilon_z \mu} \right]. \hspace{1cm} \text{(7)}$$

The same result we get for the inverse piezoelectric effect.
TABLE I: Numerical estimate of $\Delta \varepsilon_{33}$, $\Delta s_{66}$ and $\Delta d_{36}$ for different values of surface layer thickness.
The following numerical constants have been used: $P_0 = 4 \cdot 10^{-2} \text{C m}^{-2}$, $\varepsilon_z = 100$, $\varepsilon_0 = 0.015$, $\mu = 6 \cdot 10^9 \text{Pa}$, $\sigma_w = 5 \cdot 10^{-3} \text{J m}^{-2}$, $h = 5 \cdot 10^{-4} \text{m}$.

|               | $d = 0.5 \cdot 10^{-6} \text{m}$ | $d = 2.5 \cdot 10^{-6} \text{m}$ | $d = 5 \cdot 10^{-6} \text{m}$ |
|---------------|----------------------------------|----------------------------------|----------------------------------|
| $\Delta \varepsilon_{33}$ [1] | 12 000                           | 2 500                            | 1 200                            |
| $\Delta d_{36}$ [C m$^{-2}$]    | $4.1 \cdot 10^{-8}$              | $8.3 \cdot 10^{-9}$              | $4.1 \cdot 10^{-9}$              |
| $\Delta s_{66}$ [Pa$^{-1}$]     | $1.6 \cdot 10^{-8}$              | $3.2 \cdot 10^{-9}$              | $1.6 \cdot 10^{-9}$              |

V. DISCUSSION

The above calculation leads to explicit formulae (1) to (3) for extrinsic permittivity, extrinsic elastic compliance and extrinsic piezoelectric coefficient, respectively. Numerical values for all involved material coefficients are available for single crystals of RbH$_2$PO$_4$: $P_0 = 4 \cdot 10^{-2} \text{C m}^{-2}$, $\varepsilon_z = 100$, $\varepsilon_0 = 0.015$ and $\mu = 6 \cdot 10^9 \text{Pa}$. To obtain numerical estimates for particular samples we put $\sigma_w = 5 \cdot 10^{-3} \text{J m}^{-2}$ and $h = 5 \cdot 10^{-4} \text{m}$ and choose three values of surface layer thickness, namely $d = 0.5 \cdot 10^{-6} \text{m}$, $d = 2.5 \cdot 10^{-6} \text{m}$ and $d = 5 \cdot 10^{-6} \text{m}$. Table I shows resulting values of all three extrinsic variables. These numbers appear very realistic and confirm the applicability of the model presented in this paper.

It is appropriate to pay some attention to the fact that also the formula (2) gives a reasonable numerical estimation for the width of equilibrium domain pattern. With numerical values specified at Tab. I we obtain $a_{eq} \approx 1 \mu m$.

In the approach analyzed above, the source of the restoring force acting on domain walls is the interaction of ferroic sample with a passive surface layer. Very often, the origin of restoring forces is connected with domain wall pinning to defects. Understandably, the latter mechanism cannot be excluded for ferroics of any chemical composition. On the other hand, passive surface layers can be formed during sample preparations and in particular for water-soluble crystals their appearance is a very likely: samples are polished in water-containing media, the procedure obviously leading to the presence of a passive surface layer. The example analyzed numerically above, crystals of RbH$_2$PO$_4$, falls into this category. However, extrinsic properties of a number of other crystals have been studied. Thus, e.g.,
for LiTIC$_4$H$_4$O$_6$ ⋅ H$_2$O (species 222-\(P\varepsilon ds\)-2$y$) very strong and nonhysteretic dependence of $s_{44}^E$ as a function of applied field $E$ was measured. This is possible to explain by a strong contribution of domain walls with a pronounced restoring force. The above model would lead to such behavior. Similarly, large extrinsic contributions to $s_{11}$ have been measured for (NH$_4$)$_4$LiH$_3$(SO$_4$)$_4$, species 4-\(P\varepsilon ds\)-2.

Acknowledgments

This work has been supported by the Ministry of Education of the Czech Republic (Projects No. VS 96006 and No. MSM 242200002) and by the Grant Agency of the Czech Republic (Project No. 202/00/1245).

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