

Technical University in Liberec
Faculty of Education

Department of Physics

Ph. D. THESIS

The Role of Domain Structures in Piezoelectrically Active Systems

Role doménových struktur v piezoelektricky aktivních systémech

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Role doménových struktur v piezoelektricky aktivních systémech

The Role of Domain Structures in Piezoelectrically Active Systems

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Role doménových struktur v piezoelektricky aktivních systémech

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Pavel Mokřý, MSc.

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Role of the Domain Structures in Piezoelectrically Active Systems

Resume:

The subject of this Ph.D. Thesis is to theoretically investigate the role of the domain structures in piezoelectrically active systems. It is well known that the response of domain structure to external electric field and mechanical stress influences, to large extent, dielectric, elastic and electromechanical properties of ferroic samples. Domain wall motion is a basis of extrinsic contributions to e.g. dielectric constant, elastic and piezoelectric coefficients, which are frequently much higher than intrinsic ones.

We start with a simple thermodynamic theory of anomalous temperature dependencies of ϵ_{33}^E component of permittivity tensor at a constant strain, s_{66}^E component of elastic stiffness tensor at a constant electric field and d_{36} component of piezoelectric coefficient during first order phase transition $\bar{4}2m - mm2$. The comparison of theoretically predicted values and results of experimental measurements is discussed. The *model of passive surface layer* is introduced to explain this disagreement of a theory with an experiment.

First the equilibrium response of ferroelectric or ferroelastic domain structure to external electric field or mechanical stress is examined. On the base of this equilibrium response the restoring force acting on the domain wall can be calculated as well as extrinsic contributions to electromechanical properties of electroded ferroic samples. The effect of the passive surface layer thickness on the values of domain wall contributions is discussed.

The main results of our theoretical investigation are presented in form of collection of commented published papers. The applicability of the surface layer model is discussed as well as comparison of its theoretical predictions with experimental data.

Ing. Pavel Mokřý

Školitel: doc. RNDr. Antonín Kopal, CSc.

Role doménových struktur v piezoelektricky aktivních systémech

Resumé:

Cílem této disertační práce je teoretický výzkum role doménových struktur v piezoelektricky aktivních systémech. Je dobře známo, že reakce doménové struktury na vnější elektrické pole a mechanické napětí do značného rozsahu ovlivňuje dielektrické, elastické a elektromechanické vlastnosti feroických vzorků. Pohyby doménových stěn tvoří základ tzv. "vnějších" příspěvků k např. relativní permitivitě, elastickým a piezoelektrickým koeficientům, které převyšují často i řádově příspěvky dané vlastnostmi jednodoménového vzorku.

Vycházíme z jednoduché termodynamické teorie anomálních teplotních závislostí složky ϵ_{33}^E tenzoru permitivity při konstantní mechanické deformaci, složky s_{66}^E tenzoru elastických poddajností při konstantním elektrickém poli a složky d_{36} tenzoru piezoelektrických koeficientů při fázovém přechodu prvního druhu $\bar{4}2m - mm2$. Předpovědi termodynamické teorie jsou porovnány s výsledky experimentálních měření. Abychom se pokusili vysvětlit výsledky experimentálních měření, zavádíme tzv. *model s pasivní povrchovou vrstvou*.

Nejprve je vyšetřována rovnovážná reakce feroické doménové struktury na vnější elektrické pole a mechanické napětí. Ze znalosti této rovnovážné reakce můžeme vypočítat vratnou sílu, která působí na doménovou stěnu, a dále vnější příspěvky k elektromechanickým vlastnostem feroických vzorků opatřených elektrodami. Diskutujeme vliv tloušťky pasivní vrstvy na hodnoty příspěvků pohybu doménových stěn.

Nejdůležitější výsledky našeho teoretického vyšetřování jsou presentovány ve formě komentovaných publikovaných článků. V závěru práce je diskutována použitelnost modelu s pasivní povrchovou vrstvou, společně se srovnáním jeho teoretických předpovědí s experimentálními daty.

Proclamation

I do proclaim that I have developed this Ph.D. Thesis independently using published sources and only with a cooperation of supervisor and consultant.

In Jablonec nad Nisou, February 28th, 2001

Pavel Mokrý, MSc.

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I would like to thank the supervisor of this Ph.D. Thesis Ass. Prof. Dr. Antonín Kopal, Ph.D. and consultant Prof. Dr. Jan Fousek, DrSc. for their important help, helpful comments and critical remarks during the preparation of this work.

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List of Symbols

Domain structure parameters

w_+, w_-	domain width		m
$2w$	domain structure period with respect the x axis	$w = (w_+ + w_-)/2$	m
w_w	domain wall width		m
s	surface layer resp. electrode thickness		m
d	bulk single crystall thickness		m
D	electroded sample thickness	$D = d + 2s$	m
V	applied voltage		V
Θ	temperature		K

Material parameters

P_0, P_S	spontaneous polarization in ferroelectric axis direction		Cm ⁻²
Θ_{tr}	phase transition temperature		K
ϵ_0	vacuum permittivity		Fm ⁻¹
$\epsilon_{ij}^{(1)}$	relative permittivity tensor of the surface layers		1
$\epsilon_{ij}^{(2)}, \epsilon_{ij}$	relative permittivity tensor of the bulk		1
$\beta_{ij}^e, \beta_{ij}^f$	clamped and free impermittivity tensor		F ⁻¹ m
$d_{i\mu}, h_{i\mu}$	piezoelectric coefficients matrix		Cm ⁻²
$\lambda^{(\cdot)}, \mu^{(\cdot)}$	Lamè coefficients (components of elastic stiffness tensor in isotropic material)		Pa
$s_{e,\mu\nu}$	elastic compliances matrix components of the electrode		Pa ⁻¹
$s_{b,\mu\nu}$	elastic compliances matrix components of the bulk		Pa ⁻¹
$c^{(\cdot)}$	material parameter ($\cdot$)	$c^{(\cdot)} = \sqrt{\epsilon_1^{(\cdot)}/\epsilon_3^{(\cdot)}}$	1
$g^{(\cdot)}$	material parameter ($\cdot$)	$g^{(\cdot)} = \sqrt{\epsilon_1^{(\cdot)}\epsilon_3^{(\cdot)}}$	1
σ_w	domain wall surface energy density		Jm ⁻²
σ_0	surface charge density on the electrodes		Cm ⁻²
U_w	domain wall energy density per unit area of the sample		Jm ⁻²
U_{el}	electric field energy density		Jm ⁻²
U_{def}	elastic deformation energy density		Jm ⁻²

Geometrical parameters

A	asymmetry coefficient	$A = (w_+ - w_-)/2w$	1
R	domain pattern coefficient	$R = \pi d/2w$	1
B	slab factor	$B = 2s/d$	1

Complementary formulas

$$d = \frac{D}{1+B}, \quad s = \frac{BD}{2(1+B)}, \quad w = \frac{\pi D}{2R(1+B)}$$

Introduction

Microelectromechanical devices such as actuators, microaccelerometers, gyroscopes and other electromechanical transducers are of a very intensive interest of scientists and technicians. The piezoelectrically active systems play the fundamental role in these devices. That is why the contemporary scientific research pays attention to investigation of these systems both experimentally and theoretically.

The piezoelectric ceramics or single crystals are used for a transfer of mechanical stresses or strains to electric signals and this is the fundamental principle of their function in microelectromechanical devices. The electromechanical coupling factor is one of the most useful measure for selection of the best material. For this reason the ferroelectric piezoelectric materials, especially ceramics are often used. The influence of the domain structure to electromechanical behaviour of these materials is well known from many experimental observations.

The strong nonlinearity and very complicated time-dependent behaviour of material properties make a big challenge for theoretical analysis.

Role of the domain structures in piezoelectrically active systems

Very complicated piezoelectric active systems can appear in many microelectromechanical devices as well as they are prepared in many experimental apparatuses to observe fundamental physical properties of materials. It is clear that domain structures of many kinds are present in these elements when ferroelectric (or more general ferroic) materials are used for their preparation.

The main aim of our work is to explain the question: "How the domain structure can influence the physical properties of ferroic samples?" To answer this question we start from the fundamental physical observations of temperature dependencies of relative permittivity ϵ_{33} , elastic compliances s_{66} and piezoelectric coefficients d_{36} of KDP, DKDP, RbDP etc. single crystals. These substances undergo first order phase transition $\bar{4}2m - mm2$ close to the second order phase transition. There are values of phase transition temperatures Θ_{tr} for some materials of KDP family in fig. 1. Change of the values of material constants due to symmetry change during phase transition is shown in fig. 2. The anomalous behaviour is typical for temperature dependencies of components: ϵ_{33} of relative permittivity tensor, c_{66}^E of elastic stiffness tensor, s_{66}^E of elastic compliance and d_{36} or e_{36} of piezoelectric coefficients. We start from the simple thermodynamic theory and determine the temperature dependencies of these material constants. As we shall see the experimental observations of macroscopical values of these material constants disagree with theoretically predicted values, when they are measured on multidomain samples. Therefore we are going to discuss the influence of domain structure on macroscopic properties of electroded samples.

Crystals	Θ_{tr} K	C_{CW}/ϵ_0 10^3 K
KH_2PO_4	122.76	2.9
KD_2PO_4	207.16	3.9
RbH_2PO_4	147.66	3.7
CsH_2PO_4	146.15	2.9
KH_2AsO_4	96	2.49

FIGURE 1: Transition temperatures Θ_{tr} and Curie-Weiss constants C_{CW} for some materials of KDP family (see [15])

$$\begin{pmatrix} c_{11} & c_{12} & c_{13} & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ c_{12} & c_{11} & c_{13} & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ c_{13} & c_{13} & c_{33} & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & c_{44} & \cdot & \cdot & d_{14} & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & c_{44} & \cdot & \cdot & d_{14} & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot & c_{66}^* & \cdot & \cdot & d_{36}^* \\ \cdot & \cdot & \cdot & d_{14} & \cdot & \cdot & \epsilon_{11} & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & d_{14} & \cdot & \cdot & \epsilon_{11} & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot & d_{36}^* & \cdot & \cdot & \epsilon_{33}^* \end{pmatrix} \rightarrow \begin{pmatrix} c_{11} & c_{12} & c_{13} & \cdot & \cdot & c_{16} & \cdot & \cdot & d_{31} \\ c_{12} & c_{11} & c_{13} & \cdot & \cdot & c_{16} & \cdot & \cdot & d_{31} \\ c_{13} & c_{13} & c_{33} & \cdot & \cdot & c_{36} & \cdot & \cdot & d_{33} \\ \cdot & \cdot & \cdot & c_{44} & c_{45} & \cdot & d_{14} & d_{15} & \cdot \\ \cdot & \cdot & \cdot & \cdot & c_{45} & c_{44} & d_{15} & d_{14} & \cdot \\ c_{16} & c_{16} & c_{36} & \cdot & \cdot & c_{66}^* & \cdot & \cdot & d_{36}^* \\ \cdot & \cdot & \cdot & d_{14} & d_{15} & \cdot & \epsilon_{11} & \epsilon_{12} & \cdot \\ \cdot & \cdot & \cdot & d_{15} & d_{14} & \cdot & \epsilon_{12} & \epsilon_{11} & \cdot \\ d_{31} & d_{31} & d_{33} & \cdot & \cdot & d_{36}^* & \cdot & \cdot & \epsilon_{33}^* \end{pmatrix}$$

tetragonal $\bar{4}2m$ orthorhombic $mm2$

FIGURE 2: Change of the values of material properties due to symmetry lowering that occurs during $\bar{4}2m - mm2$ phase transition. Values written with respect to the parent phase. Star "*" marks the material constants with anomalous temperature dependencies.

Simple thermodynamic theory

It is known that KDP or RbDP crystals undergo the first order phase transition. Nevertheless, the discontinuous change of spontaneous polarization P_S is relatively small (see fig. 3). Moreover, all material constants ϵ_{33} , d_{36} , s_{66}^E fulfill the *Curie-Weiss law* in a wide temperature region over transition temperature. Therefore we can say that the most of crystals from KDP and RbDP families undergo the first order phase transition, which is close to the second order phase transition. Then we can adopt the following thermodynamic potential of a clamped crystal as an acceptable approximation:

$$\begin{aligned}
\Phi(\Theta, P_3, e_6; E_3, \tau_6) = & \\
& \Phi_0 + \frac{1}{2} \alpha_0 (\Theta - \Theta_{tr}^*) P^2 + \frac{1}{4} \beta P^4 + \\
& + \frac{1}{2} c_{66}^P e_6^2 - h_{36} P_3 e_6 - P_3 E_3 - \tau_6 e_6,
\end{aligned} \tag{1}$$

where E_3 resp. P_3 is the electric field resp. polarization along the ferroelectric axis. e_{66} resp. τ_{66} represents the shear strain resp. stress in the plane perpendicular to the ferroelectric axis. It is well known from experiment that the inverse dielectric constant β_{33}^E of this crystal along the ferroelectric axis at a constant shear strain e_6 vanishes at transition temperature and at the same time the elastic compliance s_{66}^P of the crystal at a constant polarization P_3 is practically temperature independent. It is therefore natural to assume that the polarization in the expansion of the thermodynamic potential is the primary order parameter; this assumption has been used as the basis for simple development of phenomenological theory of a phase transition in KDP, RbDP crystals.

The strong anomalous behaviour of temperature dependence can be easily derived for the ϵ_{33}^E component of permittivity tensor, d_{36} component of the piezoelectric coefficients matrix and s_{66}^E resp. c_{66}^E components of the elastic compliance resp. stiffness matrices at a constant electric field. Simultaneous solution of the equations that determine the equilibrium value of two parameters

$$\frac{\partial \Phi}{\partial P_3} = \alpha_0 (\Theta - \Theta_{tr}^*) P_{0,3} + \beta P_{0,3}^3 - h_{36} e_{0,6} - E_3 = 0, \tag{2}$$

$$\frac{\partial \Phi}{\partial e_6} = c_{66}^P e_{0,6} - h_{36} P_{0,3} - \tau_6 = 0 \tag{3}$$

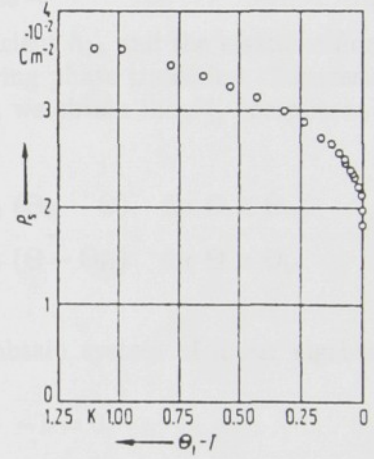


FIGURE 3: Temperature dependence of spontaneous polarization for KDP single crystal (see [15])

yields to temperature dependencies of polarization and shear strain. In the absence of any external electric field $E_3 = 0$ and mechanical stress $\tau_6 = 0$ we get the well known temperature dependencies of spontaneous polarization and shear strain

$$P_{0,3}(\Theta) = \begin{cases} \sqrt{\frac{\alpha_0 (\Theta_{tr} - \Theta)}{\beta}} & \text{for } \Theta < \Theta_{tr}, \\ 0 & \text{for } \Theta > \Theta_{tr}, \end{cases} \quad (4)$$

$$e_{0,6}(\Theta) = \begin{cases} \frac{h_{36}}{c_{66}^P} \sqrt{\frac{\alpha_0 (\Theta_{tr} - \Theta)}{\beta}} & \text{for } \Theta < \Theta_{tr}, \\ 0 & \text{for } \Theta > \Theta_{tr}, \end{cases} \quad (5)$$

where

$$\Theta_{tr} = \Theta_{tr}^* + \frac{h_{36}^2}{c_{66}^P \alpha_0}$$

is the transition temperature of a free crystal.

From equations (2,3) we can easily express the electric field E_3 and shear stress τ_6 as functions of polarization P_3 and shear strain e_6 :

$$E_3 = \alpha_0 (\Theta - \Theta_{tr}^*) P_3 + \beta P_3^3 - h_{36} e_6, \quad (6)$$

$$\tau_6 = -h_{36} P_3 + c_{66}^P e_6. \quad (7)$$

It is easy to show from equation (7) that the piezoelectric coefficient h_{36} and the elastic stiffness at a constant polarization c_{66}^P are temperature independent during phase transition. Expressing the derivative of electric field E_3 with respect to polarization P_3 we obtain the β_{33}^e component of impermeability tensor

$$\beta_{33}^e = \frac{\partial E_3}{\partial P_{0,3}} = \alpha_0 (\Theta - \Theta_{tr}^*) + 3\beta P_{0,3}^2(\Theta) = \begin{cases} \frac{h_{36}^2}{c_{66}^P \alpha_0} + 2\alpha_0 (\Theta_{tr} - \Theta) & \text{for } \Theta < \Theta_{tr}, \\ \frac{h_{36}^2}{c_{66}^P \alpha_0} + \alpha_0 (\Theta - \Theta_{tr}) & \text{for } \Theta > \Theta_{tr}. \end{cases} \quad (8)$$

Differentiating the equations (2,3) with respect to E_3 we obtain system of linear algebraic equations

$$\begin{aligned} [\alpha_0 (\Theta - \Theta_{tr}^*) + \beta P_{0,3}^2] \frac{\partial P_{0,3}}{\partial E_3} - h_{36} \frac{\partial e_{0,6}}{\partial E_3} - 1 &= 0, \\ -h_{36} \frac{\partial P_{0,3}}{\partial E_3} + c_{66}^P \frac{\partial e_{0,6}}{\partial E_3} &= 0. \end{aligned} \quad (9)$$

Solving the system of linear algebraic equations (9) for unknown partial derivatives $\partial P_3 / \partial E_3$ and $\partial e_6 / \partial E_3$, we find formulae for relative permittivity ε_{33}

$$\varepsilon_{0,33}^e \approx \frac{\partial P_{0,3}}{\partial E_3} = \frac{1}{\alpha_0 (\Theta - \Theta_{tr}^*) + 3\beta P_{0,3}^2(\Theta)} = \begin{cases} \frac{1}{2\alpha_0 (\Theta_{tr} - \Theta)} & \text{for } \Theta < \Theta_{tr}, \\ \frac{1}{\alpha_0 (\Theta - \Theta_{tr})} & \text{for } \Theta > \Theta_{tr} \end{cases} \quad (10)$$

and piezoelectric coefficient d_{36}

$$d_{36} = \frac{\partial e_{0,6}}{\partial E_3} = \frac{h_{36}}{c_{66}^P \alpha_0 (\Theta - \Theta_{tr}^*) + 3\beta P_{0,3}^2(\Theta)} = \begin{cases} \frac{h_{36}}{2c_{66}^P \alpha_0 (\Theta_{tr} - \Theta)} & \text{for } \Theta < \Theta_{tr}, \\ \frac{h_{36}}{c_{66}^P \alpha_0 (\Theta - \Theta_{tr})} & \text{for } \Theta > \Theta_{tr}. \end{cases} \quad (11)$$

We can express the temperature dependencies of c_{66}^E and s_{66}^E using transformation rules

$$c_{ijkl}^E = c_{ijkl}^P - \varepsilon_{mn}^e h_{mij} h_{nkl}, \quad s_{ijkl}^E = s_{ijkl}^P + \beta_{nm}^r d_{mij} d_{nkl}, \quad \beta_{ij}^r = \beta_{ij}^e - h_{ikl} h_{jmn} s_{klmn}^P. \quad (12)$$

Substituting equations (10) and (11) into (12) we can express the anomalous temperature dependencies of elastic stiffness

$$c_{66}^E = c_{66}^P - \begin{cases} \frac{h_{36}^2}{2\alpha_0 (\Theta_{tr} - \Theta)} & \text{for } \Theta < \Theta_{tr}, \\ \frac{h_{36}^2}{\alpha_0 (\Theta - \Theta_{tr})} & \text{for } \Theta > \Theta_{tr} \end{cases} \quad (13)$$

and elastic compliance

$$s_{66}^E = s_{66}^P + \begin{cases} \frac{4 h_{36}^4 (s_{66}^P)^2}{\alpha_0^2 (\Theta - \Theta_{tr})^2} + \frac{h_{36}^2 (s_{66}^P)^2}{2\alpha_0 (\Theta_{tr} - \Theta)} & \text{for } \Theta < \Theta_{tr}, \\ \frac{16 h_{36}^4 (s_{66}^P)^2}{\alpha_0^2 (\Theta - \Theta_{tr})^2} + \frac{h_{36}^2 (s_{66}^P)^2}{\alpha_0 (\Theta - \Theta_{tr})} & \text{for } \Theta > \Theta_{tr} \end{cases} \quad (14)$$

at a constant electric field.

The theoretically predicted and experimentally observed [15] temperature dependencies of relative permittivity ϵ_{33} for the KDP multidomain single crystal is shown in dashed line shows the values of permittivity according to the theoretical formula (10). The solid lines represent the experimentally observed ones. These observed values of ϵ_{33} differs extremely from theoretical predictions of classical Landau theory in the 35 K temperature region below the transition temperature Θ_{tr} . On the other hand, the measurements match perfectly with the theory if they are performed on single-domain single crystals.

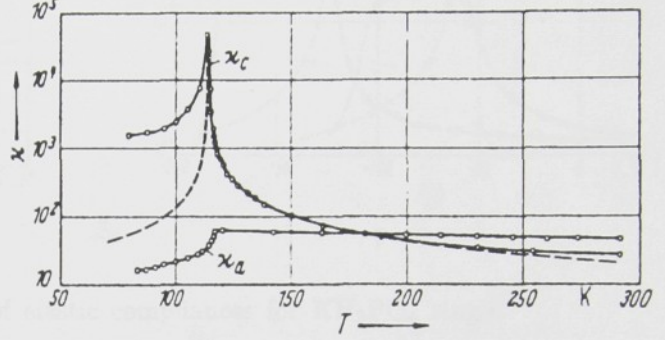


FIGURE 4: Theoretical (dashed lines) and experimental (full lines) temperature dependence of relative permittivity ϵ_{33} for KDP single crystal (see [15])

Similar temperature dependencies have been observed for elastic compliance s_{66}^E of simultaneously ferroelectric and ferroelastic KDP crystals. Nakamura and Kuramoto measured the elastic stiffness c_{66}^E as a function of temperature for potassium dihydrogen phosphate [6]. Two types of KDP samples were prepared for this measurement, see fig. 5. First, the ordinary KDP crystals (filled circles) and second, the lossy ones (empty circles). Adding the extra additives they produced the samples with extremely high dielectric losses. The secondary effect could happen due to this procedure. The number of crystal lattice defects could extremely increase and, therefore, the mobility of domain walls could diminish. The dashed line represents theoretically predicted values of temperature dependence of elastic stiffness c_{66}^E at a constant electric field. The minimum values of elastic stiffness in fig. 5 corresponds to maximum values of elastic compliance in fig. 6.

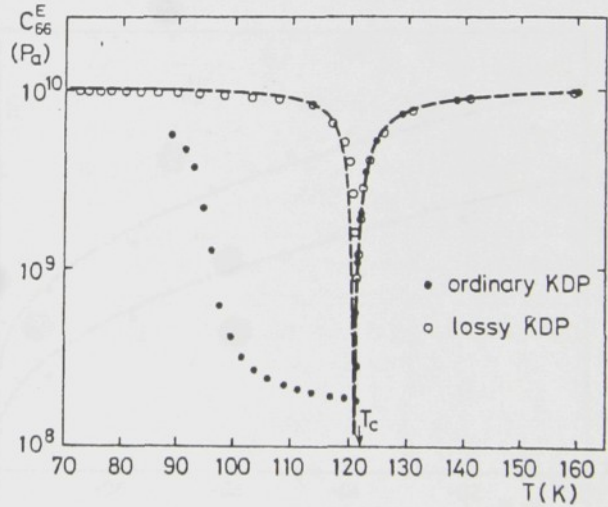
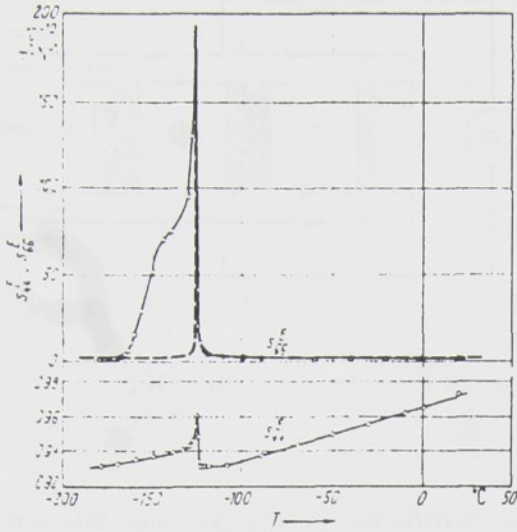
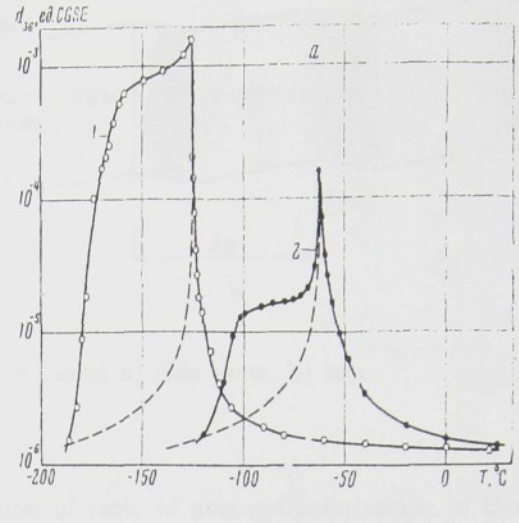


FIGURE 5: Nakamura's and Kuramoto's measurements of elastic stiffness [6]

Moreover, record values were measured for piezoelectric coefficient d_{36} for RbDP single crystal in a 35 K temperature range below phase transition point. An example of such experimental data of temperature dependence of d_{36} for RbDP single crystal taken by Shuvalov et al. [7] is shown in fig. 7. Also, the theoretical values are represented by the dashed curve.



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FIGURE 6: Measurements of elastic compliances for KH_2PO_4 single crystal [15].

FIGURE 7: Measurements of piezoelectric coefficients for (1-pure, 2-doped) RbH_2PO_4 single crystal taken by Shuvalov (see [7]).

Disagreements of theoretical temperature dependencies with experimental data measured on multidomain samples lead to following conclusion: the existence of 180° lamellar domain structure in ferroelectrics and the possibility of a small domain wall shifts can contribute to observed macroscopic values of ϵ_{33}^E , s_{66}^E and d_{36} of multidomain samples. For example, the effective permittivity of a ferroelectric crystal below the transition temperature can be regarded as composed of two contributions:

$$\epsilon^{\text{eff}} = \epsilon_{\text{s.d.s.}} + \Delta\epsilon_w,$$

where $\epsilon_{\text{s.d.s.}}$ is the permittivity of the single domain sample and the $\Delta\epsilon_w$ contribution of the displacements of the 180° domain walls. It is suitable to assume that $\epsilon_{\text{s.d.s.}}$ fulfils the *Curie-Weiss law* (10). The similar domain wall shifts in ferroelastics contributes to the value of elastic compliance s_{66}^E at a constant electric field. Moreover the extrinsic piezoelectricity Δd_w is assumed if the sample is simultaneously spontaneously polarized and deformed.

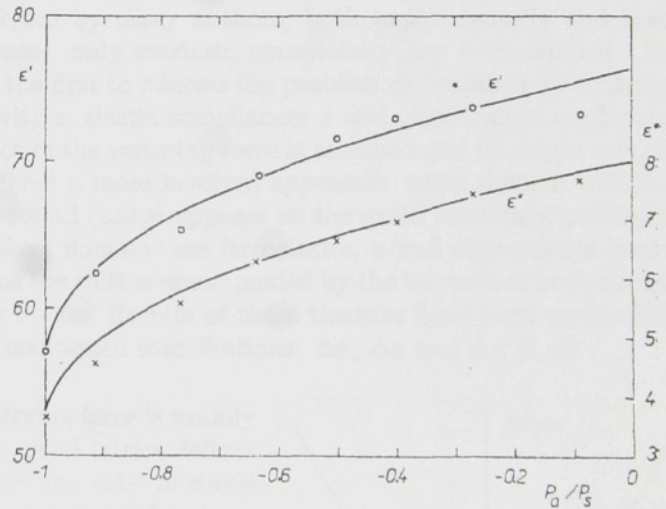


FIGURE 8: Measurements of the complex permittivity of BaTiO_3 single crystal (Meitzer [4]).

The question of existence of $\Delta\epsilon_w$ has been discussed many times in the literature. One of the first works was [1] discussing the aging of ferroelectrics and [2, 3] with the frequency dependencies of permittivity. Fousek was one of the first who proposed the method for determining the exact value of $\Delta\epsilon_w$ [5] in barium titanate single crystal: The existence of $\Delta\epsilon_w$ would be apparent if the permittivity ϵ is an increasing function of area of the 180° domain walls. This method is particularly based on measurements of Meitzler and Stadler [4]. Fig. 8 shows the two dependencies

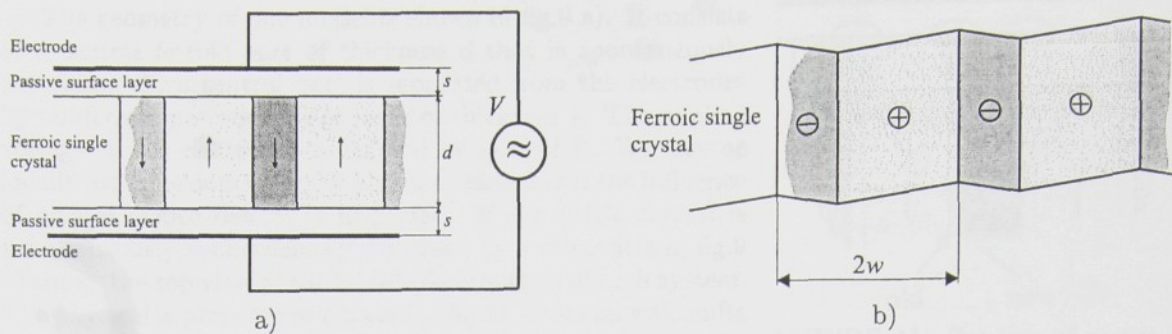


FIGURE 9: Geometry of the surface layer model a) side view, b) top view

of real and imaginary part of permittivity as a function of ratio of average polarization of the sample P_a to spontaneous polarization P_S . The permittivity reaches to its minimum, when the sample is single domain and $P_a/P_S = -1$. Situation when $P_a/P_S = 0$ is connected with the highest number of domain walls and the permittivity reaches to its maximum. Contributions of small domain walls shifts to macroscopic properties are often referred to as *extrinsic contributions*.

Surface layer model

The most interesting question is: "How we can explain disagreement of theoretically predicted temperature dependencies of ϵ_{33}^E , s_{66}^E and d_{36} with experimental data measured on multidomain samples?" This problem 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.[8] were the first to address the problem of domain wall contributions to all involved properties: permittivity ϵ , 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 [9] 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 of all three mentioned contributions: $\Delta\epsilon$, Δs and Δd [8, 9].

In single crystals, the origin of the restoring force is usually connected with domain wall pinning on crystal lattice defects (see fig.10). Other origin of restoring force can exist in single crystalline samples. The idea of *model of a passive surface layer* or, shortly *surface layer model* is introduced in this work. The restoring force acting on domain walls and the resulting extrinsic contributions can be calculated using this model. In fact, the influence of 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.

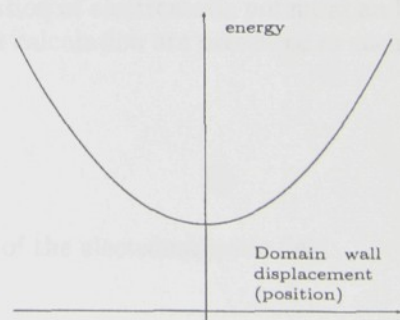


FIGURE 10: The condition for extrinsic contribution – the existence of restoring force

The geometry of one model is shown in fig.9 a). It consists of a central ferroic part of thickness d that is spontaneously polarized. This central part is separated from the electrodes by nonferroic passive surface layer of thickness s . The applied voltage on the electrodes is denoted by symbol V . We assume ideally movable domain walls of zero thickness and the influence of crystal lattice defects is neglected. If the single crystal is simultaneously spontaneously deformed by a shear strain, fig.9 b) shows the top view of the typical deformation of such system. The physical aspects are illustrated in fig.11. Domain wall shifts create regions of electrical and mechanical mismatch near the *old* and *new* domain wall positions on the interface of the central ferroic part and the surface layer (see dashed ovals in the fig.11). This mismatch is connected with a high increase of both electric and elastic energies and this is the source of restoring force (see fig.10). Our task is to calculate explicitly the spatial distribution of electric field and the spatial distribution of elastic stress caused by the shift of the domain wall. On the base of these electric fields and mechanical stresses and by integration over the volume of the sample we calculate the electrostatic and elastic energy and thus the restoring force acting on the domain wall. Then we are able to determine the domain wall shifts contributions to relative permittivity ϵ_{33}^E , elastic compliance s_{66}^E and piezoelectric coefficient d_{36} .

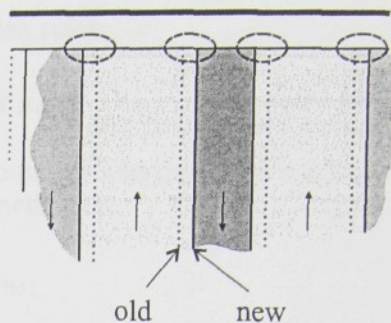


FIGURE 11: Sources of restoring forces due to increase of electric and mechanical energies

Mathematical approach

However, our model seems to be simple, the correct mathematical approach is very complicated. We have to solve the Maxwell equations for electric potential in the surface layer and the central ferroic part. Also the Lamé equations for the vector of mechanical displacement have to be solved. We can also include the intrinsic piezoelectric effect into our considerations. It is possible to solve the system of partial differential equations with the system of boundary and transition conditions analytically, but the resulting formulae become very complicated and cannot be easily published.

We give exact mathematical formulations of boundary problems for systems of partial differential equations in following three subsections. The first mathematical model was used to calculate the electrostatic potential in articles A to F. The second mathematical model was used to determine the spatial distribution of components of vector of mechanical displacement in article F. The intrinsic piezoelectric effect was taken into consideration in the last mathematical model. The numerical results of the last one is published in the article G.

However, we don't present the concrete procedures of the solution of electrostatic potential and the vector of mechanical displacement in detail, the results of our calculation are presented in each article or in its comment.

Ferroelectric samples

The system of *Maxwell equations* sets the fundamental features of the electromagnetic field:

$$\begin{aligned} \operatorname{div} \mathbf{E} &= \frac{\rho}{\epsilon_0}, & \operatorname{div} \mathbf{B} &= 0, \\ \operatorname{rot} \mathbf{E} &= -\frac{\partial \mathbf{B}}{\partial t}, & \operatorname{rot} \mathbf{B} &= \mu_0 \mathbf{j} + \frac{1}{c^2} \frac{\partial \mathbf{E}}{\partial t}. \end{aligned} \quad (15)$$

System of partial differential equations (15) enables one to express vector fields $\mathbf{E}$, $\mathbf{B}$ as function of scalar potential φ and vector potential $\mathbf{A}$. Using relations $\operatorname{div} \mathbf{B} = 0$, $\operatorname{rot} \mathbf{E} = 0$ and using

principles of vector analysis it is easy to obtain the transformation rules:

$$\mathbf{E} = -\text{grad } \varphi - \frac{\partial \mathbf{A}}{\partial t}, \quad \mathbf{B} = \text{rot } \mathbf{A}.$$

The system of partial differential equations with the system of boundary and transition conditions can be derived using these fundamental equations of electromagnetic field.

1. We have to solve the system of *anisotropic Laplace equations*:

$$\begin{aligned} \varepsilon_1^{(1)} \frac{\partial^2 \varphi^{(1)}}{\partial x_1^2} + \varepsilon_3^{(1)} \frac{\partial^2 \varphi^{(1)}}{\partial x_3^2} &= 0, \\ \varepsilon_1^{(2)} \frac{\partial^2 \varphi^{(2)}}{\partial x_1^2} + \varepsilon_3^{(2)} \frac{\partial^2 \varphi^{(2)}}{\partial x_3^2} &= 0, \\ \varepsilon_1^{(1)} \frac{\partial^2 \varphi^{(3)}}{\partial x_1^2} + \varepsilon_3^{(1)} \frac{\partial^2 \varphi^{(3)}}{\partial x_3^2} &= 0. \end{aligned} \quad (16)$$

2. The continuity of electric potential φ must be fulfilled:

$$\begin{aligned} \varphi^{(1)}|_{x_3=\frac{d}{2}+s} &= -\frac{V}{2}, & \varphi^{(1)}|_{x_3=\frac{d}{2}} &= \varphi^{(2)}|_{x_3=\frac{d}{2}}, \\ \varphi^{(2)}|_{x_3=-\frac{d}{2}} &= \varphi^{(3)}|_{x_3=-\frac{d}{2}}, & \varphi^{(3)}|_{x_3=-\frac{d}{2}-s} &= \frac{V}{2}. \end{aligned} \quad (17)$$

3. The condition can be easily expressed for tangential components of electric field on the planar interface of central ferroic part and the surface layer:

$$E_t^{(1)} - E_t^{(2)} = 0.$$

We can transform the preceeding rule to conditions for electric potential:

$$\begin{aligned} \frac{\partial \varphi^{(1)}}{\partial x_1} \Big|_{x_3=\frac{d}{2}+s} &= 0, & \frac{\partial \varphi^{(1)}}{\partial x_1} \Big|_{x_3=\frac{d}{2}} &= \frac{\partial \varphi^{(2)}}{\partial x_1} \Big|_{x_3=\frac{d}{2}}, \\ \frac{\partial \varphi^{(2)}}{\partial x_1} \Big|_{x_3=-\frac{d}{2}} &= \frac{\partial \varphi^{(3)}}{\partial x_1} \Big|_{x_3=-\frac{d}{2}}, & \frac{\partial \varphi^{(1)}}{\partial x_1} \Big|_{x_3=-\frac{d}{2}-s} &= 0. \end{aligned} \quad (18)$$

4. The next condition (*Gauß's theorem*)

$$D_n^{(1)} - D_n^{(2)} = \sigma_f, \quad (19)$$

where σ_f is free charge surface density on the interface of the central ferroelectric part and the surface layer, lead to transition condition:

$$\varepsilon_0 \varepsilon_3^{(2)} \frac{\partial \varphi^{(2)}}{\partial x_3} \Big|_{x_3=\frac{d}{2}} = \varepsilon_0 \varepsilon_3^{(1)} \frac{\partial \varphi^{(1)}}{\partial x_3} \Big|_{x_3=\frac{d}{2}} + P_0(x_1) + \sigma_f^{(1)}(x_1), \quad (20)$$

$$\varepsilon_0 \varepsilon_3^{(1)} \frac{\partial \varphi^{(3)}}{\partial x_3} \Big|_{x_3=-\frac{d}{2}} = \varepsilon_0 \varepsilon_3^{(2)} \frac{\partial \varphi^{(2)}}{\partial x_3} \Big|_{x_3=-\frac{d}{2}} - P_0(x_1) + \sigma_f^{(3)}(x_1), \quad (21)$$

where

$$\sigma_f^{(1)}(x_1) = -\sigma_f^{(3)}(x_1)$$

are *screening charges* — partial compensation of bound charges due to finite small conductivity of surface layers separating the electrodes and the sample.

5. The additional conditions can be derived from symmetry resp. antisymmetry considerations using *Laplace-Fourier transformation*. These conditions allow us to find the solution of

electrostatic potential more effectively. The periodicity and the symmetry of the model with respect to planes $x_1 = 0$ and $x_1 = w$ lead to important rules:

$$\left. \frac{\partial \varphi}{\partial x_1} \right|_{x_1=0} = 0, \quad \left. \frac{\partial \varphi}{\partial x_1} \right|_{x_1=w} = 0. \quad (22)$$

The equally important feature of electrostatic potential leading from the antisymmetry of the model with respect to plane $x_3 = 0$ is given by rule

$$\varphi(x_1, x_3) = -\varphi(x_1, -x_3), \text{ if we put } \varphi(x_1, 0) = 0. \quad (23)$$

Ferroelastic samples

The mechanical interaction of central spontaneously deformed part with the passive surface layers is considered to be one of the sources as a source of restoring force. For simplicity, we approximate the elastically anisotropic material by elastically isotropic one. Then the elastic stiffness tensor can be expressed in a very compact form

$$c_{ijkl} = \lambda \delta_{ij} \delta_{kl} + \mu (\delta_{ik} \delta_{jl} + \delta_{il} \delta_{jk}), \quad (24)$$

where λ, μ are so called *Lamè coefficients*. Mechanical properties are described by equations for stress tensor components.

$$\tau_{ij} = \lambda \delta_{ij} (\vartheta - \vartheta_0) + 2\mu (e_{ij} - e_{0,ij}), \quad (25)$$

where

$$\vartheta = \frac{\partial u_i}{\partial x_i} = e_{11} + e_{22} + e_{33} = \text{div } \vec{u}. \quad (26)$$

The system of partial differential equations for vector of mechanical displacement components can be derived from *differential conditions of equilibrium*

$$\frac{\partial \tau_{ij}}{\partial x_j} + F_i = 0 \quad \text{for } i, j = 1, 2, 3 \quad (27)$$

and using definition of strain tensor

$$e_{ij} = \frac{1}{2} \left(\frac{\partial u_i}{\partial x_j} + \frac{\partial u_j}{\partial x_i} \right). \quad (28)$$

Using equations (25, 27, 28) we can form the following system of *Lamè equations*

$$\frac{\partial}{\partial x_i} (\lambda \vartheta) + \sum_{j=1}^3 \frac{\partial}{\partial x_j} \left[\mu \left(\frac{\partial u_i}{\partial x_j} + \frac{\partial u_j}{\partial x_i} \right) \right] = -F_i + 2 \frac{\partial}{\partial x_i} (\lambda \vartheta_0) + 2 \sum_{j=1}^3 \frac{\partial}{\partial x_j} (\mu e_{0,ij}). \quad (29)$$

It is easy to show that $\vartheta_0 = e_{0,11} + e_{0,22} + e_{0,33} = 0$. Also cumbersome calculations lead to condition $\vartheta = 0$ and then equation (29) could be further simplified.

We have to solve the system of partial differential equations. The conditions for vector of mechanical displacement are summarized in the following paragraphs.

1. Mechanical displacements components u_i satisfy the *Laplace-Poisson equations*:

$$\Delta u_i^{(1)} = 0 \quad \text{on } \Omega^{(1)}, \quad (30)$$

$$\Delta u_i^{(2)} = 2 \frac{\partial e_0}{\partial x_j} \quad \text{on } \Omega^{(2)}, \quad (31)$$

$$\Delta u_i^{(3)} = 0 \quad \text{on } \Omega^{(3)}, \quad (32)$$

where $i = 1, 2, 3$.

2. We have to distinguish boundary conditions for clamped and free sample.

(a) The following boundary conditions must be fulfilled in the case of *clamped sample*:

$$u_i \Big|_{x_1=0} = 0 \quad \text{for } i = 1, 2, 3, \quad (33)$$

$$u_i \Big|_{x_1=l} = u_{l,i} \quad \text{for } i = 1, 2, 3 \quad (34)$$

and

$$u_i \Big|_{x_3=\pm(\frac{d}{2}+s)} = \frac{x_1}{l} u_{l,i}, \quad \text{where } i = 1, 2, 3. \quad (35)$$

(b) The relatively simple boundary conditions can be written for mechanically *free sample* (without electrodes)

$$u_i \Big|_{x_1=0} = 0 \quad \text{pro } i = 1, 2, 3, \quad (36)$$

$$\lim_{l \rightarrow \infty} \frac{\partial u_1}{\partial x_1} \Big|_{x_1=l} = 0, \quad (37)$$

$$\lim_{l \rightarrow \infty} \frac{\partial u_2}{\partial x_1} \Big|_{x_1=l} = \frac{\tau_{\text{ext}}}{\mu} + 2 e_{0,12}, \quad (38)$$

$$\lim_{l \rightarrow \infty} \frac{\partial u_3}{\partial x_1} \Big|_{x_1=l} = 0. \quad (39)$$

Moreover,

$$\frac{\partial u_i}{\partial x_3} \Big|_{x_3=\pm(\frac{d}{2}+s)} = 0. \quad (40)$$

3. The continuity of the vector of mechanical displacement components should be fulfilled

$$u_i^{(1)} \Big|_{x_3=\frac{d}{2}} = u_i^{(2)} \Big|_{x_3=\frac{d}{2}}, \quad \text{where } i = 1, 2, 3, \quad (41)$$

$$u_i^{(2)} \Big|_{x_3=\frac{d}{2}} = u_i^{(3)} \Big|_{x_3=-\frac{d}{2}}, \quad \text{where } i = 1, 2, 3, \quad (42)$$

4. The mechanical forces equilibrium conditions on the interface of the central ferroic part and the surface layers leads to the following conditions:

$$\mu^{(1)} \frac{\partial u_i^{(1)}}{\partial x_3} \Big|_{x_3=\frac{d}{2}} = \mu^{(2)} \frac{\partial u_i^{(2)}}{\partial x_3} \Big|_{x_3=\frac{d}{2}}, \quad \text{where } i = 1, 2, 3, \quad (43)$$

$$\mu^{(2)} \frac{\partial u_i^{(2)}}{\partial x_3} \Big|_{x_3=-\frac{d}{2}} = \mu^{(3)} \frac{\partial u_i^{(3)}}{\partial x_3} \Big|_{x_3=-\frac{d}{2}}, \quad \text{where } i = 1, 2, 3, \quad (44)$$

5. Using *elastic Green's functions* the following conditions, that reflect the periodicity of the sample and the symmetry of the sample with respect to planes $x_1 = 0$ resp. $x_1 = w$ can be expressed in form:

$$\frac{\partial u_i^{(1)}}{\partial x_1} \Big|_{x_1=0} = \frac{\partial u_i^{(1)}}{\partial x_1} \Big|_{x_1=w} = 0, \quad \text{where } i = 1, 2, 3, \quad (45)$$

$$\frac{\partial u_i^{(2)}}{\partial x_1} \Big|_{x_1=0} = \frac{\partial u_i^{(2)}}{\partial x_1} \Big|_{x_1=w} = 0, \quad \text{where } i = 1, 2, 3, \quad (46)$$

$$\frac{\partial u_i^{(3)}}{\partial x_1} \Big|_{x_1=0} = \frac{\partial u_i^{(3)}}{\partial x_1} \Big|_{x_1=w} = 0, \quad \text{where } i = 1, 2, 3. \quad (47)$$

6. The last condition follows from the symmetry of the sample with respect to the $x_3 = 0$ plane:

$$\frac{\partial u_i^{(2)}}{\partial x_3} \Big|_{x_3=0} = 0, \quad \text{where } i = 1, 2, 3. \quad (48)$$

Piezoelectric ferroic samples

A similar boundary problem for the system of partial differential equations can describe the situation, when the ferroic sample (*without* passive surface layer) of thickness d is provided with relatively thick metal electrodes of thickness s . Then we shall approximate the material of a ferroic phase by equations of state

$$D_i = P_{0,i} + \varepsilon_0 \varepsilon_{ik}^T E_k + d_{ikl} \tau_{kl}, \quad (49)$$

$$e_{ij} = e_{0,ij} + d_{kij} E_k + s_{ijkl}^E \tau_{kl}. \quad (50)$$

Using transformation rules, the equations of state (49, 50) could be written in the form:

$$D_i = P_{0,i} + \varepsilon_0 \varepsilon_{ik}^E E_k + d_{imn} c_{mnkl}^E (e_{kl} - e_{0,kl}), \quad (51)$$

$$\tau_{ij} = -d_{kmn} c_{mni}^E E_k + c_{ijkl}^E (e_{kl} - e_{0,kl}). \quad (52)$$

Substituting equations (51, 52) into *Gauß's theorem* (19) and *differential conditions of equilibrium* (27) we obtain the system of four partial differential equations

$$-\varepsilon_0 \varepsilon_{ik}^E \frac{\partial^2 \varphi}{\partial x_k \partial x_i} + d_{imn} c_{mnkl}^E \frac{\partial^2 u_k}{\partial x_i \partial x_l} = -\frac{\partial P_{0,i}}{\partial x_i} + d_{imn} c_{mnkl}^E \frac{\partial e_{0,kl}}{\partial x_i}, \quad (53)$$

$$d_{kmn} c_{mni}^E \frac{\partial^2 \varphi}{\partial x_k \partial x_j} + c_{ijkl}^E \frac{\partial^2 u_k}{\partial x_j \partial x_l} = -F_i + c_{ijkl}^E \frac{\partial e_{0,kl}}{\partial x_j}. \quad (54)$$

If we approximate the orthorhombic anisotropy of the ferroic phase by the tetragonal anisotropy of the parent phase and substitute the values of components of elastic stiffness tensor, piezoelectric coefficients and the relative permittivities to equations (53, 54) we get the system of partial differential equations, that can be solved analytically.

1. The electrostatic potential is constant

$$\varphi^{(1)} \equiv -\frac{V}{2}, \quad \varphi^{(3)} \equiv \frac{V}{2}.$$

in the metal electrodes. The system of partial differential equations for vector of mechanical displacement of the electrodes reduces to:

$$\begin{aligned} c_{e,11} \frac{\partial^2 u_1^{(1)}}{\partial x_1^2} + c_{e,44} \frac{\partial^2 u_1^{(1)}}{\partial x_3^2} + (c_{e,13} + c_{e,44}) \frac{\partial^2 u_3^{(1)}}{\partial x_1 \partial x_3} &= 0, \\ c_{e,66} \frac{\partial^2 u_2^{(1)}}{\partial x_1^2} + c_{e,44} \frac{\partial^2 u_2^{(1)}}{\partial x_3^2} &= 0, \\ c_{e,44} \frac{\partial^2 u_3^{(1)}}{\partial x_1^2} + c_{e,33} \frac{\partial^2 u_3^{(1)}}{\partial x_3^2} + (c_{e,13} + c_{e,44}) \frac{\partial^2 u_1^{(1)}}{\partial x_1 \partial x_3} &= 0. \end{aligned} \quad (55)$$

The similar system of partial differential equations can be written for the electrostatic potential and the vector of mechanical displacement of the bulk:

$$\begin{aligned} \varepsilon_0 \varepsilon_{11}^s \frac{\partial^2 \varphi^{(2)}}{\partial x_1^2} + \varepsilon_0 \varepsilon_{33}^s \frac{\partial^2 \varphi^{(2)}}{\partial x_3^2} - 4(d_{14} c_{b,44}^E + d_{36} c_{b,66}^E) \frac{\partial^2 u_2^{(2)}}{\partial x_1 \partial x_3} &= 0, \\ c_{b,11} \frac{\partial^2 u_1^{(2)}}{\partial x_1^2} + c_{b,44} \frac{\partial^2 u_1^{(2)}}{\partial x_3^2} + (c_{b,13} + c_{b,44}) \frac{\partial^2 u_3^{(2)}}{\partial x_1 \partial x_3} &= 0, \\ c_{b,66} \frac{\partial^2 u_2^{(2)}}{\partial x_1^2} + c_{b,44} \frac{\partial^2 u_2^{(2)}}{\partial x_3^2} + 4(d_{14} c_{b,44}^E + d_{36} c_{b,66}^E) \frac{\partial^2 \varphi^{(2)}}{\partial x_1 \partial x_3} &= 2 c_{b,66}^E e'_{0,12}(x_1), \\ c_{b,44} \frac{\partial^2 u_3^{(2)}}{\partial x_1^2} + c_{b,33} \frac{\partial^2 u_3^{(2)}}{\partial x_3^2} + (c_{b,13} + c_{b,44}) \frac{\partial^2 u_1^{(2)}}{\partial x_1 \partial x_3} &= 0. \end{aligned} \quad (56)$$

This system of partial differential equations must be completed by the system of boundary and transition conditions.

2. We have the only one boundary condition for electrostatic potential of the bulk:

$$\varphi^{(2)}|_{x_3=\frac{d}{2}} = -\frac{V}{2}, \quad \varphi^{(2)}|_{x_3=-\frac{d}{2}} = \frac{V}{2}. \quad (57)$$

3. We assume that electrodes are free of stress

$$\begin{aligned} \frac{\partial u_3^{(1)}}{\partial x_1} \Big|_{x_3=\frac{d}{2}+s} + \frac{\partial u_1^{(1)}}{\partial x_3} \Big|_{x_3=\frac{d}{2}+s} &= 0, \\ \frac{\partial u_2^{(1)}}{\partial x_3} \Big|_{x_3=\frac{d}{2}+s} &= 0, \\ c_{e,13}^E \frac{\partial u_1^{(1)}}{\partial x_1} \Big|_{x_3=\frac{d}{2}+s} + c_{e,33}^E \frac{\partial u_3^{(1)}}{\partial x_3} \Big|_{x_3=\frac{d}{2}+s} &= 0 \end{aligned} \quad (58)$$

and similarly for the opposite electrode.

4. The continuity of the vector of mechanical displacement components must be fulfilled according to the conditions (41, 42).
5. The equilibrium conditions on the interface of the electrodes and the central ferroic part lead to following equations:

$$\begin{aligned} c_{e,44}^E \frac{\partial u_3^{(1)}}{\partial x_1} \Big|_{x_3=\frac{d}{2}} + c_{e,44}^E \frac{\partial u_1^{(1)}}{\partial x_3} \Big|_{x_3=\frac{d}{2}} &= c_{b,44}^E \frac{\partial u_3^{(2)}}{\partial x_1} \Big|_{x_3=\frac{d}{2}} + c_{b,44}^E \frac{\partial u_1^{(2)}}{\partial x_3} \Big|_{x_3=\frac{d}{2}}, \\ c_{e,44}^E \frac{\partial u_2^{(1)}}{\partial x_3} \Big|_{x_3=\frac{d}{2}} &= c_{e,44}^E \frac{\partial u_2^{(1)}}{\partial x_3} \Big|_{x_3=\frac{d}{2}} + 4c_{e,44}^E d_{14} \frac{\partial \varphi^{(2)}}{\partial x_1} \Big|_{x_3=\frac{d}{2}}, \\ c_{e,13}^E \frac{\partial u_1^{(1)}}{\partial x_1} \Big|_{x_3=\frac{d}{2}} + c_{e,33}^E \frac{\partial u_3^{(1)}}{\partial x_3} \Big|_{x_3=\frac{d}{2}} &= c_{b,13}^E \frac{\partial u_1^{(2)}}{\partial x_1} \Big|_{x_3=\frac{d}{2}} + c_{b,33}^E \frac{\partial u_3^{(2)}}{\partial x_3} \Big|_{x_3=\frac{d}{2}}. \end{aligned} \quad (59)$$

and similarly for the second interface.

6. Aspects of symmetries of the model lead to the same conditions as (45-48). The influence of external stresses should be expressed by conditions (33-35).

The classical *Fourier method* is used to solve preceeding three boundary problems. Lengthy but very straightforward calculations lead to solution in form of Fourier series.

Outline of presented publications

In this section we give a brief overview of presented publications.

The articles A, C and the poster D give the results of our investigation of equilibrium domain structures. The analytical approximation and exact numerical results of the equilibrium domain width is presented as well as the response of the domain structure to the small external electric field. The influence of the sample thickness and the effect of the surface layer thickness is discussed.

The article B gives the information about the extrinsic contribution to relative permittivity. The effect of surface layer thickness to value of $\Delta\epsilon_w$ are discussed.

The extrinsic contribution to piezoelectric coefficient is presented in the article E.

The article F represents further development of our surface layer model. The mechanical interaction between the central ferroic part and the passive surface layer is included into our considerations. Extrinsic contributions to all three physical properties are calculated.

At last, the article G answers the very interesting question: "How the electrode thickness can affect the observations of relative permittivity, elastic compliances and the piezoelectric coefficients?" The intrinsic piezoelectric effect is considered. The exact numerical results of extrinsic contributions to all three properties are presented as a functions of the sample thickness and the electrode thickness. This makes interesting suggestions for new experiments.

Collection of Publications

Paper A

Response of Domain Structures in Electroded Ferroelectrics to External Electric Field

Poster presented at the Czech-Polish seminar on structure phase transitions. Liblice 1998.

Published in the proceedings of the Seminar.

RESPONSE OF DOMAIN STRUCTURES IN ELECTRODED FERROELECTRICS TO EXTERNAL ELECTRIC FIELD

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Abstract

Macroscopic properties of ferroelectric samples, including those in form of thin films, are, to large extent, influenced by their domain structure. In this paper electric potential and free energy are calculated for a plate-like sample composed of nonferroelectric surface layer and ferroelectric central part with antiparallel domains. The sample is provided with electrodes with a defined potential difference. The effect of applied field and its small changes on the resulting domain structure is discussed. This makes it possible to determine the restoring force acting on domain walls which codetermines dielectric and piezoelectric properties of the sample. Calculations of the potential and free energy take into account interactions of opposite surfaces and are applicable also to thin films or to samples at temperatures close to the phase transition.

A.1. INTRODUCTION

This work presents a generalization of our recent investigations of equilibrium domain patterns in thin ferroelectric films ^[A1]. The basic motivation is theoretical interpretation of latest experimental investigation of extrinsic contribution to elastic, dielectric and piezoelectric properties of RbH_2PO_4 crystals in a broad temperature range under transition temperature ^[A2] in a Liberec-Wien cooperation. A record values of d_{36} piezoelectric coefficients ($\sim 10^4$ pC/N) were measured, caused probably by domain walls response (displacement) to external electric field. In fact, the situation in thin films with the thickness $d < d_{crit} = 4\pi\sigma_w\epsilon_0\epsilon_z^{3/2}/P_0^2\epsilon_x^{1/2}$ is similar to that one under transition temperature, because $d_{crit} \rightarrow \infty$ if $T \rightarrow T_{tr}$ ^[A1]. Domain walls response was first investigated by Fedosov and Sidorkin ^[A3]. We hope, our approach is more general, because it is applicable to thin films and to temperature near the transition one and avoids some problems with convergency. Nevertheless it is simplified by neglecting the elastic interactions (see ^[A5]) and considering the wall and depolarization energy only. We also neglect the effect of crystal defects.

A.2. GEOMETRY, VARIABLES AND ENERGY OF THE SYSTEM

We consider a plate-like electroded sample of infinite area (see Fig.A.1) with major surfaces perpendicular to ferroelectric axis z . Between the central ferroelectric part with antiparallel domains (2.) and the electrodes (0.), (4.), these are two surface layers without any spontaneous polarization (1.) and (3.) $\equiv$ (1.)

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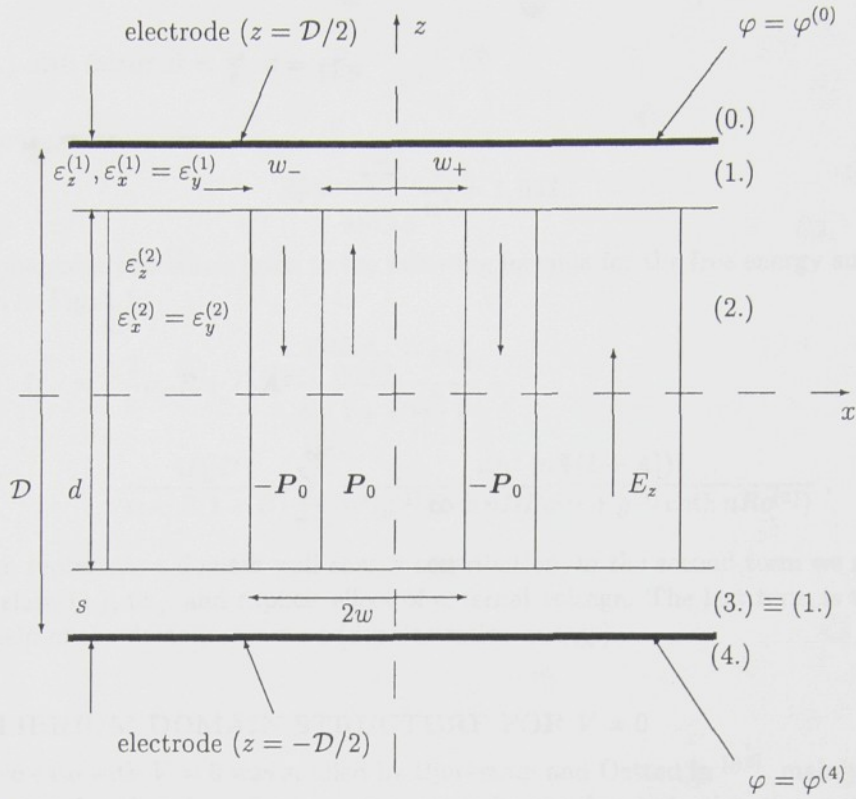


FIGURE A.1: Geometry of the Model

External parameters

- potential difference on electrodes : $V = \varphi^{(4)} - \varphi^{(0)}$
- external electric field : $E_z^{ext} = \frac{V}{D}$
- temperature T

Material parameters

- spontaneous polarization in (2.) region : P_0
- relative permittivities $\epsilon_x^{(1),(2)} = \epsilon_y^{(1),(2)}$, $\epsilon_z^{(1),(2)}$
(we assume linear relation $D_i = \epsilon_0 \epsilon_{ij} E_j + P_{0i}$ in (2.))

$$c^{(1),(2)} = \sqrt{\frac{\epsilon_x^{(1),(2)}}{\epsilon_z^{(1),(2)}}},$$

$$g^{(1),(2)} = \sqrt{\epsilon_x^{(1),(2)} \epsilon_z^{(1),(2)}}$$

- wall energy density σ_w [J/m²]
- free energy of the system per unit area of the plate surface U [J/m²]

Geometrical parameters (see Fig.A.1)

- domain pattern shape factor $R = \pi \frac{d}{2w}$
- asymmetry factor $A = \frac{w_+ - w_-}{w_+ + w_-}$

- (1.), (3.) slab factor $B = \frac{2s}{d}$, $d = \frac{\mathcal{D}}{1+B}$

Mathematical parameters

$$S_0 = \sum_{n=1,3,5}^{\infty} \frac{1}{n^3} \doteq 1,052.$$

A rather cumbersome procedure leads to the following formula for the free energy surface density of the system in Fig.A.1:

$$\begin{aligned} U = & \frac{2}{\pi} \sigma_w R + P_0 A \frac{\frac{B \mathcal{D} P_0 A}{2 \varepsilon_z^{(1)} (1+B)} - \varepsilon_0 \frac{V}{2}}{\varepsilon_0 \left(1 + B \frac{\varepsilon_z^{(2)}}{\varepsilon_z^{(1)}} \right)} + \\ & + \frac{4 P_0^2 \mathcal{D}}{\varepsilon_0 \pi^2 R (1+B)} \sum_{n=1}^{\infty} \frac{\sin^2 \left(n \frac{\pi}{2} (1+A) \right)}{n^3 (g^{(1)} \coth n B R c^{(1)} + g^{(2)} \coth n R c^{(2)})}. \end{aligned} \quad (\text{A.1})$$

The first term represents a domain wall energy contribution, in the second term we recognize the effect of the slabs (1.), (3.) and explicit effect of external voltage. The last term is the energy of the electric field of the domain structure (depolarization energy).

A.3. EQUILIBRIUM DOMAIN STRUCTURE FOR $V = 0$

A more simple case with $V = 0$ was studied by Bjorkstam and Oetted in ^[A6], mainly in the thick sample approximation $d \gg d_{crit}$. Their exact formula for the depolarization energy seems to be a bit different form (A.1). A phenomenological approach to this problem was presented in ^[A7] by Wang et. all, but with no regard to electrodes and isolating slabs (1.), (3.).

In the case of zero external field, equilibrium domain pattern is symmetric : $A_{eq}^0 = 0$. Equilibrium value of the shape factor R_{eq}^0 can be found by numerical methods. For $B R c^{(1)} \gg 1$ and $R c^{(2)} \gg 1$ (in fact for the thick sample $d > d_{crit}$), following result is valid

$$R_{eq}^0 = \frac{\sqrt{2 S_0} P_0}{\sqrt{\varepsilon_0 \pi (1+B) (g^{(1)} + g^{(2)}) \sigma_w}} \sqrt{\mathcal{D}}. \quad (\text{A.2})$$

This leads to formula for domain width

$$w_+ = w_- = w_{eq}^0 = \frac{1}{P_0} \left[\frac{\pi^3 \varepsilon_0 (g^{(1)} + g^{(2)}) \sigma_w}{8 S_0 (1+B)} \right]^{1/2} \sqrt{\mathcal{D}}. \quad (\text{A.3})$$

Formulae (A.2) and (A.3) are simple generalizations of that for the case with no electrodes and no isolating slabs ^[A1].

A.4. RESPONSE TO EXTERNAL ELECTRIC FIELD

Naturally, external field has primary effect on the asymmetry A , strong fields effect also R . We have done a numerical calculations of $A_{eq}(V)$ and $R_{eq}(V)$ for arbitrary chosen parameters $P_0 = 0,2 \text{ Cm}^{-2}$, $\sigma_w = 5 \cdot 10^{-3} \text{ Jm}^{-2}$, $B = 0,08$, $c^{(1)} = 1$, $g^{(1)} = 10$, $c^{(2)} = 5$, $g^{(2)} = 100$, $V = 12 \text{ V}$, and different $\mathcal{D}$ (see Tab.A.1). The value of d_{crit} for this special values of the parameters is $\sim 10^{-10} \text{ m}$. If $A \ll 1$, $B R c^{(1)} \gg 1$, $R c^{(2)} \gg 1$, we can approximate the $A_{eq}(V)$ as

$$A_{eq}(V) = \frac{\varepsilon_0 V}{2 P_0 \mathcal{D} \left[\frac{B}{\varepsilon_z^{(1)} (1+B)} - \frac{2 \ln 2}{R_0 (1+B) (g^{(1)} + g^{(2)})} \left(1 + B \frac{\varepsilon_z^{(2)}}{\varepsilon_z^{(1)}} \right) \right]}. \quad (\text{A.4})$$

The same approximation leads to the formula for $R_{eq}(V)$

$$R_{eq}(V) = R_{eq}^0 \sqrt{1 - \frac{\pi^2 (A_{eq}(V))^2 \ln 2}{4 S_0}}. \quad (\text{A.5})$$

$\mathcal{D}$	$A_{eq}(V)$	$R_{eq}(V)(1+B)$
10 nm	$\rightarrow 1$	$\rightarrow 0$
100 nm	0,19	17
1 μm	0,018	55
10 μm	0,0018	173
100 μm	0,00018	550

TABLE A.1: Numerical values of $A_{eq}(V)$ and $R_{eq}(V)(1+B)$ for special values of parameters $P_0, \sigma_w, B, c^{(1),(2)}, g^{(1),(2)}$ and V .

Electric field has substantial effect if E_z^{ext} is so high, that $A_{eq}(V) > 0,2$. Naturally, if the walls are pinned by crystal defects, the action of the formula (A.5) is questionable, but we hope that small deformations of the walls can be in average approximately described by the formula (A.4). For the parameters, chosen for our numerical calculations, (A.4) is in excellent agreement with numerical results for $\mathcal{D}$ from 100 μm to 100 nm. In this region, effect of voltage V on R is negligible and (A.2) is also in agreement with numerical results.

A.5. DISCUSSION

On the basis of our results, we can find the displacement of domain walls in linear response to the external field (formula (A.4)). From this, we can deduce the extrinsic contributions to dielectric permittivity and piezoelectric coefficients. Because of our approximations, we can probably get only qualitative agreement with experiment, but we can discuss a role of different parameters ($\mathcal{D}, B, R, \varepsilon_{x,z}$) using formulae (A.2)-(A.5). Numerical and analytical calculations for RbH_2PO_4 under transition temperature are in progress.

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Comment

This article was the first of our series of publications concerning with equilibrium domain structures and extrinsic contributions to macroscopic material constants in electroded multidomain samples. The Maxwell equations were solved for electric potential in the sample:

$$\varphi^{(1)}(x, z) = \frac{sP_0 A - \varepsilon_0 \varepsilon_3^{(1)} \frac{V}{2}}{\varepsilon_0 (\varepsilon_3^{(1)} + \varepsilon_3^{(2)} B)} \cdot \frac{(D-2z)}{2s} - \frac{V(z - \frac{d}{2})}{2s} + \quad (A.6)$$

$$+ \sum_{n=1}^{\infty} \frac{4P_0 w}{\varepsilon_0 n^2 \pi^2} \cdot \frac{\sin^2 n\pi \frac{A+1}{2} \cos nx \frac{\pi}{w}}{g^{(1)} \coth nBRc^{(1)} + g^{(2)} \coth nRc^{(2)}} \cdot \frac{\sinh nc^{(1)} \frac{\pi}{w} (\frac{D}{2} - z)}{\sinh nBRc^{(1)}},$$

$$\varphi^{(2)}(x, z) = \frac{sP_0 A - \varepsilon_0 \varepsilon_3^{(1)} \frac{V}{2}}{\varepsilon_0 (\varepsilon_3^{(1)} + \varepsilon_3^{(2)} \frac{2s}{d})} \cdot \frac{2z}{d} + \quad (A.7)$$

$$+ \sum_{n=1}^{\infty} \frac{4P_0 w}{\varepsilon_0 n^2 \pi^2} \cdot \frac{\sin^2 n\pi \frac{A+1}{2} \cos nx \frac{\pi}{w}}{g^{(1)} \coth nBRc^{(1)} + g^{(2)} \coth nRc^{(2)}} \cdot \frac{\sinh nc^{(2)} z \frac{\pi}{w}}{\sinh nRc^{(2)}}.$$

Formulae for the electrostatic potential (A.6, A.7) were expressed using dimensionless parameters A , B and R (see pg. 25). Values of these parameters unambiguously describe the configuration of the domain structure. Graphic representation of electric potential is shown in fig. 12. There a half of a symmetric (neutral) domain structure period (x axis) in absence of external electric field is drawn. There is a ferroelectric domain with a spontaneous polarization vector oriented in z axis direction in the centre of the drawing. There is the discontinuous change of the first order derivative with respect to z on the interface of the central ferroic part and the passive surface layer. It represents the existence of uncompensated bound charges due to discontinuous change of spontaneous polarization.

By integration over the unit volume of the sample we obtained the formula for the free energy of the sample (A.1). The equilibrium domain structure for shorted electrodes was calculated in section A.3. The partial derivative with respect to asymmetry coefficient A equals zero for $A = 0$ and $V = 0$. This means that width of neighbouring domains is equal one to each other. The equilibrium domain width

$$w_{eq}^0 = \frac{\pi D}{2R_{eq}^0(1+B)}$$

can be easily calculated. The value of equilibrium parameter R_{eq}^0 is given by expression (A.2)

After application of the voltage V on the electrodes the domain wall shifts by

$$\Delta l = \frac{w}{2} A_{eq}(V).$$

The calculation of equilibrium parameters $A_{eq}(V)$ and $R_{eq}(V)$ is described in section A.4. We have used a significant approximation to obtain the analytical results for dependencies of $R_{eq}^0(D)$, $A_{eq}(V)$ and $R_{eq}(V)$. Formulae (A.2)-(A.5) are valid in situation of *narrow domains* ($w \ll s, d$). It is possible to show that the value of equilibrium parameter $R_{eq}^0(D)$ is monotonously increasing function of the thickness of the ferroelectric sample. Table A.1 shows several values of $R_{eq}^0(D)$ for given thicknesses of the sample. It is shown that domain structure period become very small with respect to the thickness of the sample for sufficiently "thick" samples $d > d_{crit}$, where d_{crit} can be found in section A.1. Then our approximations are correct.

We found a mistake in classical work [12] of Bjorkstam and Oettel. Their formula for electrostatic potential doesn't satisfy the boundary and transition conditions. Nevertheless this mistake doesn't affect the acceptable conclusions of their calculations.

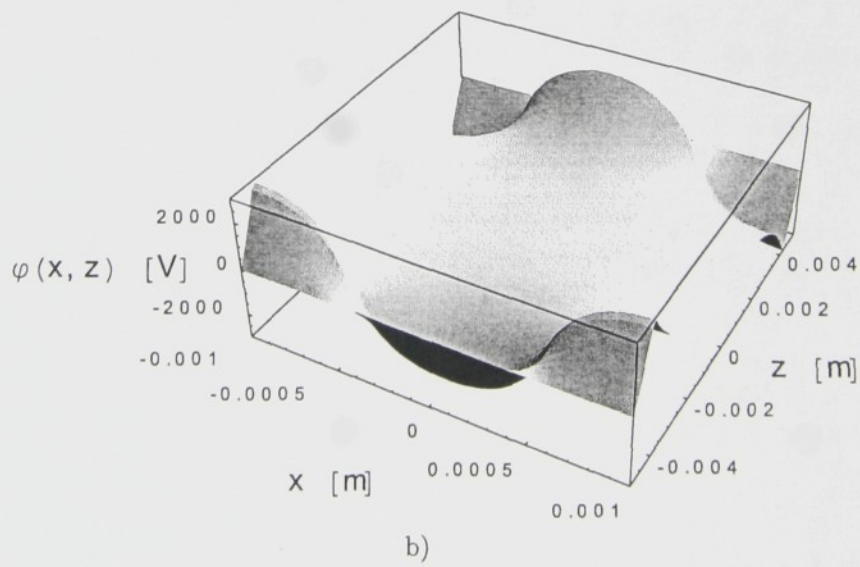
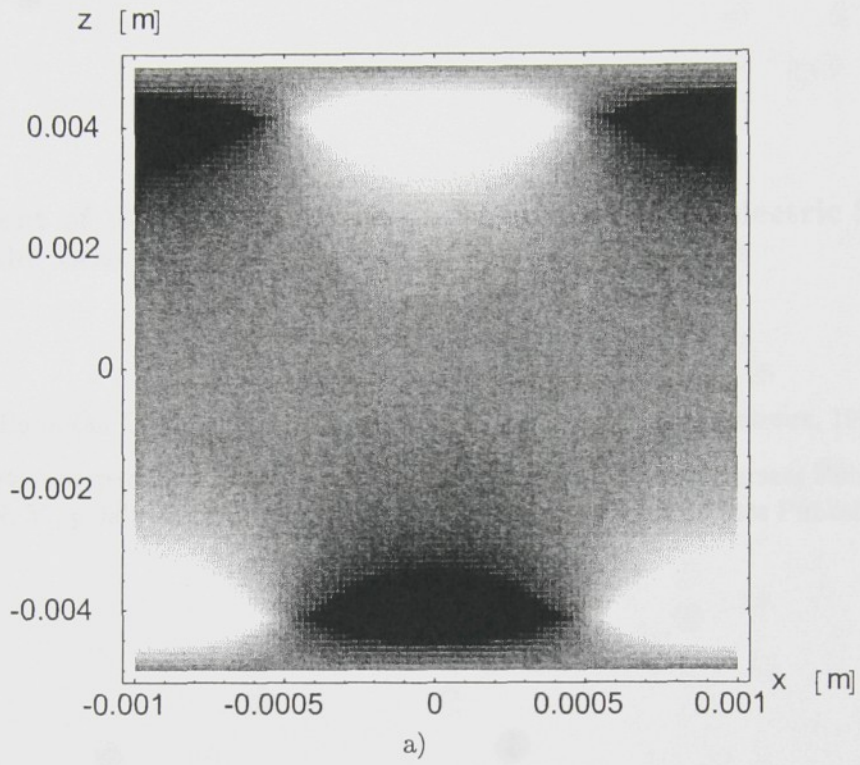


FIGURE 12: Graphic representation of electric potential: $\epsilon_z^{(1)} = 100$, $\epsilon_z^{(2)} = 100$, $\epsilon_x^{(1)} = 10$, $\epsilon_x^{(2)} = 10$, $A = 0$, $V = 0$, $P_0 = 4 \cdot 10^2 \text{ C m}^{-2}$.

Paper B

Displacement of 180° Domain Walls in Electroded Ferroelectric Single Crystals: the Effect of Surface Layers on Restoring Force

Poster at the European Conference on Applications of Polar Dielectrics, Montreux, 1998.

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DISPLACEMENTS OF 180° DOMAIN WALLS IN ELECTRODED FERROELECTRIC SINGLE CRYSTALS: THE EFFECT OF SURFACE LAYERS ON RESTORING FORCE³

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Abstract

Macroscopic properties of ferroelectric samples, including those in form of thin films, are, to large extent, influenced by their domain structure. In this paper the free energy is calculated for a plate-like sample composed of nonferroelectric surface layers and ferroelectric central part with antiparallel domains. The sample is provided with electrodes with a defined potential difference. The effect of applied field and its small changes on the resulting domain structure is discussed. This makes it possible to determine the restoring force acting on domain walls which codetermines dielectric and piezoelectric properties of the sample. Calculations of the potential and free energy take into account interactions of opposite surfaces and are applicable also to thin films.

Keywords: Ferroelectric domains; extrinsic contributions to permittivity

B.1. INTRODUCTION

It is known that samples of ferroelectric single crystals often possess a surface layer whose properties differ from those of the bulk. It may be a layer produced during the growth of a crystalline plate or produced during the preparation of a plate-like sample. Many observations gave evidence to the fact that such a layer is either nonferroelectric or does not take part in the switching process of the internal part; in any case its permittivity is believed to differ from that of a homogeneous sample in the ferroelectric phase. Its existence is expected to greatly influence macroscopic properties of bulk samples^[B1,2,3,4] as well as of thin films.^[B5] In this paper two such consequences are investigated. First we reconsider the problem of equilibrium domain structure in a ferroelectric sample possessing a surface layer, previously discussed by Bjorkstam and Oettel.^[B6] Second, we evaluate the restoring force acting on 180° domain walls due to the layer; this will make it possible to estimate the extrinsic contributions to permittivity, piezoelectric coefficients and elastic compliances of a ferroelectric sample. Investigations of crystals of the KDP family revealed the existence of huge wall contributions to these properties.^[B7,8]

In previous papers on a related subject^[B2], depolarizing field was considered as the source of energy which slows down the motion of a single domain wall in a dc electric field, as the wall departs from its original position by substantial distances. In contrast to such models we investigate very small deviations of walls forming a regular domain pattern.

B.2. GEOMETRY, VARIABLES AND ENERGY OF THE SYSTEM

We consider a plate-like electroded sample of infinite area with major surfaces perpendicular to the ferroelectric axis z . Central ferroelectric part with antiparallel domains (2.) is separated from the electrodes (0.), (4.) by nonferroelectric layers (1.), (3.) (see Fig. B.1). The spatial distribution of the electric field E is determined by the applied potential difference $V = \varphi^{(4)} - \varphi^{(0)}$ and by the

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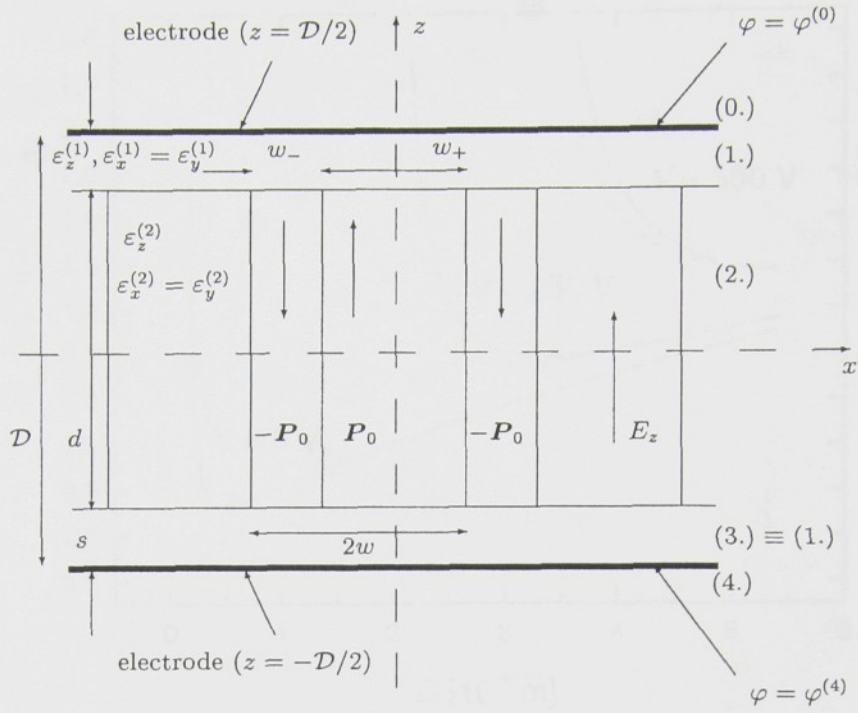


FIGURE B.1: Geometry of the model

bound charge $\text{div} \mathbf{P}_0$ on the boundary of ferroelectric material, where $\mathbf{P}_0$ stands for spontaneous polarization. Geometrical, electrical and material parameters of the system are shown in Fig. B.1. We further introduce the symbols

$$c^{(1),(2)} = \sqrt{\frac{\epsilon_x^{(1),(2)}}{\epsilon_z^{(1),(2)}}}, \quad g^{(1),(2)} = \sqrt{\epsilon_x^{(1),(2)} \epsilon_z^{(1),(2)}}, \quad S_0 = \sum_{n=1,3,5}^{\infty} \frac{1}{n^3} \doteq 1.052$$

and several geometrical parameters:

$$B = \frac{2s}{d}$$

the domain pattern factor

$$R = \pi \frac{d}{2w}, \quad 2w = w_+ + w_-$$

and the asymmetry factor

$$A = \frac{w_+ - w_-}{w_+ + w_-}.$$

The ferroelectric material itself is approximated by the equation of state

$$D_i = \epsilon_0 \epsilon_{ij} E_j + P_{0i} \quad (\text{B.1})$$

where only the component P_{0z} is nonzero. This linear approximation limits the validity of our calculations to the temperature region not very close below the transition temperature T_c . Domain walls are assumed to have surface energy density σ_w and zero thickness.

The total free energy of the system includes the domain wall energy and the electrostatic energy whose density is $(1/2) \mathbf{E} \cdot (\mathbf{D} - \mathbf{P}_0)$. First, Laplace equations have to be solved for electric potentials in the bulk and in the surface layers, fulfilling the requirement of potential continuity as well as conditions of continuity of normal components of $\mathbf{D}$ and tangential components of $\mathbf{E}$. A rather cumbersome calculation leads to the following formula for total free energy surface density (in

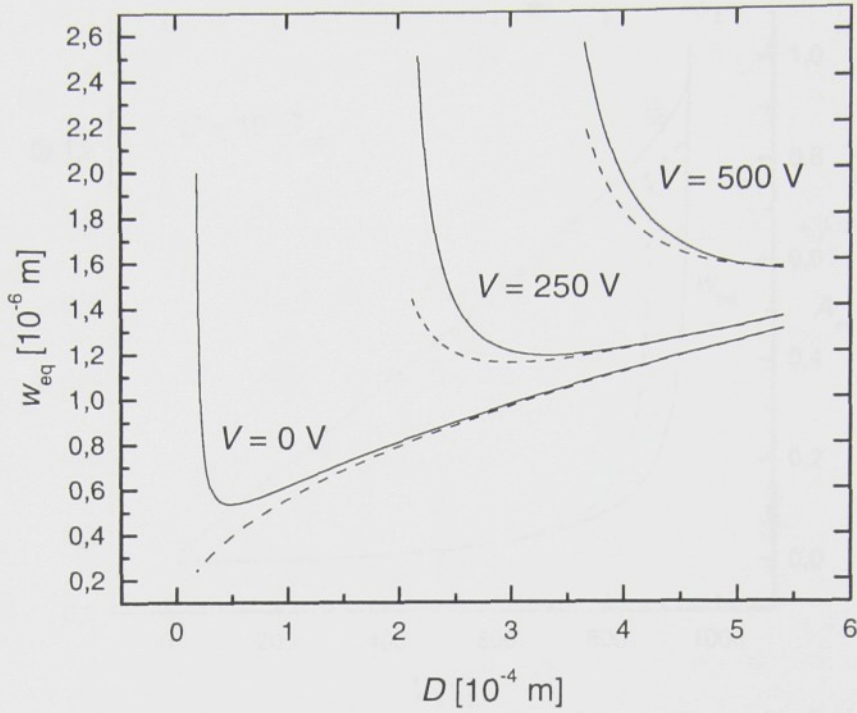


FIGURE B.2: Exact numerical (full lines) and approximate (dashed lines) results for $w_{\text{eq}}(D)$ at different values of potential difference V and $B = 0.02$.

J m^{-2}) of the system:

$$\begin{aligned}
 F = & \frac{2}{\pi} \sigma_w R + P_0 A \frac{\frac{B D P_0 A}{2 \varepsilon_z^{(1)} (1+B)} - \varepsilon_0 \frac{V}{2}}{\varepsilon_0 \left(1 + B \frac{\varepsilon_z^{(2)}}{\varepsilon_z^{(1)}} \right)} + \\
 & + \frac{4 P_0^2 D}{\varepsilon_0 \pi^2 R (1+B)} \sum_{n=1}^{\infty} \frac{\sin^2 \left(n \frac{\pi}{2} (1+A) \right)}{n^3 (g^{(1)} \coth n B R c^{(1)} + g^{(2)} \coth n R c^{(2)})} . \quad (\text{B.2})
 \end{aligned}$$

The first term represents domain wall contribution while the last one is the depolarization energy. In the second term we recognize the effect of layers (1.) and (3.) and of the applied voltage.

Let us compare expression with formulae deduced and used in previous papers. For $V = 0$ and $s \rightarrow \infty$, $\varepsilon_x^{(1)} = \varepsilon_z^{(1)} = 1$ and $A = 0$ the system goes over into an isolated ferroelectric plate with “neutral” domain structure, placed in vacuum. In this case the equation (B.2) reduces to the expression given by Kopal et al.^[B9] for ferroelectric plates of finite thickness in which the interaction of the two surfaces is accounted for. If the plate is thick this interaction can be neglected and Eq. (B.2) simplifies to the classical formula of Mitsui and Furuichi^[B10] (cf. Eq. (9) in Ref. [9]) which is often used to determine the value σ_w from the observed width of domain patterns. Finally, in the limit of $V = 0$ our formula (B.2) should converge to the expression deduced by Bjorkstam and Oettel.^[B6] In fact this is not the case and it appears that the electric displacement as expressed in Ref. [6] does not satisfy all boundary conditions.

B.3. EQUILIBRIUM DOMAIN STRUCTURE FOR $V = 0$

If the system is short-circuited, the equilibrium domain pattern is symmetric, i.e. $A_{\text{eq}} = 0$. The shape factor R_{eq}^0 and from it also the value of w_{eq}^0 can be found by numerical methods. As an example, the full lines in Fig. B.2 shows the $w_{\text{eq}}(D)$ dependence at constant d/s and different values of potential difference V . As it was shown in the previous paper^[B9], the critical thickness d_{crit} can be defined so that for $d \gg d_{\text{crit}}$ the interaction energy of sample surfaces can be neglected. Then

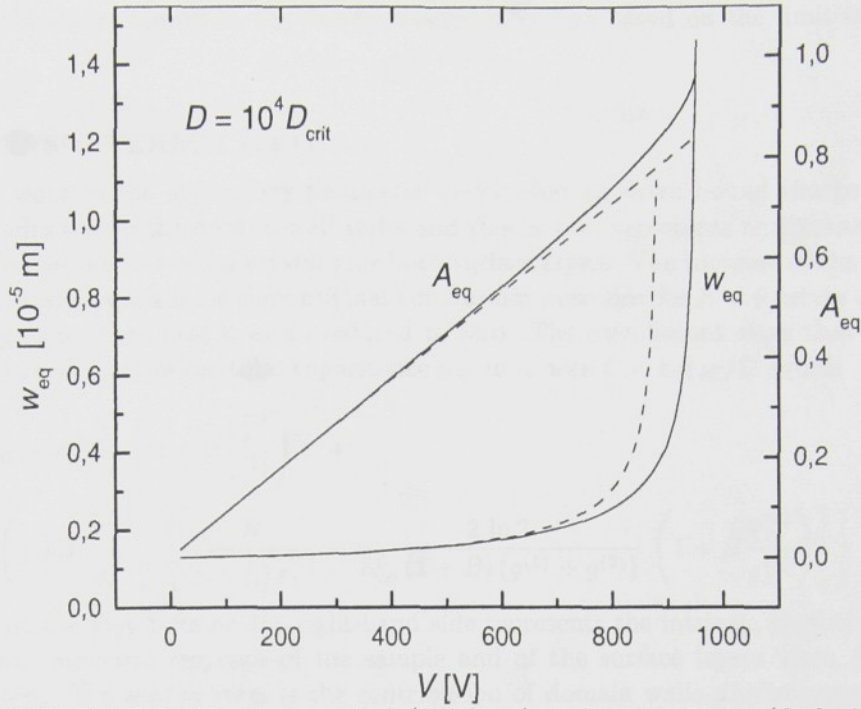


FIGURE B.3: Exact numerical (full lines) and approximate (dashed lines) results for $w_{eq}(V)$ and $A_{eq}(V)$ at $B = 0.02$ and $D = 10^4 D_{crit}$.

the minimum energy occurs for

$$w_{eq}^0 = \frac{1}{P_0} \left[\frac{\pi^3 \epsilon_0 (g^{(1)} + g^{(2)}) \sigma_w}{8 S_0 (1 + B)} \right]^{1/2} \sqrt{D}. \quad (B.3)$$

and the dependence $w_{eq}^0(D)$ in this approximation is shown by a dashed line with $V = 0$ V in the Fig. B.2. The approximate results in the Fig. B.2 with $V = 250$ V and $V = 500$ V are based on Eqs. (B.4) and (B.5). In these numerical calculations we have used the following values which roughly apply to crystals of RbH_2PO_4 below the transition temperature: $P_0 = 5.7 \times 10^{-2} \text{ C m}^{-2}$, $\epsilon_x^{(2)} = 10$, $\epsilon_z^{(2)} = 100$, $d_{crit} = 5.4 \times 10^{-8} \text{ m}$. The value $\sigma_w = 5 \times 10^{-3} \text{ J m}^{-2}$ is often considered typical for ferroelectrics. For simplicity we put $\epsilon_x^{(1)} = \epsilon_x^{(2)}$, $\epsilon_z^{(1)} = \epsilon_z^{(2)}$.

B.4. RESPONSE OF DOMAIN STRUCTURE TO EXTERNAL ELECTRIC FIELD

When an external potential difference V is applied, the asymmetry parameter becomes nonzero and at the same time the period $w = (w_+ + w_-)/2$ changes. Both these quantities can be found again by determining the minimum of F given by Eq. (B.2) numerically. Full lines in Fig. B.3 demonstrate both these dependencies for the following numerical values: $B = 0.02$, $D = 10^4 D_{crit} = 10^4 (1 + B) d_{crit}$. Starting from a certain applied voltage the period w grows very fast with increasing V . To discuss the macroscopic properties of the sample such as permittivity, the dependence $A_{eq}(V)$ is more important. We recognize that in a considerable region of the applied voltage this dependence is almost linear.

The $A_{eq}(V)$, $w_{eq}(V)$ resp. $R_{eq}(V)$ dependence can be approximated by an explicit formula if the following inequalities are satisfied: $A \ll 1$, $B R c^{(1)} \gg 1$ and $R c^{(2)} \gg 1$. Then it holds

$$A_{eq}(V) \cong \frac{\epsilon_0 V}{2 P_0 D \left[\frac{B}{\epsilon_z^{(1)} (1 + B)} - \frac{2 \ln 2}{R_{eq}^0 (1 + B) (g^{(1)} + g^{(2)})} (1 + B \frac{\epsilon_z^{(2)}}{\epsilon_z^{(1)}}) \right]} \quad (B.4)$$

$$R_{eq}(V) \cong R_{eq}^0 \sqrt{1 - \frac{\pi^2 (A_{eq}(V))^2 \ln 2}{4 S_0}}. \quad (B.5)$$

These approximations, shown in Fig.B.3 by dashed lines, are based on the limit of the sum in Eq. (B.2).

B.5. EXTRINSIC PERMITTIVITY

The nonzero value of the asymmetry parameter means that an extra bound charge is deposited on the electrodes due to the domain wall shifts and this in turn represents an increase of effective permittivity of the whole system crystal plus both surface layers. The increase of the electrostatic energy when domain walls leave their original equilibrium positions for $E \neq 0$ serves as the source of a restoring force when field is again reduced to zero. The calculations show that the effective permittivity ϵ_{eff} defined by the total capacitance per unit area $C = \epsilon_0 \epsilon_{\text{eff}} / D$ equals

$$\epsilon_{\text{eff}} = \epsilon_z^{(2)} \frac{D}{d} \left(1 + B \frac{\epsilon_z^{(2)}}{\epsilon_z^{(1)}} \right)^{-1} + \left\{ \left(1 + B \frac{\epsilon_z^{(2)}}{\epsilon_z^{(1)}} \right) \left[\frac{B}{(1+B)\epsilon_z^{(1)}} - \frac{2 \ln 2}{R_{\text{eq}}^0 (1+B)(g^{(1)} + g^{(2)})} \left(1 + B \frac{\epsilon_z^{(2)}}{\epsilon_z^{(1)}} \right) \right] \right\}^{-1} \quad (\text{B.6})$$

In this formula the first term on the right-hand side represents the intrinsic part of permittivity, given by linear dielectric response of the sample and of the surface layers when domain walls are kept at rest. The second term is the contribution of domain walls displacement to effective permittivity, often referred to as extrinsic part of permittivity.

B.6. DISCUSSION

Numerous data are available on domain wall contributions to permittivity in single crystals of ferroelectrics and also on extrinsic contributions to piezoelectric coefficients in ferroelectrics which are simultaneously ferroelastic. Our calculations indicate that depolarizing energy can be an effective source of restoring force whose existence is a condition for such contributions. In fact since the model assumes a regular system of planar domain walls, it is suitable in particular for ferroelastic ferroelectrics such as crystals of the KDP family in which a dense pattern of 180° domains is known to exist.^[B11,12] It was found that in a wide temperature range below the Curie point of crystals of RbH_2PO_4 and deuterated KDP, the piezoelectric coefficient d_{36} is greatly enhanced compared to its expected value for single domain samples.^[B13] Recently, this was confirmed by simultaneous measurements of permittivity ϵ_3 , elastic compliance s_{66} and piezoelectric coefficient d_{36} of RbH_2PO_4 . A thorough discussion of d_{36} in this case will be the subject of a forthcoming paper Kopal et al.. Here we comment on the extrinsic part of ϵ_3 . For simplicity, let us assume that $\epsilon_x^{(1)} \cong \epsilon_x^{(2)} \equiv \epsilon_x$ and $\epsilon_z^{(1)} \cong \epsilon_z^{(2)} \equiv \epsilon_z$. This is not an unreasonable assumption since the assumed surface layer for KDP-type samples can be supposed to have a similar chemical composition as the bulk. Then the extrinsic part of Eq. (B.6) reduces to

$$\left(\frac{B}{\epsilon_z} - \frac{\ln 2 (1+B)}{R_{\text{eq}}^0 \sqrt{\epsilon_z \epsilon_x}} \right)^{-1}.$$

Numerically, the second term in the brackets represents a small correction to the first term when approximations (B.4) and (B.5) are valid. If it is neglected, we obtain as an approximation

$$\epsilon_{z,\text{extrinsic}} \cong \frac{\epsilon_z}{B} = \epsilon_z \frac{d}{2s}. \quad (\text{B.7})$$

This shows that a very thin surface layer can lead to a considerable extrinsic enhancement of permittivity. Nevertheless, the simple implication: $s \rightarrow 0 \Rightarrow \epsilon_{z,\text{extrinsic}} \rightarrow \infty$ is not correct, because the assumptions needed for validity of (B.4), (B.5), (B.6) and (B.7) are violated if s is small enough.

A more general formulation of the restoring force can be used to calculate the extrinsic part of d_{36} for the same geometry of domains. In a recent paper^[B14] Sidorkin deduced the dispersion law

of wall contributions to permittivity, however, in his treatment the existence of a surface layer is not explicitly considered.

It was shown beyond any doubt that small motions of 90° domain walls are responsible for a considerable enhancement of permittivity ϵ_3 and piezoelectric coefficients d_{31} , d_{33} in poled ferroelectric ceramics.^[B15,16] One of the sources of the restoring force responsible for these wall contributions is the elastic energy at grain boundaries.^[B17] Since these boundaries may differ in chemical composition from the bulk of grains^[B18], surface layers can be expected to form so that the mechanism proposed in the present paper may also play a role in ceramic samples.

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Comment

The theory based on the surface layer model was proposed for estimation of extrinsic contribution to relative permittivity.

Sections B.2-B.4 show the preceeding results of our investigation of equilibrium domain structure. The comparison is drawn for exact numerical results and analytical approximations of equilibrium domain width, resp. domain structure period, and asymmetry coefficient in fig. B.2 and fig. B.3.

The section B.5 gives the analytical approximations for effective value of relative permittivity "along" the ferroelectric axis (see formula (B.7)). The effect of passive surface layer on the value of relative permittivity is discussed. It is necessary to stress that calculation of limit $s \rightarrow 0$ is not valid since the condition for correctness of analytical approximations are violated.

The applicability of our results should be also noted. Fig. 13 shows the temperature dependencies of ϵ_{33} for a given frequency f of an oscillatory electric field for DKDP. The domain wall shifts contributions are apparent for frequencies less than 30 MHz. On the other hand the influence of domain wall motions to macroscopic physical properties vanish for frequencies greater than 1 GHz. The limited movability of domain walls in a real samples is the reason for vanishing of extrinsic contributions. Also the equilibrium domain structure is not formed when the high-frequency fields are applied on the sample. Sidorkin [13] deduced the dispersion law for extrinsic contributions, however, the existence of surface layer is not explicitly considered in his treatment.

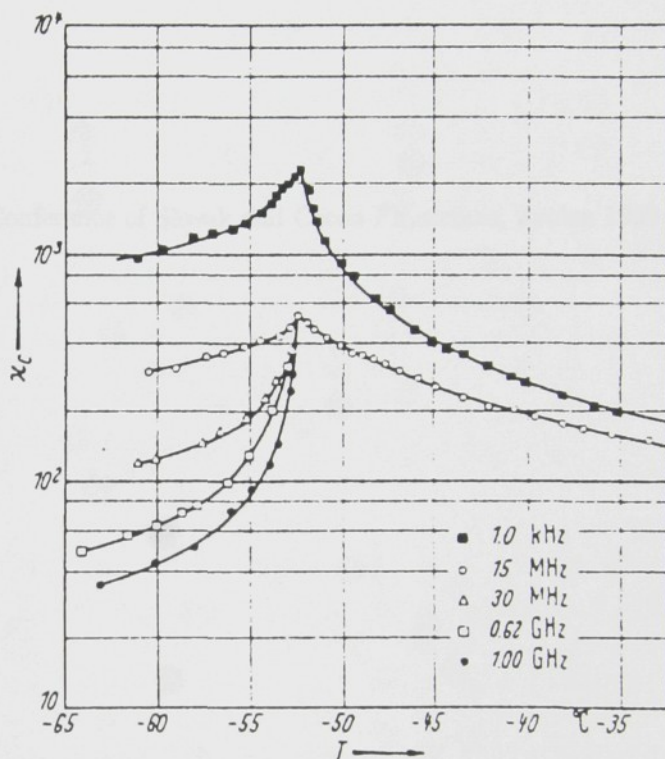


FIGURE 13: Temperature dependencies of relative permittivity for KD_2PO_4 (DKDP) single crystal. Parameter is a frequency f (see [15])

The change of the domain structure period is also questionable (see fig. B.3). The formula (B.5) should not be interpreted as increasing of the domain structure period $w_{eq}(V) = \pi D / (2R_{eq}(V) (1 + B))$ when sufficiently high external field is applied. The domain wall pinning to crystal lattice defects is the more important effect. The formula (B.5) describes the domain structure period which would be formed if the external field is applied during ferroelectric phase transition.

Exact Calculations of the Equilibrium Domain Structure Response to External Electric Field

Article version

Article in the Proceedings of the 13th Conference of Slovak and Czech Physicists, Zvolen 1999.

1. ÚVOD, GEOMETRIE MODELU

Pracujeme s modelom jednosmerného polarizovaného ferroelektrického materiálu s doménovou štruktúrou. Domény sú predstavené ako oblasti s konštantnou polarizáciou P a sú oddelené od seba vrstvou s nulovou polarizáciou. Tento model je vhodný na štúdium rovnovážnej doménovej štruktúry v závislosti od vonkajšieho elektrického poľa. V práci sa zaoberáme s výpočtom rovnovážnej doménovej štruktúry pre dané vonkajšie elektrické pole. Výsledky sú porovnané s experimentálnymi údajmi.

$$P = \frac{2\epsilon_0}{\pi} \frac{A}{B} \quad A = \frac{\epsilon_0}{\epsilon_1 + \epsilon_2} \quad B = \frac{\epsilon_1 + \epsilon_2}{\epsilon_1 - \epsilon_2}$$

Číslo ϵ_1 je permitivita vzduchu ($\epsilon_1 = 1$), číslo ϵ_2 je permitivita materiálu. Číslo A je koeficient závislosti od vonkajšieho elektrického poľa. Číslo B je koeficient závislosti od vonkajšieho elektrického poľa. Číslo P je polarizácia materiálu.

2. PRINCÍPY VÝPOČTU ODSZVY DOMÉNOVÉ STRUKTÚRY

Pracujeme s modelom jednosmerného polarizovaného ferroelektrického materiálu s doménovou štruktúrou. Domény sú predstavené ako oblasti s konštantnou polarizáciou P a sú oddelené od seba vrstvou s nulovou polarizáciou. Tento model je vhodný na štúdium rovnovážnej doménovej štruktúry v závislosti od vonkajšieho elektrického poľa. V práci sa zaoberáme s výpočtom rovnovážnej doménovej štruktúry pre dané vonkajšie elektrické pole. Výsledky sú porovnané s experimentálnymi údajmi.

$$P = \frac{2\epsilon_0}{\pi} \frac{A}{B} \quad A = \frac{\epsilon_0}{\epsilon_1 + \epsilon_2} \quad B = \frac{\epsilon_1 + \epsilon_2}{\epsilon_1 - \epsilon_2}$$

EXAKTNÍ VÝPOČTY ROVNOVÁŽNÉ REAKCE DOMÉNOVÉ STRUKTURY FEROELEKTRIKA NA VNĚJŠÍ ELEKTRICKÉ POLE

EXACT CALCULATIONS OF THE EQUILIBRIUM FERROELECTRIC DOMAIN STRUCTURE RESPONSE TO EXTERNAL ELECTRIC FIELD

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Abstract

Práce je prvním přiblížením v teoretickém vyšetřování reakce doménových stěn na vnější pole. Uvažuje ideálně pohyblivé 180° stěny, není započtena mechanická interakce složek systému – vzorku, elektrod a izolujících mezivrstev. Uvažuje se vliv částečného stínění polarizačního náboje. Výsledky platí i pro tenké vrstvy.

A theory of equilibrium response of a ferroelectric domain structure to external field is presented. Ideally moveable 180° domain walls are considered, mechanical interactions of the components of the system – sample, electrodes and surface layers are not taken into account. Effect of partial screening of polarization charges is discussed. Results are valid also for thin films.

Klíčová slova: doménová struktura, tenké vrstvy.

C.1. ÚVOD, GEOMETRIE MODELU

Studovaná reakce podstatně ovlivňuje dielektrické a elektromechanické vlastnosti feroelektrik. Pohyb doménových stěn je příčinou tzv. vnějších (extrinsic) příspěvků k permitivitě, elastickým a piezoelektrickým koeficientům. Tyto příspěvky jsou v poslední době intenzívně experimentálně zkoumány např. v [C1,2]. Exaktní výpočty studované odezvy jsou založeny na vztahu pro hustotu volné energie systému, viz obr.1, tvořeného centrální spontánně polarizovanou deskovou doménovou strukturou (2), izolujícími mezivrstvami (1,3), elektrodami (0,4) a zdrojem napětí velikosti V . Označení geometrických a materiálových parametrů je zřejmé z obr.1. Dále zavedeme parametry

$$B = \frac{2s}{d} \quad A = \frac{w_+ - w_-}{w_+ + w_-}.$$

Předpokládáme, že v počátečním symetrickém ($A = 0$) stavu je polarizační náboj plošné hustoty $\pm P_0$ částečně stíněn opačným nábojem plošné hustoty $\mp aP_0$, kde a je koeficient stínění $0 \leq a < 1$. Při rychlých posuvech doménových stěn se stínící náboje nestačí přemístit, v dlouhodobé rovnováze naopak kopíruje stínění doménovou strukturu.

C.2. PRINCIPY VÝPOČTU ODEZVY DOMÉNOVÉ STRUKTURY

Detaily odvození vztahu pro volnou energii jsou uvedeny v práci [C3], pro nulové stínění ($a = 0$) je výsledek uveden v [C4]. Předpokládáme, že rovnovážná struktura minimalizuje volnou energii při daném napětí V . Volné parametry jsou w – půlperioda struktury ve směru osy x a koeficient asymetrie A . Pro dostatečně tlusté vzorky, viz diskuse v [C5], lze nalézt rovnovážné parametry analyticky. Např. pro dlouhodobou statickou rovnováhu, kdy stínění kopíruje doménovou strukturu, platí pro koeficient asymetrie

$$A_{eq}(V) \cong \frac{\varepsilon_0 V}{2(1-a)P_0 \mathcal{D} \left[\frac{B}{\varepsilon_x^{(1)}(1+B)} - X \right]}, \quad (C.1)$$

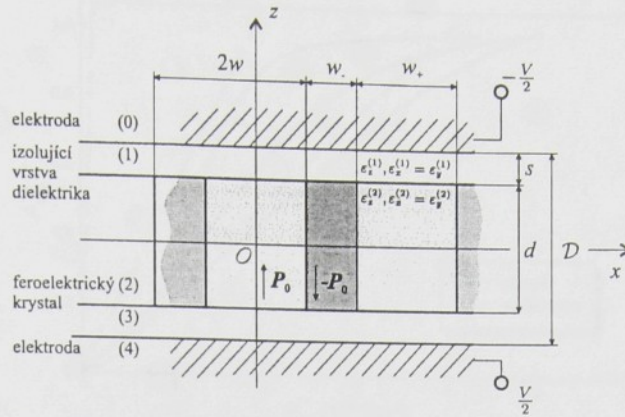


FIGURE C.1: Geometrie modelu

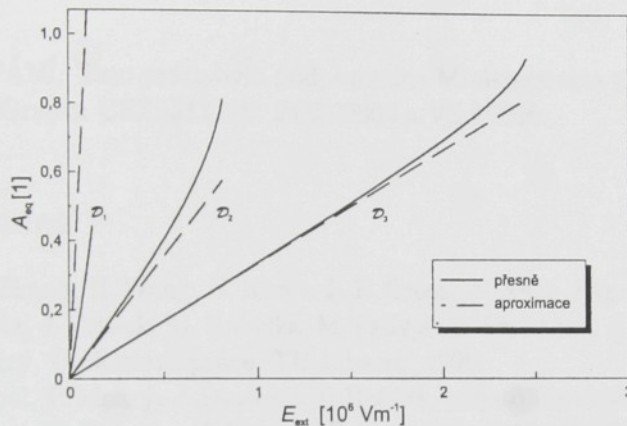


FIGURE C.2: Závislost A_{eq} na vnějším poli pro tři různé tloušťky, ustálený stav.

kde X je malá korekce, závislá na geometrických a materiálových parametrech vzorku viz. [C4]. Pro rychlé změny, kdy stínění zůstává symetrické a nestačí reagovat, platí

$$A_{eq}(V) \cong \frac{\varepsilon_0 V}{2P_0 D \left[\frac{B}{\varepsilon_x^{(1)}(1+B)} - X \right]}. \quad (C.2)$$

Pro daný vzorek lze najít rovnovážné parametry numerickými metodami.

C.3. VÝSLEDKY NUMERICKÝCH A ANALYTICKÝCH VÝPOČTŮ

Obr. 2,3 ukazují výsledky numerických výpočtů: závislost A_{eq} na vnějším poli $E_{ext} = \frac{V}{D}$ pro tři tloušťky $D_1 = 8 \mu\text{m}$, $D_2 = 20 \mu\text{m}$, $D_3 = 200 \mu\text{m}$. Materiál je RbH_2PO_4 , $B = 0,04$, $a = 0,25$. Čárkovaně jsou vyznačeny křivky vycházející z přiblížení (C.1) resp. (C.2). Obr. 2 představuje případ statické rovnováhy, obr. 3 případ relativně rychlých změn kdy stínění zůstává konstantní a symetrické.

C.4. DISKUSE

Přibližné analytické vztahy (C.1), (C.2) vyjadřují lineární odezvu doménové struktury na vnější pole. Přesné numerické výsledky se odlišují od analytických tím více, čím je tloušťka vzorku menší. Pro tenké vzorky je odezva obecně nelineární. Vztahy (C.1), (C.2) upozorňují na úlohu mezivrstvy (koeficient B).

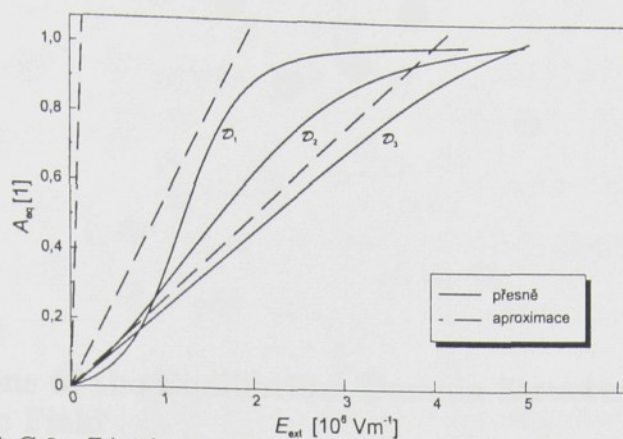


FIGURE C.3: Závislost A_{eq} na vnějším poli při konstantním symetrickém stínění, pro tři různé tloušťky.

PODĚKOVÁNÍ: Tato práce byla podporována Ministerstvem školství, mládeže a tělovýchovy ČR na základě Grantu CEZ: J11/98: 242200002 a VS 96006.

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Paper D

Exact Calculations of the Equilibrium Domain Structure Response to External Electric Field

Poster version

Poster presented at the 13th Conference of Slovak and Czech Physicians, Zvolen 1999.

EXAKTNÍ VÝPOČTY ROVNOVÁŽNÉ REAKCE DOMÉNOVÉ STRUKTURY FEROELEKTRIKA NA VNĚJŠÍ ELEKTRICKÉ POLE

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Abstract

Reakce doménových stěn feroelektrické doménové struktury na vnější elektrické pole podstatně ovlivňuje dielektrické a elektromechanické vlastnosti feroelektrik. Pohyb doménových stěn je základem tzv. vnějších (extrinsic) příspěvků, např. k relativní permitivitě, elastickým koeficientům a piezoelektrickým koeficientům, které často i řádově převyšují vnitřní (intrinsic) příspěvky, dané vlastnostmi jednodoménového vzorku. Vnější příspěvky jsou v poslední době předmětem intenzivního experimentálního výzkumu, viz např. [D1], [D2].

Tato práce je prvním přiblížením v exaktním teoretickém vyšetřování rovnovážné reakce doménových stěn na vnější pole za některých zjednodušujících předpokladů: uvažuje ideálně pohyblivé 180° stěny, vliv defektů krystalové mřížky není započten, neuvažuje mechanickou interakci jednotlivých složek systému (vzorek, elektrody, izolující mezivrstvy). Na druhé straně je vyjádřen efekt částečného stínění polarizačních nábojů v důsledku konečné malé vodivosti mezivrstvy, oddělující elektrody a vzorek a vliv tloušťky této mezivrstvy.

D.1. ÚVOD

Exaktní výpočty rovnovážné reakce doménové struktury na vnější pole jsou založeny na vztahu pro hustotu volné energie systému (viz obr. D.1), tvořeného centrální spontánně polarizovanou deskovou doménovou strukturou (2), izolujícími mezivrstvami (1), (3), elektrodami (0), (4) a zdrojem napětí V . Označení geometrických a materiálových parametrů je zřejmé z obrázku. Dále zavádíme veličiny

$$c^{(1),(2)} = \sqrt{\frac{\varepsilon_x^{(1),(2)}}{\varepsilon_z^{(1),(2)}}}, \quad g^{(1),(2)} = \sqrt{\varepsilon_x^{(1),(2)} \varepsilon_z^{(1),(2)}},$$

$$B = \frac{2s}{d}, \quad R = \pi \frac{d}{2w}, \quad 2w = w_+ + w_-,$$

$$A = \frac{w_+ - w_-}{w_+ + w_-}.$$

Feroelektrický materiál je charakterizován stavovou rovnicí

$$D_i = \varepsilon_0 \varepsilon_{ij} E_j + P_{0i},$$

kde pouze z -složka spontánní polarizace je nenulová a je rovna $\pm P_0$. Plošná hustota energie doménových stěn je označena σ_w . Předpokládáme, že polarizační náboj plošné hustoty $\pm P_0$ je na rozhraní mezivrstvy—feroelektrický vzorek stíněn v důsledku malé konečné vodivosti opačným nábojem plošné hustoty $\mp a P_0$, kde a je koeficient stínění, $0 \leq a < 1$. Při rychlých posuvech doménových stěn se stínící náboj nestačí přemístit, takže koeficient asymetrie doménové struktury A je obecně odlišný od koeficientu asymetrie rozložení stínících nábojů A_c . Při dlouhodobé rovnováze kopíruje stínění doménovou strukturu a platí $A = A_c$.

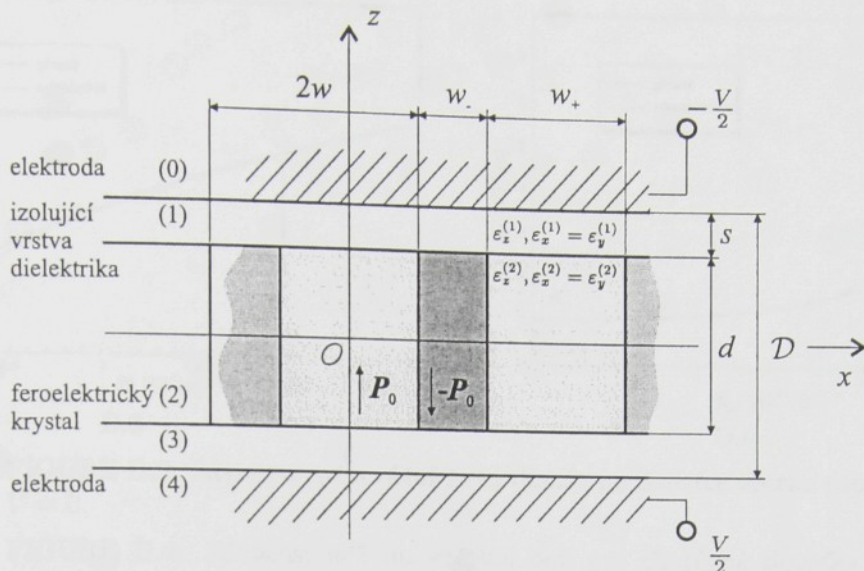
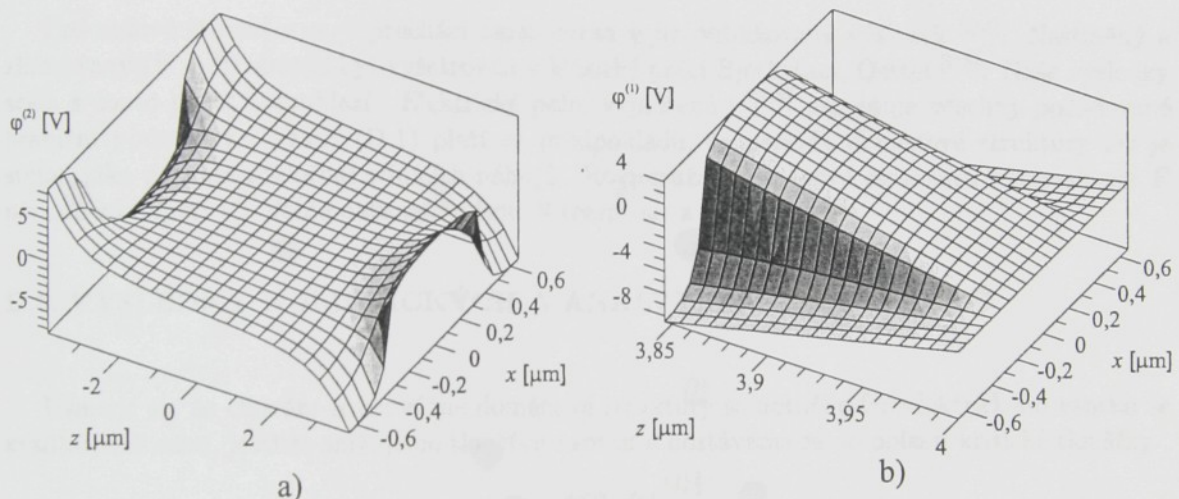


FIGURE D.1: Geometrie modelu


FIGURE D.2: Průběh potenciálu ve a) feroelektrické vrstvě a b) mezivrstvě pro $A_c = 0$, $a = 0,25$, $B = 0,04$, $A = 0,11$, $V = 5V$, $D = 8\mu m$, $R = 18,32$

D.2. VOLNÁ ENERGIE SYSTÉMU

Celková volná energie systému zahrnuje v našem modelu elektrostatickou energii a energii doménových stěn. Řešením Laplaceovy rovnice Fourierovou metodou byl nalezen elektrický potenciál, jehož typický průběh ve feroelektrickém vzorku a mezivrstvě je znázorněn na obr. D.2

Z potenciálu je vypočtena energie elektrického pole. Detaily poměrně zdlouhavých výpočtů jsou uvedeny v práci [D3]. Zde uvedeme výsledný vztah pro plošnou hustotu volné energie (volná energie na $1m^2$ plochy vzorku):

$$F = \frac{2}{\pi} \sigma_w R + P_0 (A - aA_c) \frac{\frac{P_0 D B}{2(1+B)} (A - aA_c) - \epsilon_0 \epsilon_3^{(1)} \frac{V}{2}}{\epsilon_0 (\epsilon_3^{(1)} + \epsilon_3^{(2)} B)} \quad (D.1)$$

$$+ \frac{4P_0^2 D}{\epsilon_0 \pi^2 (1+B) R} \sum_{n=1}^{\infty} \frac{1}{n^3} \cdot \frac{(\sin n\pi \frac{A+1}{2} - a \sin n\pi \frac{A_c+1}{2})^2}{g^{(1)} \coth nBRc^{(1)} + g^{(2)} \coth nRc^{(2)}}.$$

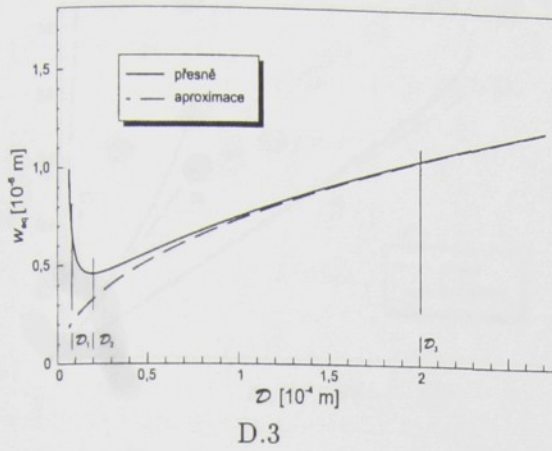


FIGURE D.3: Závislost rovnovážné šířky domén na tloušťce vzorku pro $V = 0$.

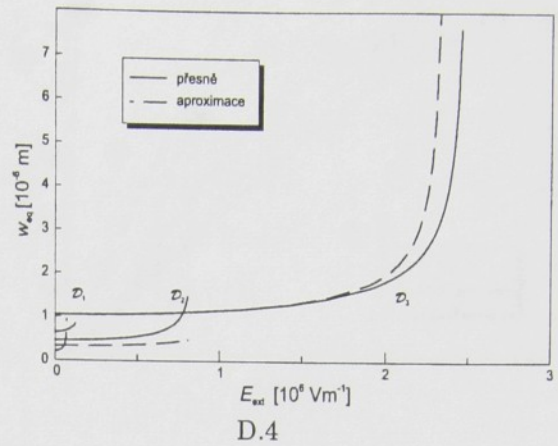


FIGURE D.4: Závislost w^{eq} na vnějším poli pro tři různé tloušťky, ustálený stav, $A = A_c$.

Pro nulové stínění $a = 0$ přechází tento vztah v již publikovaný výsledek [D4]. Nestíněný a zkratovaný ($V = 0$) vzorek byl vyšetřován v klasické práci Bjorkstam, Oettel [D5]. Naše výsledky zcela s touto prací nesouhlasí. Elektrické pole, vyjádřené v [D5] nesplňuje všechny požadované hraniční podmínky. Vztah (D.1) platí za předpokladu, že perioda doménové struktury $2w$ je stejná jako perioda rozložení stínících nábojů. Rovnovážná doménová struktura minimalizuje F při daném napětí V . Volné parametry jsou R (resp. w) a A (resp. A_c).

D.3. VÝSLEDKY NUMERICKÝCH A ANALYTICKÝCH VÝPOČTŮ

Ukazuje se, že chování rovnovážné doménové struktury samotného feroelektrického vzorku se kvalitativně mění, jestliže snižujeme tloušťku vzorku a dostáváme se do oblasti kritické tloušťky

$$\mathcal{D}_{crit} = \frac{4\pi\sigma_w\epsilon_0\epsilon_z^{(2)\frac{3}{2}}}{P_0^2\epsilon_x^{(2)}},$$

viz [D6].

U elektrovaných vzorků nastává tato změna již u tlouštěk o jeden až dva řády vyšších. Na obr. D.3 vidíme závislost rovnovážné půlperiody w^{eq} na tloušťce elektrovaného a zkratovaného vzorku pro RbH_2PO_4 ($\sigma_w = 5 \cdot 10^{-3} \text{ Jm}^{-2}$, $P_0 = 5,7 \cdot 10^{-2} \text{ Cm}^{-2}$, $\epsilon_x = 10$, $\epsilon_z = 100$, $\mathcal{D}_{crit} = 0,053 \cdot 10^{-6} \text{ m}$).

V dalším uvedeme výsledky vždy pro tento materiál a tři tloušťky

$$\begin{aligned} \mathcal{D}_1 &= 150 \mathcal{D}_{crit} = 8 \mu\text{m} \\ \mathcal{D}_2 &= 370 \mathcal{D}_{crit} = 20 \mu\text{m} \\ \mathcal{D}_3 &= 3700 \mathcal{D}_{crit} = 200 \mu\text{m}, \end{aligned}$$

které jsou též vyznačeny na obr. D.3. Ve všech výpočtech volíme koeficient stínění $a = 0,25$ a koeficient $B = 0,04$. Pro relativně tlusté vzorky $\mathcal{D} \gg \mathcal{D}_{crit}$ je možné rovnovážné hodnoty R , A aproximovat analyticky (tzv. aproximace tlustých krystalů). Uvedeme zde dva takové vztahy pro A^{eq} ,

Za předpokladu, že stínění kopíruje doménovou strukturu ($A = A_c$) platí

$$A^{eq} = \frac{\epsilon_0\epsilon_z^{(1)}(1+B)V}{2(1-a)\mathcal{D}P_0 \left[B - 2 \ln 2 \frac{\epsilon_z^{(1)} + B\epsilon_z^{(2)}}{R_0^{eq}(g^{(1)} + g^{(2)})} \right]}. \quad (\text{D.2})$$

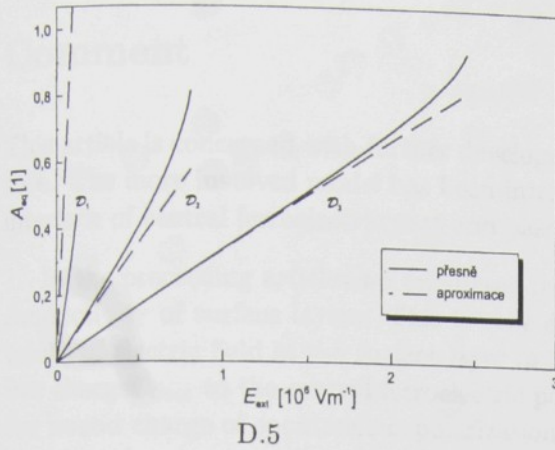


FIGURE D.5: Závislost A^{eq} na vnějším poli pro tři různé tloušťky, ustálený stav, $A = A_c$.

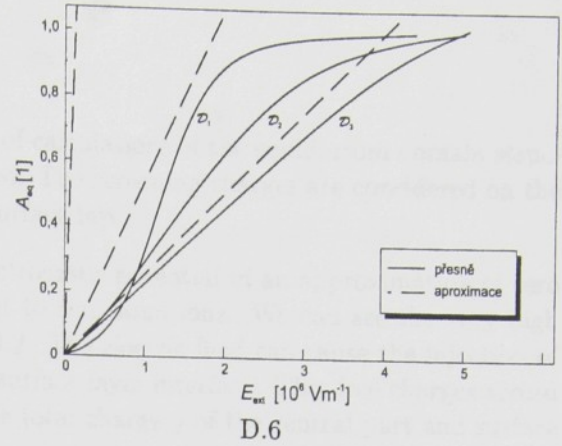


FIGURE D.6: Závislost A^{eq} na vnějším poli při konstantním symetrickém stínění, $A_c = 0$ pro tři různé tloušťky.

Za předpokladu rychlých změn napětí, kdy stínění nestačí sledovat všechny změny doménové struktury a zůstává stále symetrické ($A_c = 0$), platí

$$A^{eq} = \frac{\varepsilon_0 \varepsilon_z^{(1)} (1 + B) V}{2DP_0 \left[B - 2 \ln 2 \frac{\varepsilon_z^{(1)} + B \varepsilon_z^{(2)}}{R_0^{eq} (g^{(1)} + g^{(2)})} \right]}, \quad (D.3)$$

R_0^{eq} je rovnovážná hodnota parametru R při nulovém napětí.

Obr. D.4 ukazuje srovnání numerických a přibližných analytických výsledků závislosti w^{eq} na vnějším poli $E_{ext} = V/D$ pro tři zmíněné tloušťky za předpokladu, že $A = A_c$ (dlouhodobá rovnováha, stínění kopíruje doménovou strukturu).

Obr. D.5 představuje totéž pro závislost $A^{eq}(E_{ext})$.

Obr. D.6 ukazuje závislost $A^{eq}(E_{ext})$ při konstantním symetrickém stínění $A_c = 0$ opět pro tři různé tloušťky. Analytické přiblížení je srovnáno s exaktními numerickými výpočty.

D.4. DISKUSE

Přibližné analytické vztahy (D.2), (D.3) vyjadřují lineární odezvu doménové struktury na vnější pole. Přesné numerické výsledky se odlišují od analytických tím více, čím je tloušťka vzorku menší. Pro tenké vzorky je odezva obecně nelineární.

D.5. PODĚKOVÁNÍ

Tato práce byla podporována Ministerstvem školství, mládeže a tělovýchovy ČR na základě Grantu CEZ: J11/98: 242200002 a VS 96006.

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Comment

This article is concerned with further development of calculations of the equilibrium domain structure. The more involved model has been introduced. The screening charges are considered on the interface of central ferroelectric part and passive surface layer.

In the preceeding articles we calculated the electrostatic potential in an approximation of zero conductivity of surface layers. This is very distant to real situations. We can see the very high values of electric field in the surface layer in fig. D.2. The electric field can cause the injection of free charges ϱ_{scr} to the central ferroelectric part—surface layer interface. This free charges screen the bound charge of spontaneous polarization. The total charge ϱ of the central part and surface layer interface is

$$\varrho = -\operatorname{div} P_0(A) + \varrho_{scr}.$$

If the screening charges reflect the profile of spontaneous polarization at some instant time, we can put $\varrho_{scr} = a \operatorname{div} P_0(A_c)$, where A_c is the analogy of the asymmetry coefficient of the domain structure for the screening charge. Coefficient $a \in (0, 1)$ can be called *screening coefficient*. The following formulae for the electric potential can be derived:

$$\varphi^{(1)}(x, z) = \frac{sP_0(A - aA_c) - \varepsilon_0\varepsilon_3^{(1)}\frac{V}{2}}{\varepsilon_0(\varepsilon_3^{(1)} + \varepsilon_3^{(2)}B)} \cdot \frac{(D-2z)}{2s} - \frac{V(z-\frac{d}{2})}{2s} + \quad (D.4)$$

$$+ \sum_{n=1}^{\infty} \frac{4P_0w}{\varepsilon_0n^2\pi^2} \cdot \frac{(\sin n\pi\frac{A+1}{2} - a \sin n\pi\frac{A_c+1}{2}) \cos nx\frac{\pi}{w}}{g^{(1)} \coth nBRc^{(1)} + g^{(2)} \coth nRc^{(2)}} \cdot \frac{\sinh nc^{(1)}\frac{\pi}{w}(\frac{D}{2} - z)}{\sinh nBRc^{(1)}},$$

$$\varphi^{(2)}(x, z) = \frac{sP_0(A - aA_c) - \varepsilon_0\varepsilon_3^{(1)}\frac{V}{2}}{\varepsilon_0(\varepsilon_3^{(1)} + \varepsilon_3^{(2)}\frac{2s}{d})} \cdot \frac{2z}{d} + \quad (D.5)$$

$$+ \sum_{n=1}^{\infty} \frac{4P_0w}{\varepsilon_0n^2\pi^2} \cdot \frac{(\sin n\pi\frac{A+1}{2} - a \sin n\pi\frac{A_c+1}{2}) \cos nx\frac{\pi}{w}}{g^{(1)} \coth nBRc^{(1)} + g^{(2)} \coth nRc^{(2)}} \cdot \frac{\sinh nc^{(2)}z\frac{\pi}{w}}{\sinh nRc^{(2)}},$$

The effect of screening charges on profile of electrostatic potential is shown in fig. 14, which can be taken as the result of following physical process: it started with a situation depicted in fig. 12. Then the free screening charges was injected on the interface of the central ferroelectric and passive surface layer from the electrodes due to high local electric fields of the bound charges of spontaneous polarization. When the screening reached to approximately 80% the external voltage was applied and domain walls shifted. Then uncompensated bound charges appeared on the interface due to small conductivity of the sample.

The values of critical sample thickness D_{crit} are discussed for free-standing and electroded thin films. The dependencies of the asymmetry coefficient and the domain structure period on external electric field or on the sample thickness are shown in figs. D.3-D.6.

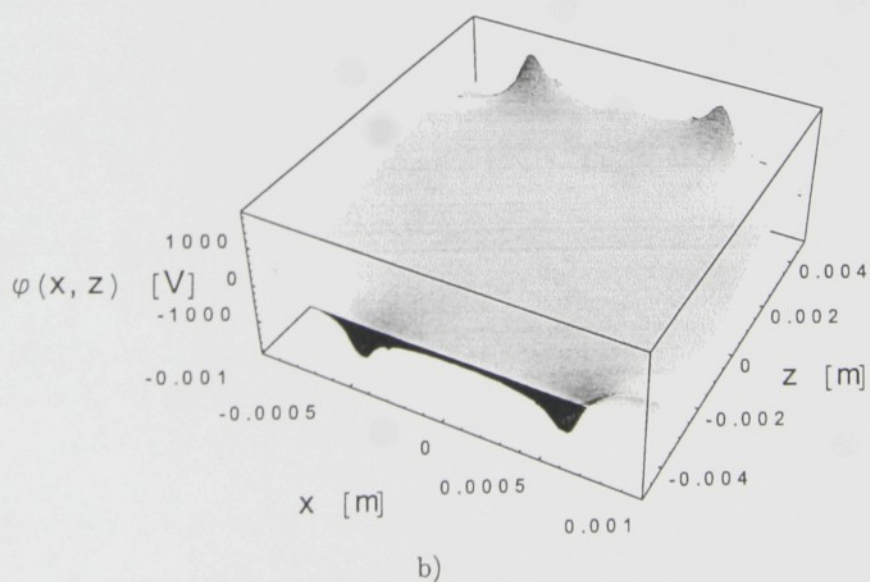
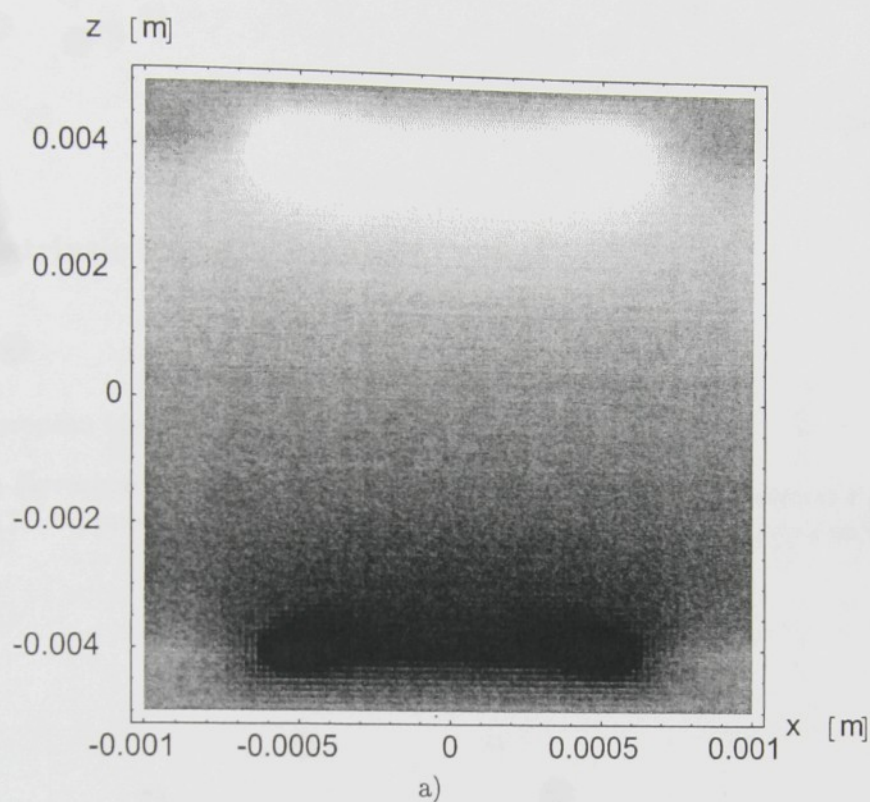


FIGURE 14: Graphic representation of electric potential, the effect of screening charges: $\epsilon_z^{(1)} = 100$, $\epsilon_z^{(2)} = 100$, $\epsilon_x^{(1)} = 10$, $\epsilon_x^{(2)} = 10$, $A = 0.2$, $V = 5 \text{ V}$, $P_0 = 4 \cdot 10^2 \text{ C m}^{-2}$, $a = 0.8$, $A_c = 0$.

Paper E

On the Extrinsic Piezoelectricity

Poster on European Meeting on Ferroelectricity, Prague 1999.

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ON THE EXTRINSIC PIEZOELECTRICITY

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Abstract

This work presents a continuation of our last paper, concerning the theory of the response of an antiparallel domain structure in a plate-like electroded sample to external electric field. The theory is based on the exact formula for free energy of the system, formed of a central ferroelectric part, isolated from electrodes (with a defined potential difference) by a surface layers. Our calculations are applicable also to thin films. It is usual to use the term 'extrinsic' for the contribution of domain walls displacement to macroscopic properties of a sample. In our last paper we discussed the extrinsic contribution to permittivity. In this work we concentrate on extrinsic contribution to piezoelectric coefficients in ferroelectrics which are simultaneously ferroelastics. As an example, we calculate the extrinsic contribution to d_{36} piezoelectric coefficient of RbH_2PO_4 , that was recently measured in a wide range of temperature below Curie point.

Keywords: Ferroelectric domains; extrinsic contributions to piezoelectricity

E.1. INTRODUCTION

Samples of ferroelectric single crystals often possess a surface layers. Its existence greatly influences properties of bulk samples^[E1,2,3,4] as well as of thin films.^[E5] Equilibrium domain structure in the system, mentioned above in the abstract, and the role of the surface layers was first discussed by Bjorkstam and Oettel^[E6] in a special case of shorted electrodes. In our recent paper^[E7] we reconsidered this problem in a general case of nonzero voltage between electrodes, discussing the response of the domain structure to external electric field. Our calculations are valid also for thin films and present, in fact, continuation of our discussion of domain structures of thin films^[E8].

In^[E7] we used our theoretical results for prediction of extrinsic contribution to permittivity of the sample. In the next two sections we give a short review of notation, description of the model and basic results from^[E7]. In last two sections we discuss as an example the extrinsic contribution to d_{36} piezoelectric coefficient of RbH_2PO_4 . We compare our predictions with the recent measurements of record values $\sim 4000 \text{ pC/N}$ in temperature range 35 K under critical temperature 146 K^[E9] (see also^[E10]).

E.2. DESCRIPTION OF THE MODEL

We consider a plate-like electroded sample of infinite area with major surfaces perpendicular to the ferroelectric axis z . Central ferroelectric part with antiparallel domains (2.) is separated from the electrodes (0.), (4.) by nonferroelectric layers (1.), (3.) (see Fig. E.1). The spatial distribution of the electric field E is determined by the applied potential difference $V = \varphi^{(4)} - \varphi^{(0)}$ and by the bound charge $\text{div} \mathbf{P}_0$ on the boundary of ferroelectric material, where $\mathbf{P}_0$ stands for spontaneous polarization. Geometrical, electrical and material parameters of the system are shown in Fig. E.1.

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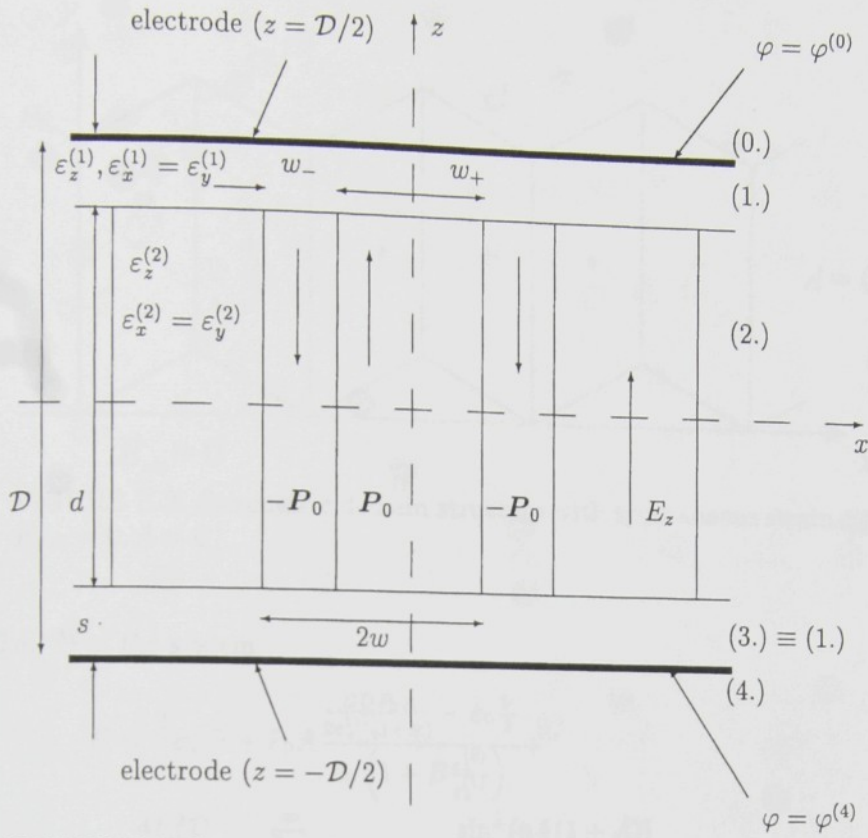


FIGURE E.1: Geometry of the model

We further introduce the symbols

$$c^{(1),(2)} = \sqrt{\frac{\epsilon_z^{(1),(2)}}{\epsilon_z^{(1),(2)}}}, \quad g^{(1),(2)} = \sqrt{\epsilon_x^{(1),(2)} \epsilon_z^{(1),(2)}},$$

and several geometrical parameters:

$$B = \frac{2s}{d}$$

the domain pattern factor

$$R = \pi \frac{d}{2w}, \quad 2w = w_+ + w_-$$

and the asymmetry factor

$$A = \frac{w_+ - w_-}{w_+ + w_-}.$$

The ferroelectric material itself is approximated by the equation of state

$$D_i = \epsilon_0 \epsilon_{ij} E_j + P_{0i} \quad (\text{E.1})$$

where only the component P_{0z} is nonzero. This linear approximation limits the validity of our calculations to the temperature region not very close below the transition temperature T_c . Domain walls are assumed to have surface energy density σ_w and zero thickness.

E.3. FREE ENERGY OF THE SYSTEM, EQUILIBRIUM DOMAIN STRUCTURE

Rather cumbersome calculations^[E7] lead to the following formula for total free energy surface

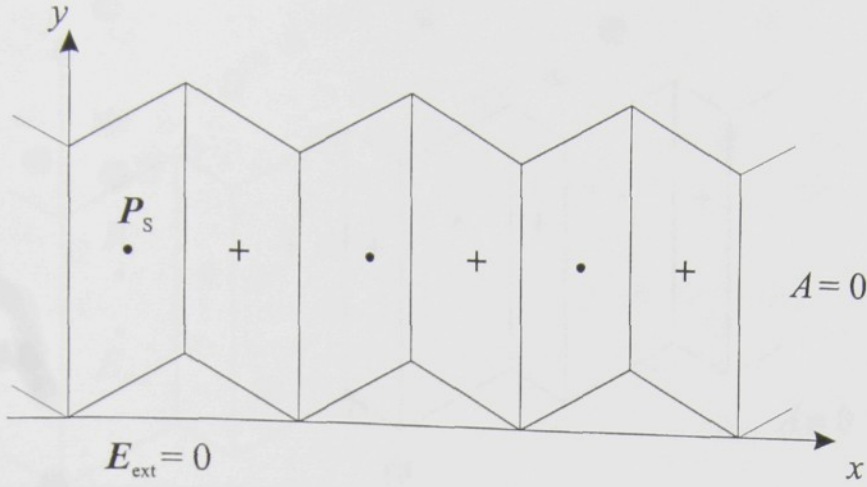


FIGURE E.2: Symmetric domain structure with spontaneous strain S_6^s , $E_{ext} = 0$, $A = 0$

density (in J m^{-2}) of the system

$$F = \frac{2}{\pi} \sigma_w R + P_0 A \frac{\frac{B D P_0 A}{2 \epsilon_z^{(1)} (1+B)} - \epsilon_0 \frac{V}{2}}{\epsilon_0 \left(1 + B \frac{\epsilon_z^{(2)}}{\epsilon_z^{(1)}} \right)} + \frac{4 P_0^2 D}{\epsilon_0 \pi^2 R (1+B)} \sum_{n=1}^{\infty} \frac{\sin^2 \left(n \frac{\pi}{2} (1+A) \right)}{n^3 (g^{(1)} \coth n B R c^{(1)} + g^{(2)} \coth n R c^{(2)})} \quad (\text{E.2})$$

The first term represents domain wall contribution while the last one is the depolarization energy. In the second term we recognize the effect of layers (1.) and (3.) and of the applied voltage.

In this model we neglect the mechanical interactions between components of the system. For given slab factor B and voltage V , the equilibrium domain structure, characterized by $R_{eq}(V)$ and $A_{eq}(V)$, corresponds to local minimum of F . In general a minimum can be found by numerical methods, but for $B R c^{(1)} \gg 1$ and $R c^{(2)} \gg 1$, the $R_{eq}(V)$ and $A_{eq}(V)$ can be approximated by explicit formulae. For purpose of this paper we use the following formula for $A_{eq}(V)$

$$A_{eq}(V) \cong \frac{\epsilon_0 V}{2 P_0 D \left[\frac{B}{\epsilon_z^{(1)} (1+B)} - X \right]} \quad (\text{E.3})$$

where

$$X = \frac{2 \ln 2}{R_{eq}^0 (1+B) (g^{(1)} + g^{(2)})} \left(1 + B \frac{\epsilon_z^{(2)}}{\epsilon_z^{(1)}} \right)$$

is considered as a small correction and R_{eq}^0 is equilibrium value of R for zero voltage V . For the extrinsic contribution to permittivity of the sample we get from (E.3) (see also^[E7])

$$\epsilon_{ext} = \left\{ \left(1 + B \frac{\epsilon_z^{(2)}}{\epsilon_z^{(1)}} \right) \left[\frac{B}{(1+B) \epsilon_z^{(1)}} - X \right] \right\}^{-1} \quad (\text{E.4})$$

E.4. EXTRINSIC PIEZOELECTRICITY

As an example, in this section we work out the approximate prediction of extrinsic contribution to d_{36} of RbH_2PO_4 (RDP), based on our simple model. RDP is a ferroelastic with spontaneous strain S_6^s , opposite in opposite polarized domains. In the Fig.E.2 there is $x-y$ cut through symmetric domain structure ($A = 0$, $E_{ext} = \frac{V}{D} = 0$). The situation after application of E_{ext} is shown in

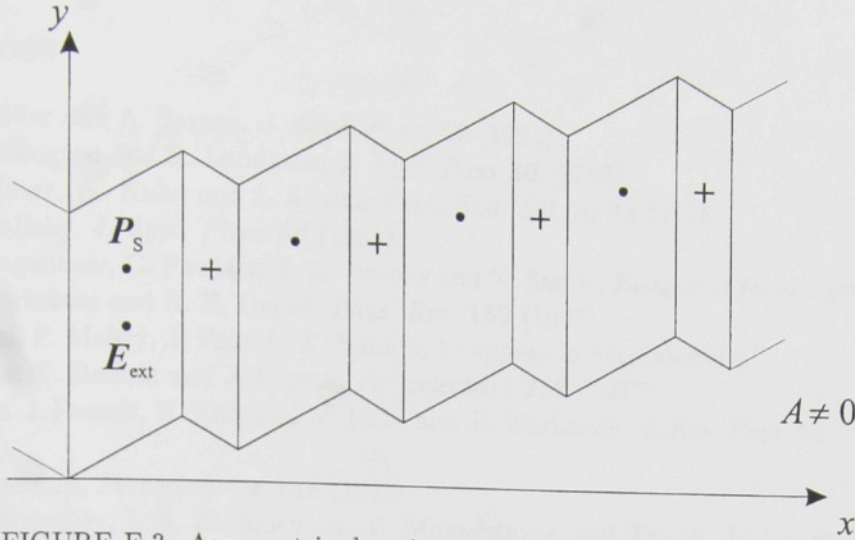


FIGURE E.3: Asymmetric domain structure with average strain $S_6 = AS_6^s$, $E_{ext} \neq 0$, $A \neq 0$

Fig.E.3 ($A \neq 0$). A simple geometric consideration leads to the formula for average strain S_6 of the sample (we neglect the mechanical coupling of the central part with the rest of the sample)

$$S_6 = S_6^s A \quad (\text{E.5})$$

For the extrinsic coefficient d_{36} we get from (E.3) and (E.5)

$$d_{36} \equiv \frac{S_6}{E_3} = \frac{\varepsilon_0 S_6^s}{2 P_0 \left[\frac{B}{(1+B) \varepsilon_z^{(1)}} - X \right]} \quad (\text{E.6})$$

neglecting the small X and for $B \ll 1$ we get more simple formula⁶

$$d_{36} = \frac{\varepsilon_0 \varepsilon_z^{(1)} S_6^s}{2 P_0 B} . \quad (\text{E.7})$$

E.5. DISCUSSION

An extremely high d_{36} under T_c for RDP was first reported in^[E11]. In a recent paper^[E12], Sidorkin deduced the dispersion law of domain wall vibrations, however, in his treatment the existence of a surface layers is not explicitly considered. We can fit our theoretical results to measured ones^[E9] - $d_{36,ext} \doteq 4 \cdot 10^{-9}$ C/N, $\varepsilon_{z,ext} = 2000$ in the 35 K range plateau under T_c . Using values that roughly apply to RDP⁷ in (E.7) resp. (E.4) we come to an agreement for reasonable value of $B \doteq 0.04$. Naturally for lower temperatures, the motion of the walls is limited by "freezing" and both $d_{36,ext}$ and $\varepsilon_{z,ext}$ decrease to zero. It is also interesting, for measurements in^[E9] with alternating $E_{ext} \doteq 20$ V/m, that corresponding amplitude of alternating A from (E.3) is only 10^{-5} and displacement of the walls with $w \doteq 10 \mu\text{m}$ is of the order 10^{-10} m.

Acknowledgements

This work has been supported by the Ministry of Education of the Czech Republic grants CEZ: J11/98:242200002 and VS 96006.

⁶The limit $B \rightarrow 0$ in (E.7) is not correct, because the assumptions needed for validity of (E.3) are violated if B is very small.

⁷ $P_0 = 4 \cdot 10^{-2}$ C/m², $\varepsilon_z^{(1)} \doteq \varepsilon_z^{(2)} \doteq 100$, $S_6^s \doteq 0.015$, see^[E9].

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Comment

The existence of effective piezoelectric response in ferroelectric ferroelastic multidomain single crystal was proposed in this article. The effect of domain wall shifts to average shear strain of the sample is clearly shown in fig. E.2 and E.3.

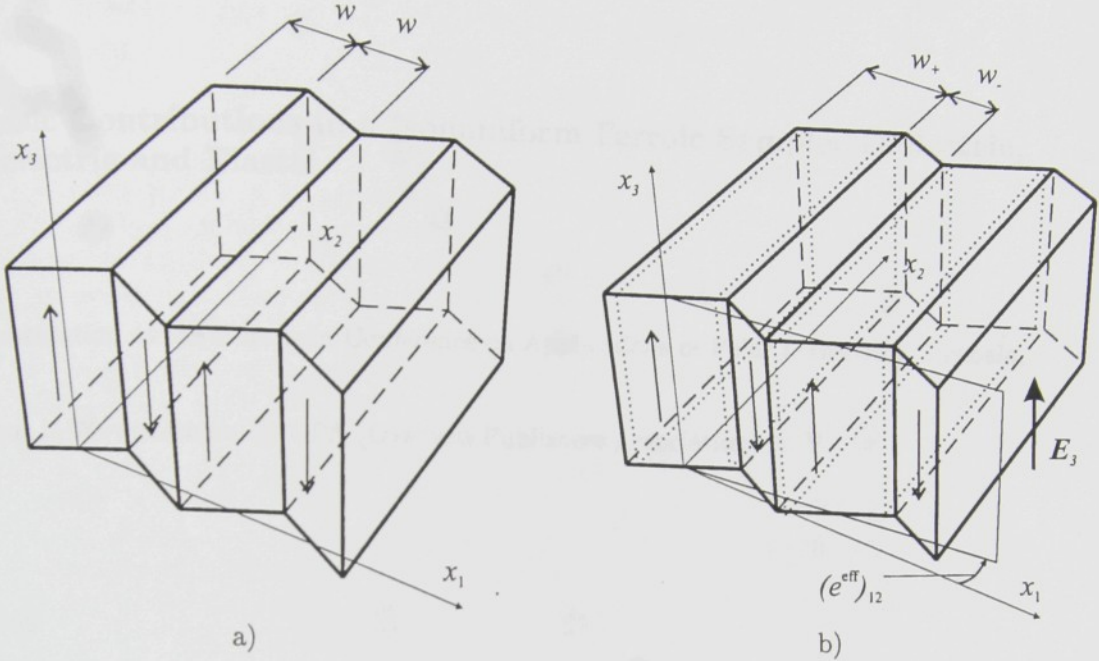


FIGURE 15: The contributions of domain wall shifts to piezoelectric coefficient d_{36} .

The ferroelectric ferroelastic domain structure is shown in the fig. 15. The domain walls shift from their original positions (dotted lines), when the external electric field is applied. Then the average shear strain e_{12}^{eff} of the ferroelastic sample changes from zero in the plane x_1x_2 perpendicular to the ferroelectric axis x_3 . Domain walls shifts cause the contribution to the piezoelectric coefficient Δd_{36} . Therefore, the existence of passive surface layer can be taken as a source of the extrinsic contribution to d_{36} . Using values that roughly apply to RDP (see fig. 16) in (E.7) resp. (E.4) we come to an agreement for reasonable value of $B \doteq 0.04$. This means that the thickness of the passive surface layer is about $20 \mu\text{m}$ for the sample of thickness 1 mm. Also the "tiny" value of domain wall displacements of the order 10^{-10} m in a small external electric fields should be stressed.

Nevertheless, the very important condition have to be taken into account for existence of extrinsic piezoelectricity: crystal must be piezoelectric in the paraelectric phase. Then the value (and the sign) of spontaneous polarization is interconnected with the value (and the sign) of spontaneous strain in each domain by equation, see eqs. (4, 5)

$$P_{0,3} = \frac{h_{36}}{c_{66}^P} e_{0,6}.$$

This is the very limiting fact that restricts the choice of materials where the depicted mechanism can show itself. We can say that the KDP family is the only one class of materials with these property, which we know.

Material constant	Value
P_0	$4 \cdot 10^{-2} \text{ C/m}^2$
S_6^s	0.015
ε_z	100
ε_x	10

FIGURE 16: Material constants roughly applying to RDP (see [15]).

Paper F

Extrinsic Contributions in a Nonuniform Ferroic Sample: Dielectric, Piezoelectric and Elastic

Oral presentation at the European Conference on Applications of Polar Dielectrics, Jurmala, 2000.

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EXTRINSIC CONTRIBUTIONS IN A NONUNIFORM FERROIC SAMPLE: DIELECTRIC, PIEZOELECTRIC AND ELASTIC

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Abstract

The contribution $\Delta\epsilon$ 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 Δd) and elastic (by Δs) properties. Data about their simultaneous existence are scarce but those available point to mutual proportionality of $\Delta\epsilon$, Δd and Δs , 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.

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

1. 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.^[F1] were the first to address the problem of wall contributions to all involved properties: permittivity ϵ , 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^[F2] 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: $\Delta\epsilon$, Δs and Δd .^[F1,2]

While there exist a number of such data for ceramic materials^[F1,3,4], information for single crystals is rather scarce. Understandably, for nonferroelastic ferroelectrics such as TGS only data on $\Delta\epsilon$ are available;^[F5] on the other hand for crystals which are both ferroelectric and ferroelastic with more than two domain states, dense domain systems are rather chaotical, 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_2PO_4 family belong to this category and have been intensively studied. Nakamura et al.^[F6,7] determined $\Delta\epsilon_{33}$ for KH_2PO_4 , CsH_2PO_4 and CsH_2AsO_4 . For KH_2PO_4 , Nakamura and Kuramoto^[F8] proved the existence of both $\Delta\epsilon_{33}$ and Δs_{66} while Δd_{36} was measured for RbH_2PO_4 .^[F9] For the same material, all quantities $\Delta\epsilon_{33}$, Δd_{36}

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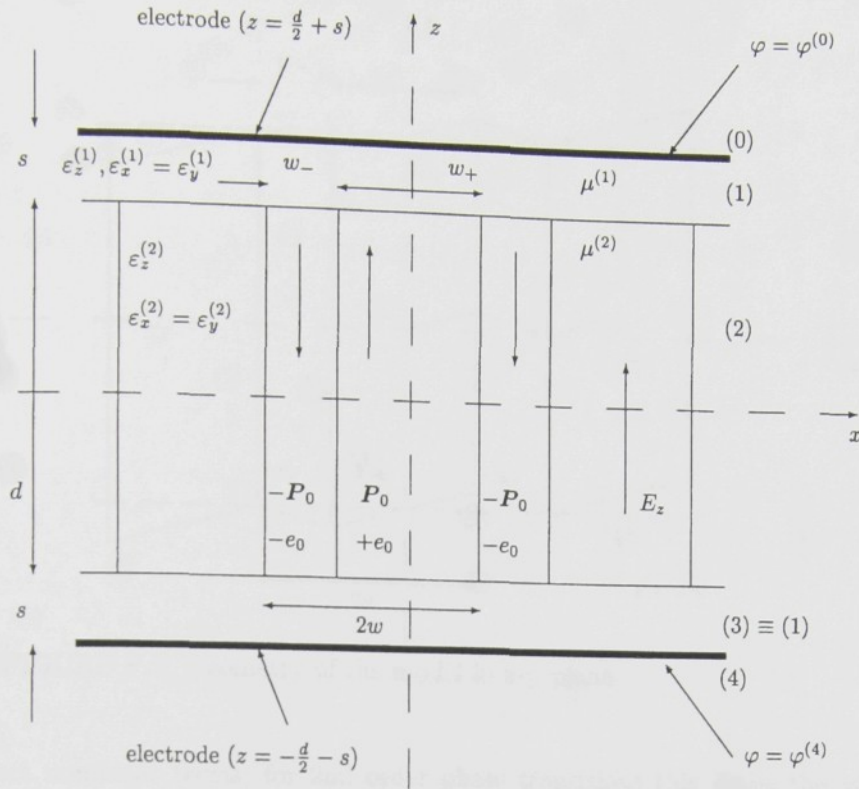


FIGURE F.1: Geometry of the model in x - z plane

and Δs_{66} have been measured by Štula et al.^[F10] 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^[F11,12] 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 $\Delta \epsilon_{33}$, Δs_{66} and Δd_{36} . Their dependence on the sample properties will be discussed.

F.2. DESCRIPTION OF THE MODEL

We consider a plate-like sample electrode sample of infinite area with major surfaces perpendicular to the ferroelectric axis z . The material is both ferroelectric and ferroelastic; 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

$$D_i = \epsilon_0 \epsilon_{ij} E_j + P_{0,i},$$

neglecting the intrinsic piezoelectricity. As we shall see, this does not suppress the existence the extrinsic piezoelectricity, which is one of the aims of our calculations. In the preceding equation,

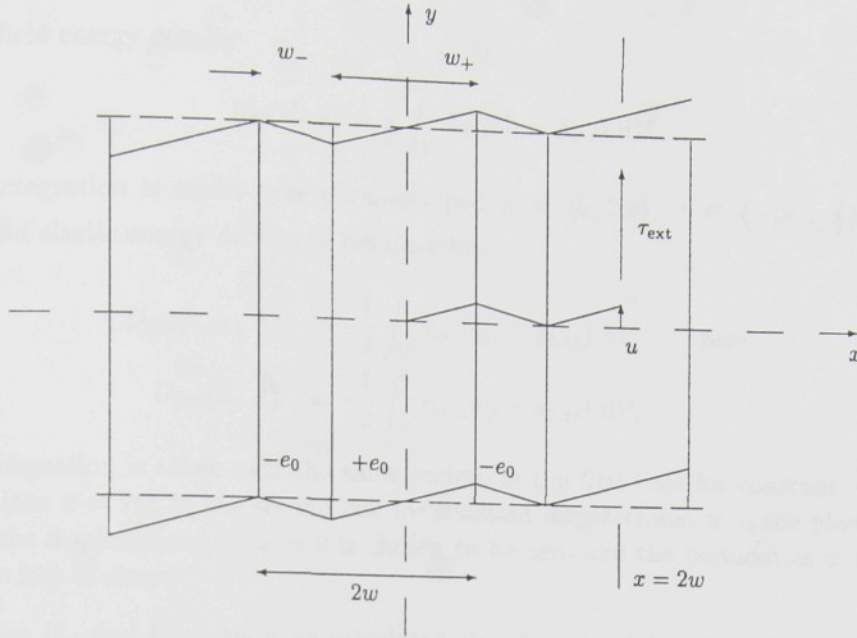


FIGURE F.2: Geometry of the model in x - y plane

we also neglect nonlinear terms; for 2nd order phase transitions this limits the validity of our calculations to the temperature region not very close below the temperature T_C . Domain walls are assumed to have surface energy density σ_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

$$\begin{aligned}\tau_{ij}^{(1)} &= 2\mu^{(1)}e_{ij}^{(1)}, \\ \tau_{ij}^{(2)} &= 2\mu^{(2)}(e_{ij}^{(2)} - e_{0,ij}),\end{aligned}$$

where $\mu^{(1,3)}$ are Lamé 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 w_+ resp. w_- domain, see Fig. F.2. We introduce the asymmetry factor

$$A = \frac{w_+ - w_-}{w_+ + w_-}.$$

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.

F.3. SURFACE ENERGY DENSITY

In what follows we consider three kinds of energy, calculated per unit surface area of the plate-like sample (in the x - y plane):

The domain wall energy density

$$U_w = \sigma_w \frac{d}{w} \quad [\text{J} \cdot \text{m}^{-2}],$$

the electric field energy density

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

where the integration is taken over parallelepiped $x \in \langle 0, 2w \rangle$, $z \in \langle -(s + \frac{d}{2}), s + \frac{d}{2} \rangle$, $y \in \langle 0, \frac{1}{2w} \rangle$, and elastic energy density of deformation:

$$\begin{aligned} U_{def}(\tau_{ext}, A) &= \frac{1}{2} \int_V \tau_{ij} (e_{ij} - e_{0,ij}) dV, \quad \text{resp.} \\ U_{def}(u, A) &= \frac{1}{2} \int_V \tau_{ij} (e_{ij} - e_{0,ij}) dV, \end{aligned}$$

where the integration is taken over the same region, in the first case for constant external stress τ_{ext} in the plane $x = 2w$, in the second one for constant displacement u in the plane $x = 2w$. 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_{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 "thick sample", that is for $s, d \gg w$:

$$\begin{aligned} U_{el}(V, A) &= \frac{sd A^2 P_0^2 + \frac{1}{2} V^2 \epsilon_0^2 \epsilon_z^{(1)} \epsilon_z^{(2)}}{\epsilon_0 (\epsilon_z^{(1)} d + \epsilon_z^{(2)} 2s)}, \\ U_{def}(\tau_{ext}, A) &= \frac{d(d+2s)^2 \mu^{(2)} \tau_{ext}^2}{2 (\mu^{(1)} 2s + \mu^{(2)} d)^2} + s \mu^{(1)} \left(2Ae_0 + \frac{(d+2s) \tau_{ext}}{\mu^{(1)} 2s + \mu^{(2)} d} \right)^2, \\ U_{def}(u, A) &= \frac{\frac{1}{2} \mu^{(1)} s u^2 + \mu^{(2)} d (\frac{1}{2} u - 2Ae_0 w)^2}{2w^2}. \end{aligned}$$

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

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

where σ_0 is constant Fourier component of the free charge density on the positive electrode, calculated as

$$\sigma_0(V, A) = \frac{\epsilon_z^{(1)} P_0 A + \epsilon_0 \epsilon_z^{(1)} \epsilon_z^{(2)} \frac{V}{d}}{\epsilon_z^{(1)} + \epsilon_z^{(2)} \left(\frac{2s}{d} \right)}. \quad (\text{F.1})$$

Infinitesimal work of the mechanical source, deforming the parallelepiped is

$$\delta W_{def} = \tau_{ext} \frac{d+2s}{2w} \delta u \quad [\text{J} \cdot \text{m}^{-2}],$$

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

$$w_{eq} = \sqrt{3.68} d \sigma_w \left[4e_0^2 \frac{\mu^{(1)} \mu^{(2)}}{\mu^{(1)} + \mu^{(2)}} + \frac{P_0^2}{\epsilon_0 \left(\sqrt{\epsilon_x^{(1)} \epsilon_z^{(1)}} + \sqrt{\epsilon_x^{(2)} \epsilon_z^{(2)}} \right)} \right]^{-\frac{1}{2}}. \quad (\text{F.2})$$

It can be shown (see e.g.^[F11]) that within a large interval of the applied voltage the average width

$$w = \frac{w_+ + w_-}{2}$$

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

F.4. EXTRINSIC CONTRIBUTIONS $\Delta\epsilon_{33}$, Δs_{66} and Δd_{36}

We calculate the equilibrium effective $\epsilon_{33}^{\text{eff}}$ of the sample from the relations

$$D_3^{\text{eff}} = \sigma_0(V, A) = \epsilon_{33}^{\text{eff}} E_3^{\text{ext}} = \epsilon_{33}^{\text{eff}} \frac{V}{2s + d}. \quad (\text{F.3})$$

We keep $\tau_{\text{ext}} = 0$, $V = \text{constant}$ and we take into account that variation of "the total energy of the sample + electric source" is zero in equilibrium:

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

Solving this standard problem, we get $A = A(V)$ and from the Eqs. (F.1), (F.3) the effective $\epsilon_{33}^{\text{eff}}$. For $\mu^{(1)} = \mu^{(2)} = \mu$, $\epsilon_{x,z}^{(1)} = \epsilon_{x,z}^{(2)} = \epsilon_{x,z}$ we obtain the relatively simple result:

$$\epsilon_z^{\text{eff}} = \epsilon_z + \epsilon_z \frac{d}{2s} \cdot \left[\frac{P_0^2 d}{P_0^2 d + 4 e_0^2 \epsilon_0 \epsilon_z \mu (d + 2s)} \right]. \quad (\text{F.4})$$

The effective elastic compliance of the sample is

$$s_{66}^{\text{eff}} = 4s_{1212}^{\text{eff}} = \frac{2e_{12}^{\text{eff}}}{\tau_{\text{ext}}} = \frac{u}{2w \tau_{\text{ext}}}.$$

We put $V = 0$ (shorted sample), apply constant external shear stress τ_{ext} and postulate, that variation of "the energy of the sample + mechanical source" is zero in equilibrium

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

Solving this problem, we get $u = u(\tau_{\text{ext}})$ and we get for $\mu^{(1)} = \mu^{(2)} = \mu$, $\epsilon_{x,z}^{(1)} = \epsilon_{x,z}^{(2)} = \epsilon_{x,z}$:

$$s_{66}^{\text{eff}} = \frac{1}{\mu} + \frac{1}{\mu} \cdot \frac{d}{s} \left[\frac{2 e_0^2 \epsilon_0 \epsilon_z}{(P_0^2/\mu) + 4 e_0^2 \epsilon_0 \epsilon_z} \right]. \quad (\text{F.5})$$

To find the effective piezoelectric coefficient of the sample

$$d_{36}^{\text{eff}} = \frac{D_3^{\text{eff}}}{\tau_{\text{ext},6}} = \frac{\sigma_0}{\tau_{\text{ext},6}},$$

we put $V = 0$, apply τ_{ext} and solve the problem

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

From here we obtain $A = A(\tau_{\text{ext}})$. Inserting this result into Eq. (F.1) we obtain $\sigma_0 = \sigma_0(\tau_{\text{ext}})$. For $\mu^{(1)} = \mu^{(2)} = \mu$, $\epsilon_{x,z}^{(1)} = \epsilon_{x,z}^{(2)} = \epsilon_{x,z}$ we get finally for the effective piezoelectric coefficient

$$d_{36}^{\text{eff}} = \frac{d}{s} \cdot \left[\frac{e_0 P_0 \epsilon_0 \epsilon_z}{P_0^2 + 4 e_0^2 \epsilon_0 \epsilon_z \mu} \right]. \quad (\text{F.6})$$

The same result we get for the inverse piezoelectric effect.

F.5. DISCUSSION

The above calculation leads to explicite formulae (F.4) to (F.6) for extrinsic permittivity, extrinsic

	$s = 1 \cdot 10^{-6} \text{ m}$	$s = 5 \cdot 10^{-6} \text{ m}$	$s = 10 \cdot 10^{-6} \text{ m}$
$\Delta \varepsilon_{33}$ [1]	12000	2500	1200
Δd_{36} [C m^{-2}]	$4.1 \cdot 10^{-8}$	$8.3 \cdot 10^{-9}$	$4.1 \cdot 10^{-9}$
Δs_{66} [Pa^{-1}]	$1.6 \cdot 10^{-8}$	$3.2 \cdot 10^{-9}$	$1.6 \cdot 10^{-9}$

TABLE F.1: Numerical estimate of $\Delta \varepsilon_{33}$, Δs_{66} and Δd_{36} for different values of surface layer thickness. The following numerical constants have been used: $P_0 = 4 \cdot 10^{-2} \text{ C m}^{-2}$, $\varepsilon_z = 100$, $e_0 = 0.015$, $\mu = 6 \cdot 10^9 \text{ Pa}$, $\sigma_w = 5 \cdot 10^{-3} \text{ J m}^{-2}$, $d = 5 \cdot 10^{-4} \text{ m}$.

elastic compliance and extrinsic piezoelectric coefficient, resp. Numerical values for all involved material coefficients are available for single crystals of RbH_2PO_4 : $P_0 = 4 \cdot 10^{-2} \text{ C m}^{-2}$, $\varepsilon_z = 100$, $e_0 = 0.015$ 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 $d = 5 \cdot 10^{-4} \text{ m}$ and choose three values of surface layer thickness, namely $s = 1 \cdot 10^{-6} \text{ m}$, $s = 5 \cdot 10^{-6} \text{ m}$ and $s = 10 \cdot 10^{-6} \text{ m}$. Table F.1 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 (F.2) gives a reasonable numerical estimation for the width of equilibrium domain pattern. With numerical values specified at Tab. F.1 we obtain $w_{\text{eq}} \cong 1 \mu\text{m}$.

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_2PO_4 , falls into this category. However, extrinsic properties of a number of other crystals have been studied. Thus, e.g., for $\text{LiTiC}_4\text{H}_4\text{O}_6 \cdot \text{H}_2\text{O}$ (species 222- $P\bar{e}ds-2_y$) ^[F13] 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^[F14] for $(\text{NH}_4)_4\text{LiH}_3(\text{SO}_4)_4$, species 4- $\bar{e}ds-2$.

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Comment

A qualitatively more general approach has been used in this article. The mechanical interaction between the central ferroic part and the surface layers is included into our considerations.

First the Maxwell equations were solved for the electrostatic potential in the bulk and the surface layer. Second, solution for the vector of mechanical displacement was found from the Lammé equations. We can choose from two types of boundary conditions for vector of mechanical displacement. When we define the values of mechanical force acting on the boundary of the sample (Neumann-type boundary condition), the components of vector of mechanical displacement is of form:

$$\begin{aligned}
 u_1^{(1)}(x_1, x_3) &= \frac{\tau_{\text{ext}}(2s+d)}{\mu^{(1)}2s + \mu^{(2)}d} x_2, \\
 u_1^{(2)}(x_1, x_3) &= \frac{\tau_{\text{ext}}(2s+d)}{\mu^{(1)}2s + \mu^{(2)}d} x_2, \\
 u_2^{(1)}(x_1, x_3) &= \left[2Ae_0 + \frac{\tau_{\text{ext}}(2s+d)}{\mu^{(1)}2s + \mu^{(2)}d} \right] x_1 + \\
 &\quad + \sum_{n=1}^{\infty} \frac{8e_0w}{n^2\pi^2} \sin n\pi \frac{A+1}{2} \sin \frac{n\pi x_1}{w} \frac{\mu^{(2)} \cosh \frac{n\pi}{w} \left(\frac{d}{2} + s - x_3 \right) \operatorname{sech} \frac{n\pi s}{w} \tanh \frac{n\pi d}{2w}}{\mu^{(2)} \tanh \frac{n\pi d}{2w} + \mu^{(1)} \tanh \frac{n\pi s}{w}}, \\
 u_2^{(2)}(x_1, x_3) &= \left[2Ae_0 + \frac{\tau_{\text{ext}}(2s+d)}{\mu^{(1)}2s + \mu^{(2)}d} \right] x_1 + \\
 &\quad + \sum_{n=1}^{\infty} \frac{8e_0w}{n^2\pi^2} \sin n\pi \frac{A+1}{2} \sin \frac{n\pi x_1}{w} \left(1 - \frac{\mu^{(1)} \cosh \frac{n\pi x_3}{w} \operatorname{sech} \frac{n\pi d}{2w} \tanh \frac{n\pi s}{w}}{\mu^{(1)} \tanh \frac{n\pi s}{w} + \mu^{(2)} \tanh \frac{n\pi d}{2w}} \right), \\
 u_3^{(1)}(x_1, x_3) &= 0, \\
 u_3^{(2)}(x_1, x_3) &= 0.
 \end{aligned} \tag{F.7}$$

The second possibility is to define the values of the vector of mechanical displacement (Dirichlet-type boundary condition). Then the components of u_i has form:

$$\begin{aligned}
 u_1^{(1)}(x_1, x_3) &= 0, \\
 u_1^{(2)}(x_1, x_3) &= 0, \\
 u_2^{(1)}(x_1, x_3) &= \frac{x_1}{2w} u_w + \\
 &\quad + \sum_{n=1}^{\infty} \frac{8e_0w}{n^2\pi^2} \sin n\pi \frac{A+1}{2} \sin \frac{n\pi x_1}{w} \frac{\mu^{(2)} \sinh \frac{n\pi}{w} \left(\frac{d}{2} + s - x_3 \right) \operatorname{csch} \frac{n\pi s}{w} \tanh \frac{n\pi d}{2w}}{\mu^{(2)} \tanh \frac{n\pi d}{2w} + \mu^{(1)} \coth \frac{n\pi s}{w}}, \\
 u_2^{(2)}(x_1, x_3) &= \frac{x_1}{2w} u_w + \\
 &\quad + \sum_{n=1}^{\infty} \frac{8we_0}{n^2\pi^2} \sin n\pi \frac{A+1}{2} \sin \frac{n\pi x_1}{w} \left(1 - \frac{\mu^{(1)} \cosh \frac{n\pi x_3}{w} \coth \frac{n\pi s}{w} \operatorname{sech} \frac{n\pi d}{2w}}{\mu^{(1)} \coth \frac{n\pi s}{w} + \mu^{(2)} \tanh \frac{n\pi d}{2w}} \right), \\
 u_3^{(1)}(x_1, x_3) &= 0, \\
 u_3^{(2)}(x_1, x_3) &= 0.
 \end{aligned} \tag{F.8}$$

By integration of "power square" of strain tensor calculated from (F.7) we have obtained the following formula for deformation energy of a free sample:

$$\begin{aligned}
 U_{\text{def}} &= s \mu^{(1)} \left(2Ae_0 + \frac{(d+2s) \tau_{\text{ext}}}{2s \mu^{(1)} + d \mu^{(2)}} \right)^2 + \frac{d}{2} \mu^{(2)} \left(\frac{(d+2s) \tau_{\text{ext}}}{2s \mu^{(1)} + d \mu^{(2)}} \right)^2 + \\
 &\quad + \frac{32 e_0^2 w \mu^{(1)} \mu^{(2)}}{\pi^3} \sum_{n=1}^{\infty} \frac{\sin^2 n\pi \frac{A+1}{2} \tanh \frac{n\pi d}{2w} \tanh \frac{n\pi s}{w}}{n^3 (\mu^{(1)} \tanh \frac{n\pi s}{w} + \mu^{(2)} \tanh \frac{n\pi d}{2w})}
 \end{aligned} \tag{F.9}$$

Analogically, using eq. (F.8) we have got the deformation energy of a clamped sample:

$$U_{\text{def}} = \frac{2su_w^2\mu^{(1)} + d(u_w - 2Ae_0w)^2\mu^{(2)}}{2w^2} + \frac{32e_0^2w\mu^{(1)}\mu^{(2)}}{\pi^3} \sum_{n=1}^{\infty} \frac{\sin^2 n\pi \frac{A+1}{2} \tanh \frac{n\pi d}{2w} \coth \frac{n\pi s}{w}}{n^3 (\mu^{(1)} \coth \frac{n\pi s}{w} + \mu^{(2)} \tanh \frac{n\pi d}{2w})} \quad (\text{F.10})$$

The graphic representation of strain in a free sample is shown in fig.18 in the absence of external mechanical force a) and when the external mechanical stress is applied b). Four ferroelastic domains can be recognized in the center of each picture. The characteristic profile of the vector of mechanical displacement can help to accept the mechanical deformation of both central ferroic part and the passive surface layer as a source of restoring force acting on domain wall.

We can see that ratios of expressions for the effective values of $\epsilon_0\epsilon_{33}$, d_{36} and s_{66} are independent on the geometry of the sample. Evaluating these ratios we get a very realistic results which suggest that our model could be applicable to real samples; see the comparison of surface model theoretical predictions with experimental data taken by Štula et. al. [14].

		Exp. Data	Theory
$\frac{\epsilon_0\epsilon_{33}}{d_{36}}$	$[\text{C m}^{-2}]$	4.6	2.7
$\frac{\epsilon_0\epsilon_{33}}{s_{66}}$	$[\text{C}^2 \text{m}^{-4}]$	20.3	6.9
$\frac{d_{36}}{s_{66}}$	$[\text{C m}^{-2}]$	4.4	2.6

FIGURE 17: Theoretical prediction of the surface layer model and experimental data comparison.

We have to point out that our model could be improved. We assume that surface layer permittivity and elastic stiffness equal ones of the central part, which is a crude approximation. Spatial distribution of the material constants is more complicated than in a simple surface model. We also neglect the intrinsic piezoelectric effect in this article.

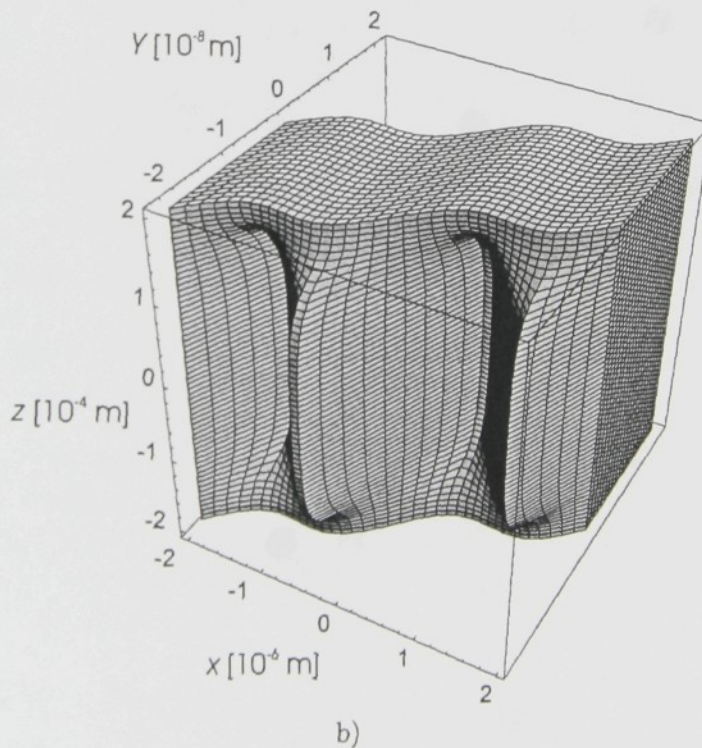
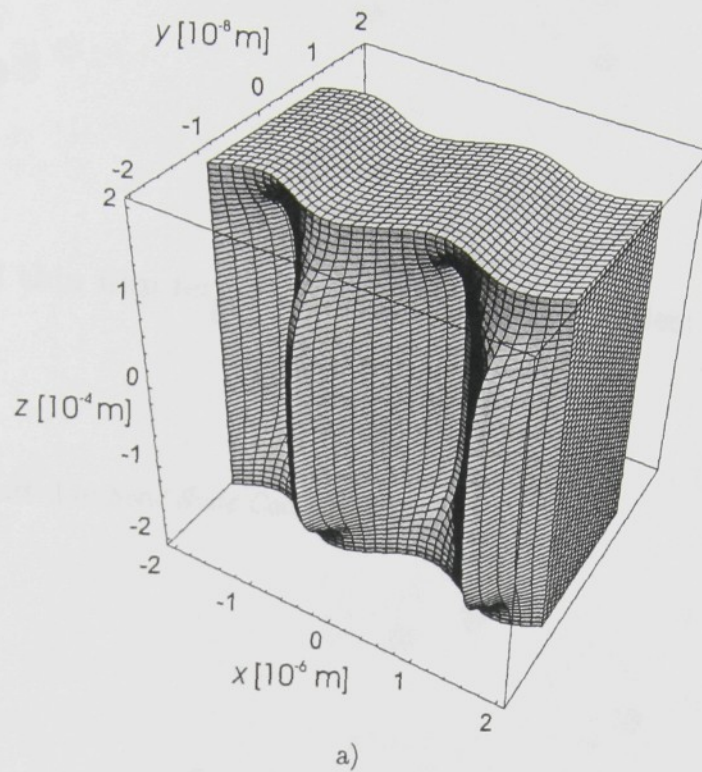


FIGURE 18: Graphic representation of strain in a free sample a) in the absence of external mechanical force, b) when the external mechanical stress is applied.

Paper G

Plate-like and thin film ferroelectric-ferroelastic samples: Extrinsic properties

Paper will be submitted to *Solid State Communications*

PLATE-LIKE AND THIN FILM FERROELECTRIC-FERROELASTIC SAMPLES: EXTRINSIC PROPERTIES

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Abstract

The influence of electrode thickness on the values of extrinsic (i.e. domain wall) contributions to relative permittivity ϵ_{33} , piezoelectric coefficients d_{36} and elastic moduli s_{66} in electroded free-standing KDP and BT samples including those in form of thin films are examined theoretically on the basis of rigorous solution of the associated electrostatics and elasticity problems. Moreover, the intrinsic piezoelectric effect is taken into account. The both electric and elastic energies are calculated. The condition for the equilibrium domain structure configuration is used to express analytically and numerically results of mentioned extrinsic contributions. The effect of restoring force acting on the domain wall due to mechanical interaction of the ferroelastic crystalline sample and metal electrode is discussed.

Keywords: Extrinsic contributions, free-standing films, electroded samples

G.1. INTRODUCTION

Extrinsic contributions play an essential role in macroscopic properties of ferroelectrics: extremely slight domain wall motions can strongly influence dielectric, piezoelectric as well as elastic properties measured in applied fields of very low intensity. To get nonzero contributions $\Delta\epsilon$, Δd , Δs to these properties, a restoring force must be present which keeps a domain wall in its original position. Pinning to lattice defects plays a significant role [1, 2, 3]. However, boundary conditions can be also important. A ferroelectric sample is often considered to be in contact with a ferroelectrically passive dielectric layer between the medium and the electrode. Shifts of domain walls change the electrostatic energy, providing the source of a restoring force. This situation was considered for ferroelectric single crystals both nonferroelastic [G4,5] as well as ferroelastic [G6]. While most attention was paid to extrinsic permittivity, it is known that in crystals of some ferroics all extrinsic contributions $\Delta\epsilon$, Δd , Δs play a significant role. Examples are KDP and related materials [G7]. The investigated samples are always plate-like, covered with metallic electrodes. In the present paper we discuss the extrinsic properties of a sample which is homogeneous and intend to show that the electrode-sample elastic interaction may be of importance. We consider a ferroic representing the species $\bar{4}2m - mm2$.

G.2. DESCRIPTION OF THE MODEL

We consider a plate-like sample of infinite area with major surfaces perpendicular to the ferroelectric axis z . The material of the central part (2) of thickness d is both ferroelectric and ferroelastic; with antiparallel 180° domains. This ferroic part is covered by metal electrodes (1,3)

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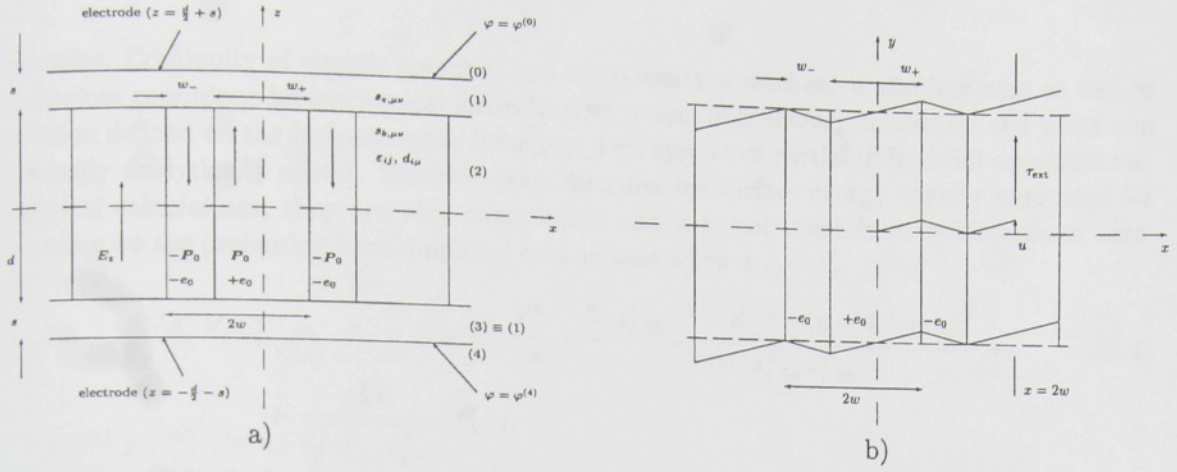


FIGURE G.1: Geometry of the model. a) side view, b) top view

of thickness s . We shall approximate the material of the ferroic phase by equations of state

$$D_i = P_{0,i} + \epsilon_0 \epsilon_{ij}^T E_j + d_{ikl} \tau_{kl}, \quad (G.1)$$

$$e_{ij} = e_{0,ij} + s_{ijkl}^E \tau_{kl} + d_{kij} E_k, \quad (G.2)$$

where e_{ij} resp. τ_{ij} is the strain resp. stress tensor, $e_{0,ij}$ is the spontaneous strain tensor. We suppose that the only $e_{0,12} = e_{0,21} = \pm e_S$ are its nonzero components in the w_+ resp. w_- domain, see Fig.G.1a). The sample is simultaneously spontaneously polarized. Spontaneous polarization P_S and spontaneous strain e_S are interconnected with relation

$$\frac{P_S}{e_S} = \frac{8 d_{36}}{s_{b,66}^E}.$$

We introduce the asymmetry factor

$$A = \frac{w_+ - w_-}{w_+ + w_-} = \frac{w_+ - w_-}{2w}, \quad (G.3)$$

where $2w = w_+ + w_-$ is domain structure period.

In the preceding equations we neglect nonlinear terms; for 2nd order phase transitions this limits the validity of our calculations to the temperature region not very close below the temperature T_C . Domain walls are assumed to have a surface energy density σ_w and zero thickness. For simplicity we approximate the elastically anisotropic material of the sample in the ferroic phase by one which reflect the anisotropy of the parent phase only; i.e. we neglect the morphic elastic moduli and piezoelectric coefficients. We assume that the material properties of neighbouring domains do not differ. 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 electric source. It is evident that metal electrode is nonpiezoelectric and ideally conducting. When we apply the constant external stress $\tau_{\text{ext},12} = \tau_{\text{ext}}$, the sample should be deformed with shear strain $e_{12}^{\text{eff}} = u/4w$.

G.3. SURFACE ENERGY DENSITY OF THE SYSTEM

In what follows we consider two kinds of energy, calculated per unit surface area. First domain wall energy and second electrostatic and elastic energy density, whose volume energy density is $\frac{1}{2} E_i (D_i - P_{0,i}) + \frac{1}{2} \tau_{ij} (e_{ij} - e_{0,ij})$.

At first the very complicated system of partial differential equations have to be solved for electric potential in the bulk and the vector of mechanical displacement in the bulk and in the

electrodes. Continuity of electric potential and components of mechanical displacement as well as equilibrium conditions for mechanical forces lead to system of boundary conditions and transition condition defined on the bulk-electrode interface. This system of partial differential equations can be exactly analytically solved. However exact formulas for surface energy density were used for numerical calculations, they are very complicated and it is not possible to publish them here. Therefore we are presenting here simplified ones in case when $d_{ijk} \equiv 0$.

$$U(A, V, u) = \sigma_w \frac{d}{w} + \varepsilon_0 \varepsilon_{33}^e \frac{V^2}{2d} + \frac{2s_{b,66}^E u^2 + d s_{e,66}^E (u - 4A e_S w)^2}{8w^2 s_{e,66}^E s_{b,66}^E} + \frac{e_S^2 w}{\sqrt{s_{b,44}^E s_{b,66}^E}} f(A), \quad (G.4)$$

where

$$f(A) = \sum_{n=1}^{\infty} \frac{32 \sin^2 n\pi \frac{A+1}{2}}{n^3 \pi^3 \left(\coth \sqrt{\frac{s_{e,44}^E}{s_{e,66}^E}} \frac{n\pi s}{w} + \sqrt{\frac{s_{e,44}^E s_{e,66}^E}{s_{b,44}^E s_{b,66}^E}} \coth \sqrt{\frac{s_{b,44}^E}{s_{b,66}^E}} \frac{n\pi d}{2w} \right)} \quad (G.5)$$

is dimensionless function. In the preceding two formulas symbols $s_{e,\mu\nu}^E$ resp. $s_{b,\mu\nu}^E$ stand for elastic compliance matrix component of the electrode resp. bulk.

The infinitesimal work of external sources should be taken into consideration when discussing the variations of the energy of the isolated system sample + sources. Infinitesimal work of the electric source at constant voltage V per unit area of the sample is

$$\delta W_{el} = V \delta \sigma_0, \quad (G.6)$$

where σ_0 is constant Fourier component of the free charge density on the positive electrode, calculated as

$$\sigma_0(A, V, u) = A P_S + \varepsilon_0 \varepsilon_{33}^e \frac{V}{d} + \frac{2 d_{36}}{s_{b,66}^E w} (u - 4A e_S w). \quad (G.7)$$

Infinitesimal work of the mechanical source deforming the sample is

$$\delta W_{def} = \tau_{ext} \frac{d}{2w} \delta u, \quad (G.8)$$

The equilibrium domain structure in the applied electric field and mechanical stress can be calculated in the following way. First, from equation

$$\frac{\partial}{\partial u} (U - V \sigma_0) = F_{ext} \quad (G.9)$$

we easily obtain mechanical response $u = u(A, V, \tau_{ext})$ of the sample to the external force per unit area of the sample $F_{ext} = \tau_{ext} \frac{d}{2w}$ at given domain structure configuration A . Second, the equilibrium domain structure we get from condition that variation of "the total energy of the sample and the energy of external sources" equals zero in equilibrium

$$\frac{\partial U}{\partial A} \delta A - \delta W_{el} - \delta W_{def} = \left(\frac{\partial U}{\partial A} - V \frac{\partial \sigma_0}{\partial A} - \tau_{ext} \frac{d}{2w} \frac{\partial u}{\partial A} \right) \delta A = 0. \quad (G.10)$$

For samples of thickness $d > d_{crit}$, where

$$d_{crit} = 36.4 \frac{\sigma_w}{e_S^2} \left(\sqrt{s_{e,44}^E s_{e,66}^E} + \sqrt{s_{b,44}^E s_{b,66}^E} \right), \quad (G.11)$$

we can approximate $f(A)$ by a more simple function and solving the problem (G.10) we finally get simplified analytical expression:

$$A^{eq} = s_{e,66}^E \frac{P_S V + 2 d e_S \tau}{8 s e_S^2 (1 - X)}, \quad (G.12)$$

where

$$X = \frac{(2 \log 2) (d s_{e,66}^E + 2s s_{b,66}^E) w^{\text{eq}}(0)}{\pi d s \left(\sqrt{s_{e,44}^E s_{e,66}^E} + \sqrt{s_{b,44}^E s_{b,66}^E} \right)}$$

is a small correction and

$$w^{\text{eq}}(A) \approx \frac{1}{e_s} \sqrt{\frac{0.92 \sigma_w d}{1 - A^2} \left(\sqrt{s_{e,44}^E s_{e,66}^E} + \sqrt{s_{b,44}^E s_{b,66}^E} \right)} \quad (\text{G.13})$$

is an approximation of equilibrium domain width for slightly asymmetric domain structure.

G.4. EFFECTIVE VALUES OF ELECTROMECHANICAL PROPERTIES, EXTRINSIC CONTRIBUTIONS

The values of D_3 component of electrical displacement vector and e_{12} component of strain tensor averaged per unit area of the sample are defined by following formulas

$$D_3^{\text{eff}} = \sigma_0(V, \tau_{\text{ext}}, A) = \varepsilon_0 \varepsilon_{33}^{\tau, \text{eff}} E_3^{\text{eff}} + d_{36}^{\text{eff}} \tau_6 = \varepsilon_0 \varepsilon_{33}^{\tau, \text{eff}} \frac{V}{d} + d_{36}^{\text{eff}} \tau_{\text{ext}}, \quad (\text{G.14})$$

$$e_6^{\text{eff}} = \frac{1}{2w} u(V, \tau_{\text{ext}}, A) = s_{66}^{E, \text{eff}} \tau_6 + d_{36}^{\text{eff}} E_3^{\text{eff}} = s_{66}^{E, \text{eff}} \tau_{\text{ext}} + d_{36}^{\text{eff}} \frac{V}{d}. \quad (\text{G.15})$$

The effective material constants are

$$\varepsilon_0 \varepsilon_{33}^{\tau, \text{eff}} = d \left(\frac{\partial \sigma_0}{\partial V} + \frac{\partial \sigma_0}{\partial A} \frac{\partial A^{\text{eq}}}{\partial V} \right) \Big|_{A=A^{\text{eq}}}, \quad (\text{G.16})$$

$$s_{66}^{E, \text{eff}} = \frac{1}{2w} \left(\frac{\partial u}{\partial \tau_{\text{ext}}} + \frac{\partial u}{\partial A} \frac{\partial A^{\text{eq}}}{\partial \tau_{\text{ext}}} \right) \Big|_{A=A^{\text{eq}}}, \quad (\text{G.17})$$

$$d_{36}^{\text{eff}} = \frac{d}{2w} \left(\frac{\partial u}{\partial V} + \frac{\partial u}{\partial A} \frac{\partial A^{\text{eq}}}{\partial V} \right) \Big|_{A=A^{\text{eq}}} = \left(\frac{\partial \sigma_0}{\partial \tau_{\text{ext}}} + \frac{\partial \sigma_0}{\partial A} \frac{\partial A^{\text{eq}}}{\partial \tau_{\text{ext}}} \right) \Big|_{A=A^{\text{eq}}}. \quad (\text{G.18})$$

In the preceeding expressions we can recognize the intrinsic contributions (the first term on the right hand side) and the extrinsic ones (the first term on the right hand side). Using eq. (G.12) in case of narrow domains in the sample we finally get

$$\varepsilon_{33}^{\tau, \text{eff}} = \varepsilon_0 \varepsilon_{33}^e + \varepsilon_0 (\varepsilon_{33}^{\tau} - \varepsilon_{33}^e) \frac{d}{2s} \frac{s_{e,66}^E}{s_{b,66}^E} \left(1 + \frac{kX}{1-X} \right), \quad (\text{G.19})$$

$$s_{66}^{E, \text{eff}} = k s_{b,66}^E + s_{e,66}^E \frac{d}{2s} \frac{k}{1-X}, \quad (\text{G.20})$$

$$d_{36}^{\text{eff}} = 4 d_{36} \frac{s_{e,66}^E}{s_{b,66}^E} \frac{d}{2s} \left(1 + \frac{kX}{1-X} \right), \quad (\text{G.21})$$

where

$$k = \left(1 + \frac{s_{b,66}^E}{s_{e,66}^E} \frac{2s}{d} \right)^{-1} \approx 1.$$

G.5. DISCUSSION

Formulae (G.19-G.21) represent the analytical approximations of the effective values of relative permittivity ε_{33} , elastic compliance s_{66} and piezoelectric coefficient d_{36} . It is possible to separate the intrinsic contribution (terms on the left hand side) from the extrinsic one (terms on the right hand side) in eqs. (G.19-G.21). We can see that the extrinsic contribution to the relative permittivity is about two orders lower than the extrinsic ones to the elastic compliance s_{66}^E . The exact numerical results are shown in fig. G.2, where the effect of the electrode thickness is represented.

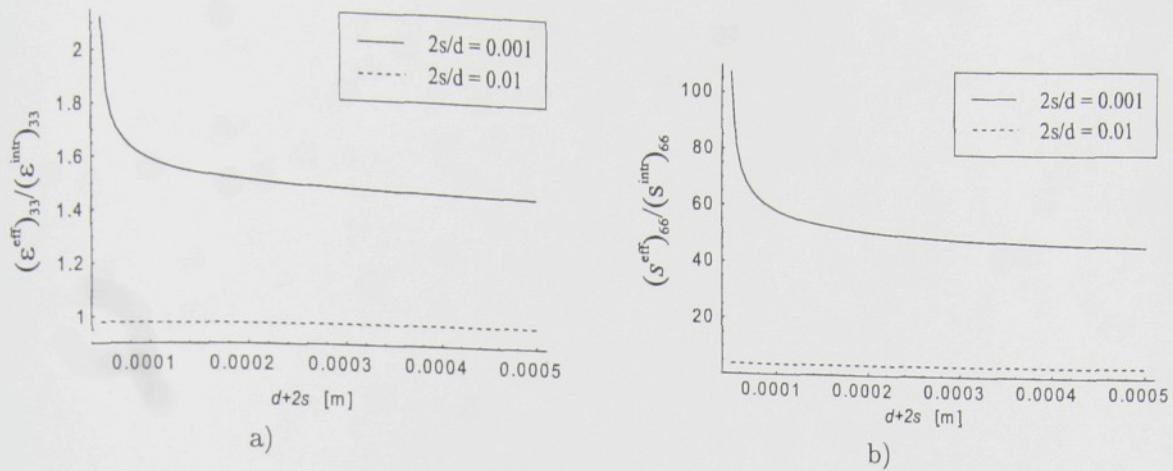


FIGURE G.2: Dependencies of effective values over intrinsic value of a) relative permittivity ϵ_{33} , b) elastic compliance s_{66}

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Summary

Resume

We have presented results of our investigation of the influence of domain structures on macroscopic properties of ferroic samples. It is known that some of these properties measured on multidomain samples frequently differ from those measured on single domain samples. The simple thermodynamic theory has been used to obtain the theoretical predictions of the anomalous temperature dependencies of ϵ_{33}^E , s_{66}^E , d_{36} for single domain samples, which undergo the first order phase transition close to the second order one $42\text{m} - \text{mm}2$. The difference between values of mentioned material constants of single domains and multidomain samples leads to one possible conclusion: the response of domain structure to the external electric field and mechanical stress influences the effective values of dielectric, elastic and electromechanical constants.

The ferroelectric domain wall shifts cause the redistribution of bound charges in the region close to the electrodes. Resulting change of electric field affect the value of free charge that is present on the electrode during measurement process. Therefore, domain wall motion can contribute to the value of dielectric constant ϵ or piezoelectric coefficient d , if the sample is simultaneously ferroelastic. The very similar situation is set in pure ferroelastic samples. The shift of the domain wall between two ferroelastic domains is interconnected with the change of average shear strain of the sample. It is evident that domain wall motion can contribute to elastic compliance s in ferroelastic samples.

One essential condition is necessary for existence of extrinsic (i.e. domain walls shifts) contributions — the restoring force acting on the domain wall when it is moved from its original position. The several origins of restoring forces can exist: first pinning to crystal lattice defects, second interaction between domain walls. Speaking about ceramics, the domain wall shifts result in a change of a shape of the grain. This grain is clamped by surrounding grains and internal stress appear. In the single crystal there exists another origin of restoring force. It is known that samples of ferroelectric single crystal often possess a nonferroelectric surface layer whose properties differ from those of the bulk. Then bound charges of spontaneous polarization are not compensated by the free charges of the electrodes. The depolarizing field is present in the sample and the increase of its energy is a source of restoring force, when the domain wall shifts from its equilibrium position.

Also the mechanical interaction between particular parts of the system "bulk + surface layer + electrode" takes an important role in a configuration of equilibrium domain structure. When the passive layer is present on a bulk crystal in the paraelectric phase, local stresses appear in the region of interface between central part and surface layer during phase transition. Then the multidomain single crystal is slightly clamped by the passive surface layers. Similarly, when the domain wall shifts from its equilibrium position the increase of elastic energy of the local stresses is a source of restoring force. An equally important situation is the case when the ferroelectric ferroelastic sample is clamped by metal electrodes.

The first step of our investigation of extrinsic contributions was the exact calculation of equilibrium response of ferroelectric domain structure to external electric field. Some simplifications have been assumed: we have considered an ideally movable 180° walls, influence of crystal defects

with the experimental data [14] is shown in fig. 17. So we get a very realistic results, which suggest that our model could be applicable to real samples.

The last thing we would like to mention is the applicability of our model. First we can apply this model on ferroics of any composition when a passive layer is formed during sample preparation. That are e.g. all crystals of KDP family and ferroelastic crystals of lithium thallium tartrate ($\text{LiTlC}_4\text{H}_4\text{O}_6 \cdot \text{H}_2\text{O}$) or ammonium lithium sulphate ($(\text{NH}_4)_4\text{LiH}_3(\text{SO}_4)_4$), which are both water-soluble.

The second group is formed by other ferroics in which the surface layer is formed during crystal growth, like Remeika-grown BaTiO_3 . We can also say that for ceramic grains our calculations are more explicit than previous qualitative approach of Arlt and Pertsev. Concretely, each ceramic grain is splitted by domain walls into many domains. This small domain structure can be also considered as lamellar ferroic domain structure, where the surrounding grains can be considered as the passive surface layer. Therefore, the similar mechanism takes place, when a domain wall shifts from its equilibrium position in a ceramic grain. Our model gives treatment for evaluation of the restoring force and therefore, the extrinsic contributions to macroscopic properties of ceramic samples. Finally, the elastic part of our calculation is applicable to thin ferroelastic films due to interaction of a film with a substrate.

Nevertheless, the extreme decrease of extrinsic contributions below the 35 K temperature range under transition temperature cannot be explained ("freezing domain wall motions") on the basis of this simple model. Some considerations of our theory are probably violated. Also quantum mechanical effects may influence the movability of the domain walls, but this goes beyond the scope of this model.

Summary

Motivace práce

Mikroelektromechanická zařízení, jako aktuátory, mikroakcelerometry, gyroskopy a další elektromechanické převodníky jsou ve velmi intenzivním zájmu vědců a techniků. Základní roli v těchto systémech hrají piezoelektricky aktivní systémy. Proto současný vědecký výzkum věnuje velkou pozornost výzkumu právě těchto systémů, a to jak experimentálnímu, tak teoretickému.

Pro převod mechanických napětí nebo deformací na elektrické signály se často používají piezoelektrické keramiky nebo krystaly, a to je také základním principem jejich funkce v mikroelektromechanických zařízeních. Důležitým měřítkem pro výběr nejlepšího materiálu je tzv. *koeficient elektromechanické vazby*. Z tohoto důvodu jsou často používány feroelektrické piezoelektrické materiály, konkrétně keramiky. Z mnoha experimentálních pozorování je dobře známý vliv doménových struktur na elektromechanické chování těchto materiálů.

Role doménových struktur v piezoelektricky aktivních systémech

Hlavním cílem této práce je vysvětlit otázku: "Jak může doménová struktura ovlivnit fyzikální vlastnosti feroických vzorků?" Abychom odpověděli na tuto otázku, vyjdeme ze základních fyzikálních pozorování teplotních závislostí relativní permitivity ϵ_{33} , elastických poddajností s_{66} a piezoelektrických koeficientů d_{36} monokrystalů KDP, DKDP, RbDP atd. Tyto látky procházejí fázovým přechodem prvního druhu $42m - mm2$, který je blízký fázovému přechodu druhého druhu. Teplotní závislosti složek tenzorů relativní permitivity ϵ_{33} , elastických poddajností s_{66} a piezoelektrických koeficientů d_{36} jeví velmi typické anomální chování. Vyjdeme z jednoduché termodynamické teorie a určíme teplotní závislosti s těchto materiálových konstant. Jak můžeme vidět z experimentálních pozorování, teplotní závislosti makroskopických hodnot těchto materiálových konstant nesouhlasí s teoreticky předpovězenými hodnotami, jsou-li měřeny na mnohodoménových monokrystalech. Budeme proto diskutovat vliv doménových struktur na makroskopické vlastnosti vzorků opatřených elektrodami.

Model s povrchovou vrstvou

Nejzajímavější otázka zní: "Jak můžeme vysvětlit nesouhlas teoreticky předpovězených teplotních závislostí s experimentálními daty, které byly pořízeny na mnohodoménových vzorcích?" Tento problém byl adresován mnoha autory jak teoreticky, tak experimentálně. Ve většině případů je studován pouze vnější příspěvek k permitivitě. V těchto pracech je předpokládána existence vratné síly — nutné podmínky existence vnějších příspěvků, ačkoli její původ není nikde specifikován. Později Arlt a Petsev [9] použili komplikovanější model: při posuvu doménových stěn se objeví na hranici zrn nekompenzovaný vázaný náboj tvořící elektrické pole. Současně, jsou-li uvažované domény feroelastické, je výsledkem tohoto posuvu vznik mechanického napětí v okolních zrnech.

Posuv doménových stěn je tedy spojen se vzrůstem energie elektrického pole a elastické deformace, který vede ke vzniku vratné síly. Výsledky těchto teorií byly úspěšně porovnány s experimentálními daty ke všem třem zmíněným příspěvkům $\Delta\epsilon$, Δs a Δd [8, 9].

V monokrystalech je zdroj vratné síly obvykle spojen se zachytáváním doménových stěn na defektech krystalové mříže. Kromě toho, může v monokrystalech existovat ještě jeden možný zdroj vratné síly, který je presentován v této práci — *Model s povrchovou vrstvou*. Geometrie modelu je zobrazena na obr.9 a). Skládá se z centrální feroické části tloušťky d , která je oddělena od elektrod neferoickou pasivní vrstvou tloušťky s . Napětí na elektrodách je označeno V . Užitím tohoto modelu může být určena vratná síla působící na doménovou stěnu, je-li vychýlena ze své rovnovážné polohy. Odtud pak vnější příspěvky k elektromechanickým vlastnostem vzorku.

Shrnutí

Prezentovali jsme výsledky našeho vyšetřování vlivu doménových struktur na makroskopické vlastnosti feroických vzorků. Je známo, že se některé z těchto vlastností měřené na mnohadoménových vzorcích liší od stejných vlastností měřených na jednodoménových vzorcích. Užili jsme jednoduchou termodynamickou teorii, abychom odvodili teoretické předpovědi anomálních teplotních závislostí ϵ_{33}^E , s_{66}^E , d_{36} jednodoménových vzorků, které procházejí fázovým přechodem $\bar{4}2m - mm2$ prvního druhu, který je blízký přechodu druhého druhu. Rozdíl mezi hodnotami uvedených materiálových konstant jednodoménových a mnohadoménových vzorků vede k jednomu možnému závěru: reakce doménové struktury na vnější elektrické pole a mechanické napětí ovlivňuje efektivní hodnoty dielektrických, elastických a elektromechanických konstant.

Posuvy feroelektrických doménových stěn způsobují redistribuci vázaných nábojů v oblasti blízko elektrod. Výsledná změna elektrického pole ovlivní hodnotu volného náboje, který je přítomen na elektrodě během procesu měření. Proto posuv doménových stěn může přispět k hodnotě relativní permitivity ϵ nebo piezoelektrického koeficientu, je-li vzorek současně feroelastický. Obdobná situace nastává v čistě feroelastických vzorcích. Posuv doménové stěny mezi dvěma feroelastickými doménami je spojen se změnou střední stříhové deformace vzorku. Je jasné, že posuv doménových stěn může přispět k hodnotě elastické poddajnosti. s ve feroelastickém vzorku.

Jedna podstatná podmínka je nezbytná pro existenci vnějších příspěvků (t.j. příspěvků posuvů doménových stěn) — vratná síla působící na doménovou stěnu, je-li vychýlena ze své původní pozice. Existuje několik zdrojů vratných sil: zaprvé zachytávání doménových stěn na defekty krystalové mříže, zadruhé interakce mezi doménovými stěnami. Mluvíme-li o keramice, výsledek posuvu doménových stěn je změna tvaru zrna. Poněvadž je toto zrno upnuto okolními zrny, objeví se vnitřní mechanická pnutí. V případě monokrystalu existuje ještě jeden zdroj vratné síly. Je známo, že vzorky feroelektrických monokrystalů často mají neferoelektrické povrchové vrstvy, jejichž vlastnosti se často velmi liší od vlastností krystalu. Vázané náboje od spontánní polarizace nejsou kompenzovány volným nábojem na elektrodách. Ve vzorku je potom přítomno depolarizační pole a nárůst jeho energie při posuvu doménových stěn z jejich rovnovážných poloh je zdrojem vratné síly.

Také mechanická interakce mezi jednotlivými částmi systému "centrální část + povrchová vrstva + elektroda" hraje důležitou úlohu v konfiguraci rovnovážné doménové struktury. V přítomnosti povrchové vrstvy krystalu v paraelastické fázi se při fázovém přechodu vytvoří lokální pnutí v oblasti rozhraní mezi centrální částí a povrchovou vrstvou. Potom je mnohadoménový vzorek slabě upínán pasivními povrchovými vrstvami. Obdobně, při vychýlení doménových stěn ze svých rovnovážných poloh se zvýší hodnota elastické energie lokálních pnutí a to je zdrojem vratné síly. Stejně důležitá situace nastane v případě feroelektrického feroelastického vzorku upnutého kovovými elektrodami.

Prvním krokem našeho vyšetřování vnějších příspěvků byl přesný výpočet rovnovážné reakce feroelektrické doménové struktury na vnější elektrické pole. Užili jsme určitá zjednodušení. V článku A jsme předpokládali ideálně pohyblivé 180° doménové stěny, vliv krystalových defektů a mechanické interakce jednotlivých částí systému byl také zanedbán. Na druhé straně byla v článcích C a D předpokládána kompenzace vázaných nábojů. Toto stínění je způsobeno injekcí volných nábojů z elektrod díky nenulové malé vodivosti povrchových vrstev oddělujících elektrody od vzorku. Také je diskutován vliv tloušťky pasivní vrstvy.

Byly provedeny určité aproximace, abychom mohli vyjádřit analytické formule (A.2 - A.5) resp. (D.2 - D.3) popisující konfiguraci rovnovážné doménové struktury. Naše zjednodušení jsou platná pro rovnovážné doménové struktury s úzkými doménami. Tyto doménové struktury jsou přítomny v relativně tlustých vzorcích, viz obr. D.3. Nalezli jsme, že rovnovážná reakce doménové struktury na vnější elektrické pole silně závisí na tloušťce povrchové vrstvy, stejně tak jako na tloušťce celého vzorku. Reakce doménových stěn je lineární vzhledem ke vnějšímu elektrickému poli. Na druhé straně přesné numerické výsledky se liší od analytických, je-li tloušťka povrchové vrstvy velmi malá. Rovnovážná reakce tenkého feroelektrického filmu je obecně nelineární.

Na základě reakce doménové struktury na vnější elektrické pole můžeme jednoduše vypočítat efektivní hodnotu vektoru elektrické indukce ve vzorku, a tedy i efektivní hodnotu relativní permittivity ϵ_{33} . Jednoduchý výsledek je prezentován v článku B. Můžeme vidět, že vnější příspěvek k relativní permittivitě je přímo úměrný $d/2s$. To znamená, že velmi tenké povrchové vrstvy mohou vést k předpokládanému zvětšení permittivity. Nicméně jednoduchý vztah $s \rightarrow 0 \Rightarrow \epsilon_{33}^{\text{extrinsic}} \rightarrow \infty$ je nesprávný. Limita $s \rightarrow 0$ popisuje nepřítomnost povrchové vrstvy, ale bez povrchové vrstvy nemohou existovat žádné vnější příspěvky.

Předpokládáme-li feroelastický vzorek, můžeme vyjádřit vnější příspěvek k elastické poddajnosti s_{66}^E při konstantním elektrickém poli. A proto jsme v článku F použili důmyslnější přístup: mechanická interakce mezi jednotlivými částmi systému je brána jako zdroj vratné síly.

Předpokládáme-li, že je vzorek současně feroelektrický a feroelastický, projeví se vnější příspěvek k piezoelektrickému koeficientu d_{36} , viz články E a F. Avšak jeden velmi limitující faktor omezuje existenci vnější piezoelektriny: materiál musí být piezoelektrický v paraelektrické fázi. To klade omezení na množinu materiálů, ve kterých se může popsaný mechanismus projevit.

Velmi důležitá otázka, kterou musíme diskutovat, je: "Jak můžeme dokázat správnost našich výpočtů?" Ve skutečnosti je pouze pro krystal RbDP dokázáno, že jako funkce teploty si jsou všechny vnější příspěvky přímo úměrné. Tento důkaz byl proveden Štulou a kol., viz obr. 19. Také naše výpočty vedou k podobnému závěru. Podíly vnějších příspěvků nezávisí na geometrii modelu. Srovnání teoretických předpovědí modelu s povrchovou vrstvou s experimentálními daty [14] je ukázáno na obr. 17. Dostali jsme tedy realistické výsledky, které naznačují, že náš model může být aplikovatelný na reálné vzorky.

Poslední věc, kterou bychom měli zmínit, je použitelnost našeho modelu. Zprvce můžeme tento model aplikovat na feroika libovolné kompozice, kdy se během přípravy vzorku vytvoří povrchová vrstva. To jest např. všechny krystaly skupiny KDP a feroelastik $\text{LiTiC}_4\text{H}_4\text{O}_6 \cdot \text{H}_2\text{O}$ nebo $(\text{NH}_4)_4\text{LiH}_3(\text{SO}_4)_4$, které jsou oba vodou rozpustné.

Druhá skupina je tvořena dalšími feroiky, ve kterých se povrchová vrstva vytvoří během růstu krystalu, jako Remeika-growth BaTiO_3 . Můžeme také říci, že pro keramické materiály je náš přístup přesnější než předchozí kvalitativní přístup Arlta a Pertseva. Konkrétně každé keramické zrno je rozděleno doménovými stěnami do mnoha domén. Tyto malé doménové struktury mohou být také považovány za deskové feroické doménové struktury, ve kterých povrchovou vrstvu tvoří okolní zrna. A proto se zde uplatní podobný mechanismus, vychýlí-li se doménové stěny ze svých rovnovážných poloh. Náš model dává návod pro výpočet vratné síly, a tedy vnější příspěvek

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Oponentský posudek disertační práce Ing. Pavla Mokrého
The role of domain structures in the piezoelectrically active systems

Tématem předložené disertační práce je odvození příspěvků pohybu doménových stěn k anomálním průběhům složek permitivity a elastického i piezoelektrického koeficientu pro model jednodoménového ferroelektrika s neferoelektrickou vrstvou. Hlavní část disertace tvoří šest publikovaných prací a jeden rukopis, připravený k odeslání do časopisu Solid State Communications. Většina publikací je doplněna krátkým vysvětlujícím komentářem a dalšími obrázky.

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V úvodu jsou pro jednodoménový krystal typu KDP odvozeny teplotní závislosti složek permitivity, elastického a piezoelektrického koeficientu s anomálními teplotními závislostmi. Jejich porovnání s experimentálními průběhy naměřenými na jednodoménových a mnohadoménových krystalech ukazuje přesvědčivě podstatný tzv. „vnější“ příspěvek doménové struktury k těmto koeficientům ve ferroelektrické fázi.

Pouze jediná stránka úvodu je věnována dosavadním interpretacím tohoto vnějšího příspěvku a modelu neferoelektrické povrchové vrstvy. Jsou zde citovány pouze dvě práce Arlta a spolupracovníků, kteří vysvětlují vnější příspěvky pohybem doménových stěn a srovnávají své teoretické závěry s experimentálními daty. I když se zabývají jiným typem ferroelektrik než je KDP, domnívám se, že jsou to výsledky natolik příbuzné s tematikou předložené práce, že by si zasloužily podrobnější zmínky. Tím spíše by se zde měly objevit výsledky získané na krystalech rodiny KDP a na příbuzných látkách, zmíněné v práci F.

Třetí část úvodu obsahuje základní rovnice a konstitutivní relace piezoelektrického ferroelektrika. Je z nich patrné, jak složitý matematický problém představuje jejich řešení

v konkrétním případě. V této části postrádám vysvětlení, jaký výchozí výraz pro elektrickou energii byl při výpočtech použit. Je známo (viz např. Landau & Lifšic: Elektrodynamika spojitého prostředí, nebo Kvasnica: Termodynamika), že tento výraz závisí na okrajových podmínkách daného problému. Je např. energie označovaná v práci A jako „free energy“ totožná s „energy density“ v práci F a jaký je vztah mezi vnějšími příspěvky odvozenými v práci F a v předchozích pracích ?

Diskuse výsledků je roztroušena hlavně v práci F, v poznámkách k této práci a v závěrečném shrnutí. Zde zůstává řada drobných, ale i závažnějších otázek otevřena. Tak např. není zřejmé proč číselné hodnoty vnějších příspěvků v Tab. F.1 nejsou porovnány se skutečně naměřenými hodnotami. Také otázka „How we can prove correctness of our calculations ?“ v závěru práce (str. 75) není správně položena, neboť o správnosti výpočtů asi autoři nepochybují, jde spíš o to, zda uvažovaný model odpovídá skutečnosti. Argument, že poměry dvou anomálních vnějších příspěvků jsou nezávislé na teplotě, což je ve shodě s experimentálními výsledky Štuly a ost., nelze - podle mého názoru - považovat za důkaz správnosti použitého modelu, neboť i jiný model může tyto vztahy splňovat (např. tzv. Pippardovy relace dávají obdobné vztahy pro anomální veličiny zcela nezávisle na modelu). Vymrzání vnějších příspěvků při nízkých teplotách je asi nejzávažnějším argumentem proti interpretaci užívající povrchové vrstvy. Ověřování oprávněnosti tohoto modelu není však předmětem této doktorské práce.

Ještě malou poznámku k citacím literatury. Autor je na ně podle mého názoru příliš skoupý. V úvodních partiích není jediná citace týkající se termodynamiky anomálních vlastností, celá obsáhla partie nazvaná „Mathematical approach“ neobsahuje žádný odkaz. V seznamu literatury se nevyskytuje jediná kniha, s výjimkou tabulek Landolt-Boernstein, ale odkaz na ně neobsahuje ani stránku ani jméno autora, jehož výsledky jsou citovány.

Těchto několik kritických poznámek by nemělo zastínit hlavní výsledek celé práce, který spočívá v nalezení explicitních výrazů pro vnější kritické příspěvky permitivity a elastického a piezoelektrického koeficientu pro jasně definovaný model jednoosého feroelektrika s neferoelektrickou povrchovou vrstvou. Tento úkol vyžadoval řešení systému parciálních diferenciálních rovnic s danými okrajovými podmínkami. Vedle numerického řešení byla nalezena i přibližná analytická řešení. Porovnáním těchto dvou přístupů byly stanoveny podmínky pro platnost analytických řešení. Tento velice pěkný výsledek dokládá značnou matematickou erudici i důkladnost a pečlivost, kterou autoři řešení věnovali. Pokud jsou výchozí rovnice správně formulovány, jsou nalezené výrazy dobrým východiskem pro

další ověřování předloženého modelu a mohou sloužit i jako podnět k novým experimentům s uměle vytvořenou mezivrstvou.

Za zmínku stojí vynikající grafická úroveň práce i to, že je napsána anglicky.

Vzhledem k tomu, že na všech publikacích figurují jména několika autorů, měl by ing. Mokřý v průběhu oponentního řízení specifikovat svůj podíl na dosažených výsledcích.

Disertační práce ing. Pavla Mokrého obsahuje podle mého názoru velmi kvalitní teoretické výsledky a splňuje po obsahové i formální stránce požadavky stanovené řádem postgraduálního studia Pedagogické fakulty Technické univerzity v Liberci. Doporučuji ji proto uznat jako práci doktorskou.

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On the Extrinsic Piezoelectricity

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This work presents a continuation of our last paper, concerning the theory of the response of an antiparallel domain structure in a plate-like electroded sample to external electric field. The theory is based on the exact formula for free energy of the system, formed of a central ferroelectric part, isolated from electrodes (with a defined potential difference) by a surface layers. Our calculations are applicable also to thin films. It is usual to use the term "extrinsic" for the contribution of domain walls displacement to macroscopic properties of a sample. In our last paper we discussed the extrinsic contribution to permittivity. In this work we concentrate on extrinsic contribution to piezoelectric coefficients in ferroelectrics which are simultaneously ferroelastics. As an example, we calculate the extrinsic contribution to d_{36} piezoelectric coefficient of RbH_2PO_4 , that was recently measured in a wide range of temperature below Curie point.

Keywords: Ferroelectric domains; extrinsic contributions to piezoelectricity

INTRODUCTION

Samples of ferroelectric single crystals often possess a surface layer. Its existence greatly influences properties of bulk samples^[1,2,3,4] as well as of thin films.^[5] Equilibrium domain structure in the system, mentioned above in the abstract, and the role of the surface layers was first discussed by Bjorkstam and Oettel^[6] in a special case of shorted electrodes. In our recent paper^[7] we reconsidered this

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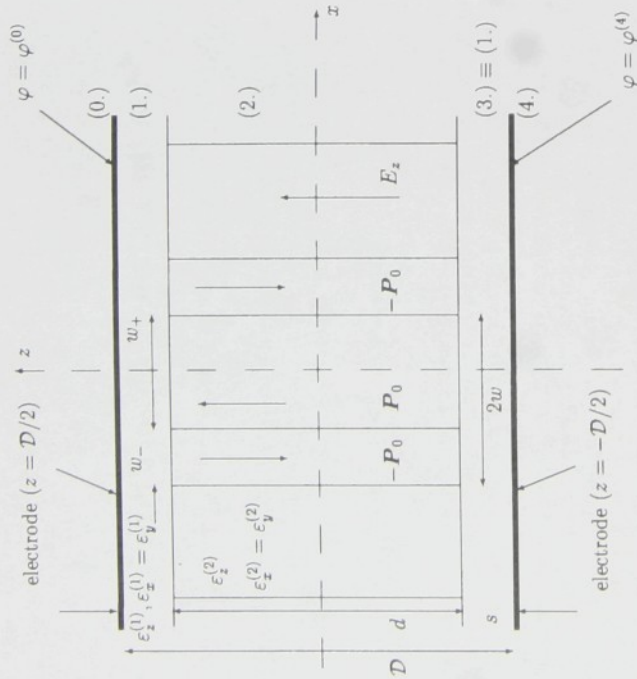


FIGURE 1: Geometry of the model

problem in a general case of nonzero voltage between electrodes, discussing the response of the domain structure to external electric field. Our calculations are valid also for thin films and present, in fact, continuation of our discussion of domain structures of thin films^[8].

In^[7] we used our theoretical results for prediction of extrinsic contribution to permittivity of the sample. In the next two sections we give a short review of notation, description of the model and basic results from^[7]. In last two sections we discuss as an example the extrinsic contribution to d_{36} piezoelectric coefficient of RbH_2PO_4 . We compare our predictions with the recent measurements of record values $\sim 4000 \text{ pC/N}$ in temperature range 35 K under critical temperature 146 K^[9] (see also^[10]).

DESCRIPTION OF THE MODEL

We consider a plate-like electroded sample of infinite area with ma-

jor surfaces perpendicular to the ferroelectric axis z . Central ferroelectric part with antiparallel domains (2.) is separated from the electrodes (0.), (4.) by nonferroelectric layers (1.), (3.) (see Fig. 1). The spatial distribution of the electric field $\mathbf{E}$ is determined by the applied potential difference $V = \varphi^{(4)} - \varphi^{(0)}$ and by the bound charge $\text{div} \mathbf{P}_0$ on the boundary of ferroelectric material, where $\mathbf{P}_0$ stands for spontaneous polarization. Geometrical, electrical and material parameters of the system are shown in Fig. 1. We further introduce the symbols

$$c^{(1),(2)} = \sqrt{\frac{\varepsilon_x^{(1),(2)}}{\varepsilon_x^{(1),(2)}}}, \quad g^{(1),(2)} = \sqrt{\varepsilon_x^{(1),(2)} \varepsilon_z^{(1),(2)}},$$

and several geometrical parameters:

$$B = \frac{2s}{d}$$

the domain pattern factor

$$R = \pi \frac{d}{2w}, \quad 2w = w_+ + w_-$$

and the asymmetry factor

$$A = \frac{w_+ - w_-}{w_+ + w_-}.$$

The ferroelectric material itself is approximated by the equation of state

$$D_i = \varepsilon_0 \varepsilon_{ij} E_j + P_{0i} \quad (1)$$

where only the component P_{0z} is nonzero. This linear approximation limits the validity of our calculations to the temperature region not very close below the transition temperature T_c . Domain walls are assumed to have surface energy density σ_w and zero thickness.

FREE ENERGY OF THE SYSTEM, EQUILIBRIUM DOMAIN STRUCTURE

Rather cumbersome calculations^[7] lead to the following formula for

total free energy surface density (in J m^{-2}) of the system

$$F = \frac{2}{\pi} \sigma_w R + P_0 A \frac{BDP_0 A}{2\epsilon_z^{(1)}(1+B)} - \epsilon_0 \frac{V}{2} + \frac{4P_0^2 D}{\epsilon_0 \pi^2 R(1+B)} \sum_{n=1}^{\infty} \frac{\sin^2(n\frac{\pi}{2}(1+A))}{n^3(g^{(1)} \coth nBRc^{(1)} + g^{(2)} \coth nRc^{(2)})}. \quad (2)$$

The first term represents domain wall contribution while the last one is the depolarization energy. In the second term we recognize the effect of layers (1.) and (3.) and of the applied voltage.

In this model we neglect the mechanical interactions between components of the system. For given slab factor B and voltage V , the equilibrium domain structure, characterized by $R_{eq}(V)$ and $A_{eq}(V)$, corresponds to local minimum of F . In general a minimum can be found by numerical methods, but for $BRc^{(1)} \gg 1$ and $Rc^{(2)} \gg 1$, the $R_{eq}(V)$ and $A_{eq}(V)$ can be approximated by explicit formulae. For purpose of this paper we use the following formula for $A_{eq}(V)$

$$A_{eq}(V) \cong \frac{\epsilon_0 V}{2P_0 D \left[\frac{B}{\epsilon_z^{(1)}(1+B)} - X \right]} \quad (3)$$

where

$$X = \frac{2 \ln 2}{R_{eq}^0 (1+B)(g^{(1)} + g^{(2)})} \left(1 + B \frac{\epsilon_z^{(2)}}{\epsilon_z^{(1)}} \right)$$

is considered as a small correction and R_{eq}^0 is equilibrium value of R for zero voltage V . For the extrinsic contribution to permittivity of the sample we get from (3) (see also⁽⁷⁾)

$$\epsilon_{ext} = \left\{ \left(1 + B \frac{\epsilon_z^{(2)}}{\epsilon_z^{(1)}} \right) \left[\frac{B}{(1+B)\epsilon_z^{(1)}} - X \right] \right\}^{-1} \quad (4)$$

EXTRINSIC PIEZOELECTRICITY

As an example, in this section we work out the approximate prediction of extrinsic contribution to d_{36} of RbH_2PO_4 (RDP), based on our simple model. RDP is a ferroelastic with spontaneous strain S_6^s ,

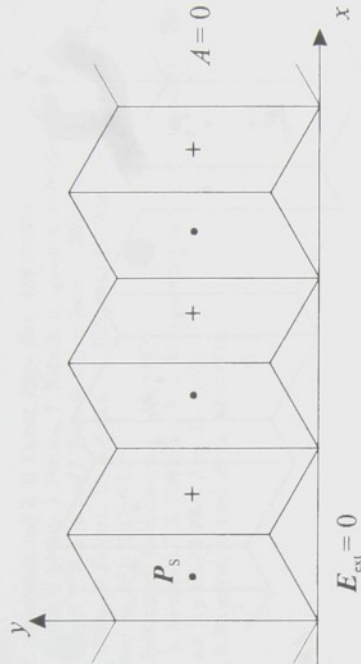


FIGURE 2. Symmetric domain structure with spontaneous strain S_6^s , $E_{ext} = 0$, $A = 0$

opposite in opposite polarized domains. In the Fig.2 there is $x - y$ cut through symmetric domain structure ($A = 0$, $E_{3ext} = \frac{V}{D} = 0$). The situation after application of E_{ext} is shown in Fig.3 ($A \neq 0$). A simple geometric consideration leads to the formula for average strain S_6 of the sample (we neglect the mechanical coupling of the central part with the rest of the sample)

$$S_6 = S_6^s A \quad (5)$$

For the extrinsic coefficient d_{36} we get from (3) and (5)

$$d_{36} \equiv \frac{S_6}{E_3} = \frac{\epsilon_0 S_6^s}{2 P_0 \left[\frac{B}{(1+B)\epsilon_z^{(1)}} - X \right]} \quad (6)$$

neglecting the small X and for $B \ll 1$ we get more simple formula[†]

$$d_{36} = \frac{\epsilon_0 \epsilon_z^{(1)} S_6^s}{2 P_0 B}. \quad (7)$$

DISCUSSION

An extremely high d_{36} under T_c for RDP was first reported in^[11].

[†]The limit $B \rightarrow 0$ in (7) is not correct, because the assumptions needed for validity of (3) are violated if B is very small.

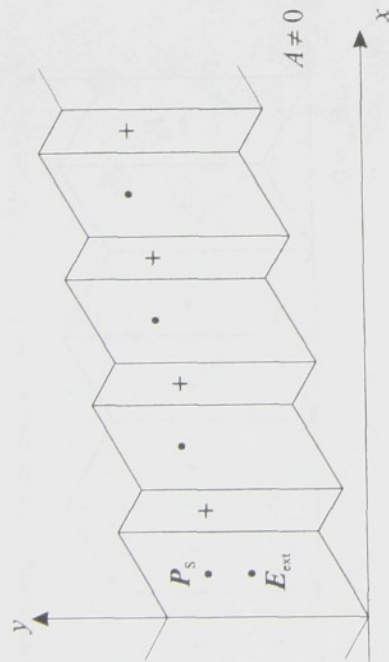


FIGURE 3: Asymmetric domain structure with average strain $S_6 = AS_6^s$, $E_{ext} \neq 0$, $A \neq 0$

In a recent paper^[12], Sidorkin deduced the dispersion law of domain wall vibrations, however, in his treatment the existence of a surface layers is not explicitly considered. We can fit our theoretical results to measured ones^[9] - $d_{36,\text{ext}} \doteq 4 \cdot 10^{-9}$ C/N, $\varepsilon_{z,\text{ext}} = 2000$ in the 35 K range plateau under T_c . Using values that roughly apply to RDPt in (7) resp. (4) we come to an agreement for reasonable value of $B = 0.04$. Naturally for lower temperatures, the motion of the walls is limited by "freezing" and both $d_{36,\text{ext}}$ and $\varepsilon_{z,\text{ext}}$ decrease to zero. It is also interesting, for measurements in^[9] with alternating $E_{\text{ext}} \doteq 220$ V/m, that corresponding amplitude of alternating A from (3) is only 10^{-5} and displacement of the walls with $w = 10 \mu\text{m}$ is of the order 10^{-10} m.

Acknowledgements

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$$P_0 = 4 \cdot 10^{-2} \text{ C/m}^2, \varepsilon_z^{(1)} \doteq \varepsilon_z^{(2)} \doteq 100, S_6^s \doteq 0.015, \text{ see } [9].$$

References

FIGURE 3: Asymmetric domain structure with average strain $S_6 = AS_6^s, E_{ext} \neq 0, A \neq 0$

In a recent paper^[12], Sidorkin deduced the dispersion law of domain wall vibrations, however, in his treatment the existence of a surface layers is not explicitly considered. We can fit our theoretical results to measured ones^[9] - $d_{36,ext} \doteq 4 \cdot 10^{-9} \text{ C/N}$, $\varepsilon_{z,ext} = 2000$ in the 35 K range plateau under T_c . Using values that roughly apply to RDP[†] in (7) resp. (4) we come to an agreement for reasonable value of $B \doteq 0.04$. Naturally for lower temperatures, the motion of the walls is limited by "freezing" and both $d_{36,ext}$ and $\varepsilon_{z,ext}$ decrease to zero. It is also interesting, for measurements in^[9] with alternating $E_{ext} \doteq 20 \text{ V/m}$, that corresponding amplitude of alternating A from (3) is only 10^{-5} and displacement of the walls with $w \doteq 10 \mu\text{m}$ is of the order 10^{-10} m .

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[†] $P_0 = 4 \cdot 10^{-2} \text{ C/m}^2$, $\varepsilon_z^{(1)} \doteq \varepsilon_z^{(2)} \doteq 100$, $S_6^s \doteq 0.015$, see^[9].

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also play a role in ceramic samples.

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Displacements of 180° Domain Walls in Electroded Ferroelectric Single Crystals: the Effect of Surface Layers on Restoring Force *

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Macroscopic properties of ferroelectric samples, including those in form of thin films, are, to large extent, influenced by their domain structure. In this paper the free energy is calculated for a plate-like sample composed of nonferroelectric surface layers and ferroelectric central part with antiparallel domains. The sample is provided with electrodes with a defined potential difference. The effect of applied field and its small changes on the resulting domain structure is discussed. This makes it possible to determine the restoring force acting on domain walls which codetermines dielectric and piezoelectric properties of the sample. Calculations of the potential and free energy take into account interactions of opposite surfaces and are applicable also to thin films.

Keywords: Ferroelectric domains; extrinsic contributions to permittivity

INTRODUCTION

It is known that samples of ferroelectric single crystals often possess a surface layer whose properties differ from those of the bulk. It may be a layer produced during the growth of a crystalline plate or produced during the preparation of a plate-like sample. Many observations gave evidence to the fact that such a layer is either nonferroelectric or does not take part in the switching process of the internal part; in any case its permittivity is believed to differ from that of a homogeneous sample in the ferroelectric phase. Its existence is expected to greatly influence macroscopic properties of bulk samples^[1,2,3,4] as well as of thin films.^[5] In this paper two such consequences are investigated. First we reconsider the problem of equilibrium domain

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structure in a ferroelectric sample possessing a surface layer, previously discussed by Bjorkstam and Oertel.^[6] Second, we evaluate the restoring force acting on 180° domain walls due to the layer; this will make it possible to estimate the extrinsic contributions to permittivity, piezoelectric coefficients and elastic compliances of a ferroelectric sample. Investigations of crystals of the KDP family revealed the existence of huge wall contributions to these properties.^[7,8]

In previous papers on a related subject^[2], depolarizing field was considered as the source of energy which slows down the motion of a single domain wall in a dc electric field, as the wall departs from its original position by substantial distances. In contrast to such models we investigate very small deviations of walls forming a regular domain pattern.

GEOMETRY, VARIABLES AND ENERGY OF THE SYSTEM

We consider a plate-like electroded sample of infinite area with major surfaces perpendicular to the ferroelectric axis z . Central ferroelectric part with antiparallel domains (2.) is separated from the electrodes (0.), (4.) by non-ferroelectric layers (1.), (3.) (see Fig. 1). The spatial distribution of the electric field $\mathbf{E}$ is determined by the applied potential difference $V = \varphi^{(4)} - \varphi^{(0)}$ and by the bound charge $\text{div} \mathbf{P}_0$ on the boundary of ferroelectric material, where $\mathbf{P}_0$ stands for spontaneous polarization. Geometrical, electrical and material parameters of the system are shown in Fig. 1. We further introduce the symbols

$$\epsilon^{(1),(2)} = \sqrt{\frac{\epsilon_x^{(1),(2)}}{\epsilon_z^{(1),(2)}}}, \quad g^{(1),(2)} = \sqrt{\epsilon_x^{(1),(2)} \epsilon_z^{(1),(2)}}, \quad S_0 = \sum_{n=1,3,5} \frac{1}{n^3} \doteq 1.052$$

and several geometrical parameters:

$$B = \frac{2s}{d}$$

the domain pattern factor

$$R = \pi \frac{d}{2w}, \quad 2w = w_+ + w_-$$

and the asymmetry factor

$$A = \frac{w_+ - w_-}{w_+ + w_-}.$$

The ferroelectric material itself is approximated by the equation of state

$$D_1 = \epsilon_0 \epsilon_{ij} E_j + P_0, \quad (1)$$

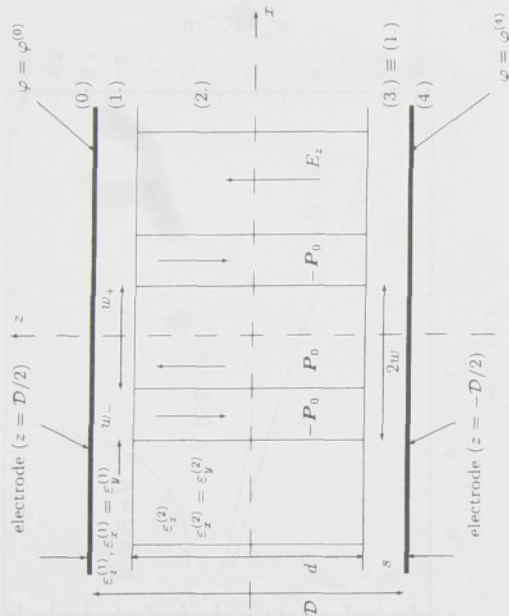


FIGURE 1: Geometry of the model

where only the component P_{0z} is nonzero. This linear approximation limits the validity of our calculations to the temperature region not very close below the transition temperature T_c . Domain walls are assumed to have surface energy density σ_w and zero thickness.

The total free energy of the system includes the domain wall energy and the electrostatic energy whose density is $(1/2)\mathbf{E} \cdot (\mathbf{D} - \mathbf{P}_0)$. First, Laplace equations have to be solved for electric potentials in the bulk and in the surface layers, fulfilling the requirement of potential continuity as well as conditions of continuity of normal components of $\mathbf{D}$ and tangential components of $\mathbf{E}$. A rather cumbersome calculation leads to the following formula for total free energy surface density (in J m^{-2}) of the system:

$$F = \frac{2}{\pi} \sigma_w R + P_0 A \frac{2\epsilon_z^{(1)}(1+B)}{\epsilon_0 \left(1 + B \frac{\epsilon_z^{(2)}}{\epsilon_z^{(1)}}\right)} + \frac{4P_0^2 D}{\epsilon_0 \pi^2 R(1+B)} \sum_{n=1}^{\infty} \frac{\sin^2(n\frac{\pi}{2}(1+A))}{n^3 (g^{(1)} \coth nBR \epsilon_z^{(1)} + g^{(2)} \coth nR \epsilon_z^{(2)})}. \quad (2)$$

The first term represents domain wall contribution while the last one is the depolarization energy. In the second term we recognize the effect of layers (1.) and (3.) and of the applied voltage.

Let us compare expression with formulae deduced and used in previous papers. For $V = 0$ and $s \rightarrow \infty$, $\epsilon_x^{(1)} = \epsilon_z^{(1)} = 1$ and $A = 0$ the system goes over into an isolated ferroelectric plate with "neutral" domain structure,

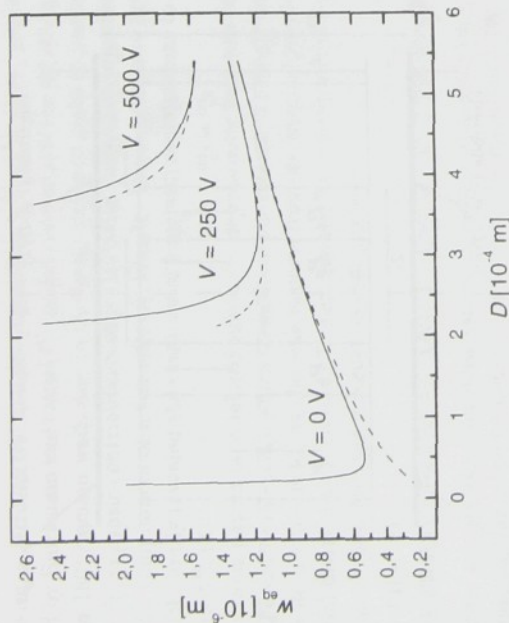


FIGURE 2: Exact numerical (full lines) and approximate (dashed lines) results for $w_{eq}(\mathcal{D})$ at different values of potential difference V and $B = 0.02$.

placed in vacuum. In this case the equation (2) reduces to the expression given by Kopal *et al.*^[9] for ferroelectric plates of finite thickness in which the interaction of the two surfaces is accounted for. If the plate is thick this interaction can be neglected and Eq. (2) simplifies to the classical formula of Mitsui and Furuichi^[10] (cf. Eq. (9) in Ref. [9]) which is often used to determine the value σ_w from the observed width of domain patterns. Finally, in the limit of $V = 0$ our formula (2) should converge to the expression deduced by Bjorkstam and Oettel.^[6] In fact this is not the case and it appears that the electric displacement as expressed in Ref. [6] does not satisfy all boundary conditions.

EQUILIBRIUM DOMAIN STRUCTURE FOR $V = 0$

If the system is short-circuited, the equilibrium domain pattern is symmetric, i.e. $A_{eq} = 0$. The shape factor R_{eq}^0 and from it also the value of w_{eq}^0 can be found by numerical methods. As an example, the full lines in Fig. 2 shows the $w_{eq}(\mathcal{D})$ dependence at constant d/s and different values of potential difference V . As it was shown in the previous paper^[9], the critical thickness d_{crit} can be defined so that for $d \gg d_{crit}$ the interaction energy of

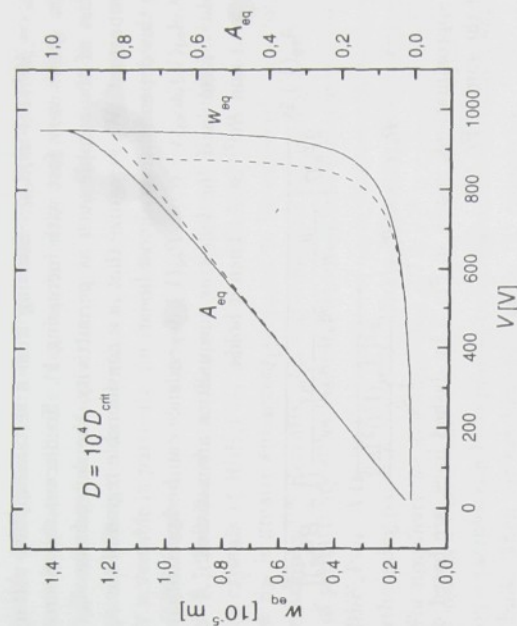


FIGURE 3: Exact numerical (full lines) and approximate (dashed lines) results for $w_{eq}(V)$ and $A_{eq}(V)$ at $B = 0.02$ and $\mathcal{D} = 10^4 \mathcal{D}_{crit}$.

sample surfaces can be neglected. Then the minimum energy occurs for

$$w_{eq}^0 = \frac{1}{P_0} \left[\frac{\pi^3 \epsilon_0 (g^{(1)} + g^{(2)}) \sigma_w}{8 S_0 (1 + B)} \right]^{1/2} \sqrt{\mathcal{D}}. \quad (3)$$

and the dependence $w_{eq}^0(\mathcal{D})$ in this approximation is shown by a dashed line with $V = 0$ V in the Fig. 2. The approximate results in the Fig. 2 with $V = 250$ V and $V = 500$ V are based on Eqs. (4) and (5). In these numerical calculations we have used the following values which roughly apply to crystals of RbH_2PO_4 below the transition temperature: $P_0 = 5.7 \times 10^{-2} \text{ C m}^{-2}$, $\epsilon_x^{(2)} = 10$, $\epsilon_z^{(2)} = 100$, $d_{crit} = 5.4 \times 10^{-8} \text{ m}$. The value $\sigma_w = 5 \times 10^{-3} \text{ J m}^{-2}$ is often considered typical for ferroelectrics. For simplicity we put $\epsilon_x^{(1)} = \epsilon_z^{(1)} = \epsilon_x^{(2)}$.

RESPONSE OF DOMAIN STRUCTURE TO EXTERNAL ELECTRIC FIELD

When an external potential difference V is applied, the asymmetry parameter becomes nonzero and at the same time the period $w = (w_+ + w_-)/2$ changes. Both these quantities can be found again by determining the minimum of F given by Eq. (2) numerically. Full lines in Fig. 3 demonstrate both these dependencies for the following numerical values: $B = 0.02$, $\mathcal{D} =$

$10^4 \mathcal{D}_{\text{ent}} = 10^4 (1 + B)d_{\text{ent}}$. Starting from a certain applied voltage the period w grows very fast with increasing V . To discuss the macroscopic properties of the sample such as permittivity, the dependence $A_{\text{eq}}(V)$ is more important. We recognize that in a considerable region of the applied voltage this dependence is almost linear.

The $A_{\text{eq}}(V)$, $u_{\text{eq}}(V)$ resp. $R_{\text{eq}}(V)$ dependence can be approximated by an explicit formula if the following inequalities are satisfied: $A \ll 1$, $BR_{\text{C}}^{(1)} \gg 1$ and $R_{\text{C}}^{(2)} \gg 1$. Then it holds

$$A_{\text{eq}}(V) \cong \frac{\varepsilon_0 V}{2P_0 \mathcal{D}} \left[\frac{B}{\varepsilon_z^{(1)}(1+B)} - \frac{2 \ln 2}{R_{\text{eq}}^0(1+B)(g^{(1)}+g^{(2)})} (1 + B \frac{\varepsilon_z^{(2)}}{\varepsilon_z^{(1)}}) \right] \quad (4)$$

$$R_{\text{eq}}(V) \cong R_{\text{eq}}^0 \sqrt{1 - \frac{\pi^2 (A_{\text{eq}}(V))^2 \ln 2}{4 S_0}} \quad (5)$$

These approximations, shown in Fig. 3 by dashed lines, are based on the limit of the sum in Eq. (2).

EXTRINSIC PERMITTIVITY

The nonzero value of the asymmetry parameter means that an extra bound charge is deposited on the electrodes due to the domain wall shifts and this in turn represents an increase of effective permittivity of the whole system crystal plus both surface layers. The increase of the electrostatic energy when domain walls leave their original equilibrium positions for $E \neq 0$ serves as the source of a restoring force when field is again reduced to zero. The calculations show that the effective permittivity ε_{eff} defined by the total capacitance per unit area $C = \varepsilon_0 \varepsilon_{\text{eff}} / \mathcal{D}$ equals

$$\varepsilon_{\text{eff}} = \varepsilon_z^{(2)} \frac{\mathcal{D}}{d} \left(1 + B \frac{\varepsilon_z^{(2)}}{\varepsilon_z^{(1)}} \right)^{-1} + \left\{ \left(1 + B \frac{\varepsilon_z^{(2)}}{\varepsilon_z^{(1)}} \right) \left[\frac{B}{(1+B)\varepsilon_z^{(1)}} - \frac{2 \ln 2}{R_{\text{eq}}^0(1+B)(g^{(1)}+g^{(2)})} \left(1 + B \frac{\varepsilon_z^{(2)}}{\varepsilon_z^{(1)}} \right) \right] \right\}^{-1} \quad (6)$$

In this formula the first term on the right-hand side represents the intrinsic part of permittivity, given by linear dielectric response of the sample and of the surface layers when domain walls are kept at rest. The second term is the contribution of domain walls displacement to effective permittivity, often referred to as extrinsic part of permittivity.

DISCUSSION

Numerous data are available on domain wall contributions to permittivity in single crystals of ferroelectrics and also on extrinsic contributions to

piezoelectric coefficients in ferroelectrics which are simultaneously ferroelastic. Our calculations indicate that depolarizing energy can be an effective source of restoring force whose existence is a condition for such contributions. In fact since the model assumes a regular system of planar domain walls, it is suitable in particular for ferroelastic ferroelectrics such as crystals of the KDP family in which a dense pattern of 180° domains is known to exist.^[11,12] It was found that in a wide temperature range below the Curie point of crystals of RbH_2PO_4 and deuterated KDP, the piezoelectric coefficient d_{36} is greatly enhanced compared to its expected value for single domain samples.^[13] Recently, this was confirmed by simultaneous measurements of permittivity ε_3 , elastic compliance s_{66} and piezoelectric coefficient d_{36} of RbH_2PO_4 . A thorough discussion of d_{36} in this case will be the subject of a forthcoming paper Kopal *et al.*. Here we comment on the extrinsic part of ε_3 . For simplicity, let us assume that $\varepsilon_x^{(1)} \cong \varepsilon_x^{(2)} \equiv \varepsilon_x$ and $\varepsilon_z^{(1)} \cong \varepsilon_z^{(2)} \equiv \varepsilon_z$. This is not an unreasonable assumption since the assumed surface layer for KDP-type samples can be supposed to have a similar chemical composition as the bulk. Then the extrinsic part of Eq. (6) reduces to

$$\left(\frac{B}{\varepsilon_z} - \frac{\ln 2 (1+B)}{R_{\text{eq}}^0 \sqrt{\varepsilon_z \varepsilon_x}} \right)^{-1}$$

Numerically, the second term in the brackets represents a small correction to the first term when approximations (4) and (5) are valid. If it is neglected, we obtain as an approximation

$$\varepsilon_{z,\text{extrinsic}} \cong \frac{\varepsilon_z}{B} = \varepsilon_z \frac{d}{2s} \quad (7)$$

This shows that a very thin surface layer can lead to a considerable extrinsic enhancement of permittivity. Nevertheless, the simple implication: $s \rightarrow 0 \Rightarrow \varepsilon_{z,\text{extrinsic}} \rightarrow \infty$ is not correct, because the assumptions needed for validity of (4), (5), (6) and (7) are violated if s is small enough.

A more general formulation of the restoring force can be used to calculate the extrinsic part of d_{36} for the same geometry of domains. In a recent paper^[14] Sidorkin deduced the dispersion law of wall contributions to permittivity, however, in his treatment the existence of a surface layer is not explicitly considered.

It was shown beyond any doubt that small motions of 90° domain walls are responsible for a considerable enhancement of permittivity ε_3 and piezoelectric coefficients d_{31} , d_{33} in poled ferroelectric ceramics.^[15,16] One of the sources of the restoring force responsible for these wall contributions is the elastic energy at grain boundaries.^[17] Since these boundaries may differ in chemical composition from the bulk of grains^[18], surface layers can be expected to form so that the mechanism proposed in the present paper may