Abstract

Acknowledgements

Contents

Chapter 1

Mechanical softening in Ferroelectric domain walls

1.1 Introduction

So far, the focus of this work was largely on the behavior of various orders in uniform domains, and how they interact with eachother. A thorough understanding of these physics is of fundamental importance, since this provides the building blocks for more complex scenarios. Reality, however, presents to us almost exclusively these more complex scenarios. The reason for this is that while going through a phase transition with an associated spontaneous symmetry breaking, different parts of the material which are separated in space will separately (and usually randomly), choose one of the degenerate states with different values of the order parameters. One could argue that second order phase transitions could happen coherently throughout the entire system, but this assumes that the crystals are completely uniform and without defects, and that the temperature variation happens at an infinitely slow rate. In reality these assumptions are almost always invalid, inevitably leading to domains separated by domain walls (DWs) in which one or more order parameters interpolate between the values in the neighboring domains. The fundamental difference between DWs and the domains themselves has led to a great amount of research interest, both from the fundamental and technological point of view. The latter can be attributed to the small size and the fact that their location can usually be controlled easily. One example are conducting DWs in a ferroelectric materials, which have are bulk insulators. However, sandwiching a ferroelectric that harbors these walls between two conducting plates allows for creating these DWs by applying electric fields. When more conducting DWs are present, current will flow more easily through the material. This fact can be exploited to efficiently store and read information. A lot of research has been focused on the functionality that DWs present, but less is known about their mechanical properties. It has been shown that ferroelectric-ferroelastic (ferroelastic walls separate domains with differing strain textures) DWs can be moved by applying stress [**Schneider2001**],[**Lee2003**]. While the influence of stress on these ferroelectric-ferroelastic DWs has been investigated theoretically [**Lee2003**], it [maybe some more examples etc?]

While domain walls offer an extremely rich behavior in the case of multi-ferroics, and hold the key to use these promising materials in spintronics applications [**Lee2014**], here we focus on domain walls in the classic ferroelectric BaTiO$_3$ (BTO).

In the previous chapter, the focus was largely on the multiferroic behavior of uniform domains. While the research towards greater understanding of this topic is fundamental to further the field, the usability in spintronics applications is difficult. A key reason for this is the fact that multiferroics are almost exclusively insulators with relatively wide band gaps. For most technological applications, some current has to be able to pass through the device in order to transfer, probe and process information. As such, domain walls have taken center stage in the search for usable multiferroic devices, since even though the domains the separate are non-conductive, their different internal configuration can allow for current to flow through.

The study of domain walls in ferroelectric and ferroelastic materials has taken the center stage in recent years. This is because they signify crossover regions between domains where the parent symmetry of the material was broken. These regions therefore often harbor effects that are markedly different from the behaviors found in the domains themselves. Here we investigate mainly 180° domain walls in ferroelectric BaTiO$_3$ (BTO). These domain walls are purely ferroelectric, i.e. the strain textures accompanying the ferroelectricity (see below for a more in depth discussion) is the same in both domains, separated by the wall. Given this fact it is fairly remarkable that it was observed that these walls are mechanically distinct from the domains they separate. In the case of BTO, they appear softer. After giving an overview of the performed experiments and the results we are trying to describe, we continue with a discription of the underlying theory, followed by the numerical results together with a discussion.

1.2 Experimental

In order to characterise the stiffness of the material, scanning probe microscopy experiments were performed on single crystal BTO, by the group of Prof. Catalan. More specifically, Contact Resonance Frequency Microscopy (CR-FM) was performed, whereby an Atomic Force Microscopy (AFM) tip is brought into contact with the material, upon which the resonance frequency is measured. The higher the frequency the stiffer is the material in contact with the tip. This allows one to produce a mapping of stiffness the entire crystalline surface where the main limit on resolution is time. This leads to images as shown in Fig. **??**, where there is a clear contrast between soft areas close to the wall and harder areas inside the domains. The softening of domain walls was previously studied for ferroelastic materials (i.e. materials where the wall separates two domains with different strain textures), where a similar effect was observed [**Lee2003**].

1.3 Theory

In order to describe the coupling between the ferroelectric order parameter P and the strain ε we use a Ginzburg-Landau-Devonshire model as described in
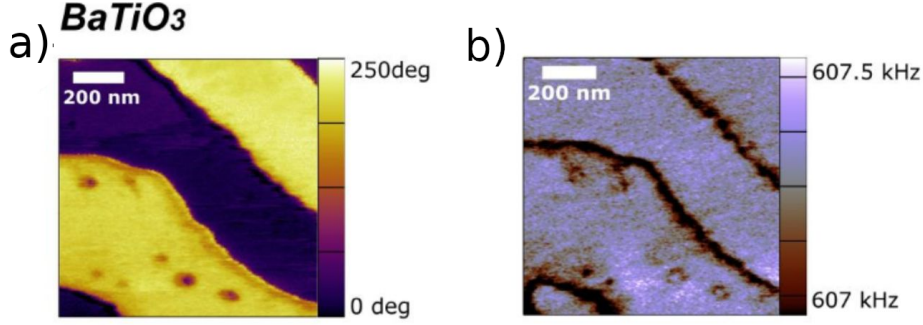
Figure 1.1: Ferroelectric polarization and stiffness maps of the surface of a single crystal of BTO. a) orientation of the ferroelectric polarization, obtained by Piezoresponse Force Microscopy (PFM). b) Mechanical response of the material as measured by CR-FM.

[**Marton2010**]. The free energy density throughout the material is given by:

$$f = f_L + f_G + f_c + f_q + f_{fl}, \tag{1.1}$$

$$f_L = \alpha_{ij}P_{ij} + \frac{1}{2}\alpha_{ijkl}P_iP_jP_kP_l + \alpha_{ijklmn}P_iP_jP_kP_lP_mP_n, \tag{1.2}$$

$$f_G = \frac{1}{2}G_{jklm}\partial_k P_j \partial_m P_l, \tag{1.3}$$

$$f_c = \frac{1}{2}\varepsilon_{jk}C_{jklm}\varepsilon_{lm}, \tag{1.4}$$

$$f_q = -\frac{1}{2}\varepsilon_{jk}q_{jklm}P_lP_m, \tag{1.5}$$

$$f_{fl} = \frac{1}{2}f_{jklm}(\varepsilon_{jk}\partial_m P_l - P_l\partial_m\varepsilon_{jk}) \tag{1.6}$$

where the indices run through x, y, z, and einstein summation is assumed. The first term is the Landau free energy for a uniform ferroelectric polarization. Up to sixth order had to be included to bound the energy, since in BTO the fourth order term turns out to be negative. The second term denotes the Ginzburg part, the energy penalty occured by spatial variations of the polarization. f_c is the elastic energy density, and f_q gives the contribution of electrostriction to the free energy. This is the main term coupling the polarization to the strain and causes the domains to be stretched along the polarization [add some panels like in the discussion of the powerpoint]. Lastly we include the flexoelectric contribution, f_{fl}, since it leads to small but possibly important effects.

The first possible source for the mechanical softening originates from the electrostriction term, and the strain texture it results in. As mentioned before, electrostriction stretches the domains in the direction of the polarization. Since we are investigating 180° domain walls, we can take the main polarization to be P_z, leading to a stretching of the domains in the z direction, or equivalently, $\varepsilon_{zz} \neq 0$ inside the domains. In the domain wall, however, P_z^2 is diminished and even zero at the center. This then causes ε_{zz} to be dimished, but never reduced to zero due to compatibility relations and the elastic coupling to neighboring unit cells. Nonetheless, this will result in an indentation that forms at the location of the domain wall, as shown pictorially in Fig. **??**(b), and more realistically in (c-

d). As it turns out, the strain texture of this indentation stretches out relatively far [actual derivation and formula for this?] from the domain wall. This long-rangedness of strain is a general fenomenon, and depends on the morfology of the strain defect [more indepth on this?]. When the tip is then applied in an area where this strain texture is present, the wall will try to bend towards the tip in order to gain on the displacement. This will thus lead to a relatively big displacement to be caused by applying the tip, making the material appear soft.

Even though the interaction between the pinning potential, Peierls-Nabarro barriers, and electrostatics, with the force applied by the tip is hard to analytically describe, we can make statements about two extremes of the behavior: i) If the force of the tip is large enough, the wall slide towards it, maximizing the possible energy gain from the interaction with the tip. ii) A bending of the wall, where it remains inside the original Peierls-Nabarro potential, but deviates from the equilibrium position. [The situation that happens in the real material is more like a mix between the two, the top part of the wall bends almost completely towards teh tip, but it's not moved as a whole because the bottom/bending electrostatics pins it. Can we say that these things are causing the potential for the entire wall to behave like the one we describe below?]

The first case can be ignored because this would mean that in the experiments, the wall would be dragged along the tip since the tip moves at a relatively slow rate, which would lose any contrast between wall and domain during the full measurement. We therefore try to formulate a simple free energy expansion for the second situation, where we assume that the wall at x_{DW} is pinned by a parabolic potential, and perturbed by a tip applying a force F_z at x_{tip},

$$E = E_0 - F_z u_z(x_{tip} - x_{DW}) + \frac{m\omega^2 x_{DW}^2}{2}. \tag{1.7}$$

We can expand this equation under the assumption of a small x_{DW}, i.e. that the wall doesn't move far from the $x_{DW} = 0$ equilibrium situation. Together with minimizing the energy we obtain $x_{DW} = -Fu'(x_{tip})/m\omega^2$, with a compliance correction $\Delta c = u'(x_{tip})^2/(m\omega^2)^2$. Thus, we can conclude that to maximize the softening, the tip should be applied where $u'(x_{tip})$ is large, i.e. within the strain variation caused by the above discussed electrostrictive coupling. This part of the effect is pictorially depicted in panel (b) of Fig. **??**.
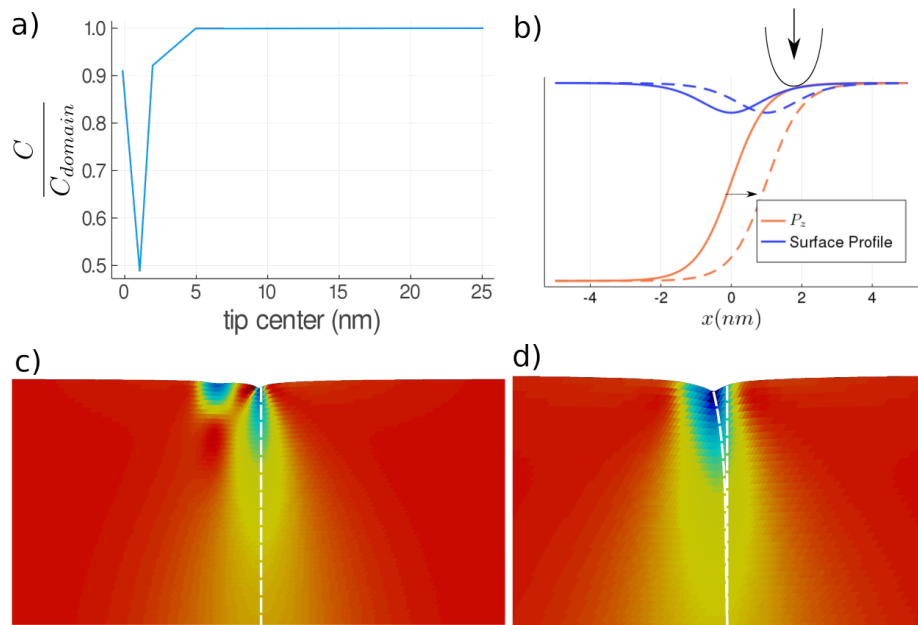
1.4   Results

Figure 1.2