Coherent Bragg Rod Analysis of Ferroelectrics

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1 Introduction

A ferroelectric crystal is a crystal which exhibits an electric dipole moment in the absence of an electric field. The spontanous polarization can be reversed by applying sufficiently large electric fields.

Ferroelectric crystals consist of domains analogous to ferromagnetic domains. The polarization, P, is in the same direction within each domain and different in adjacent domains. The net polarization is obtained by summing up the polarizations from the different domains. The domain sizes and shapes may change when an external field is applied.

Ferroelectricity is used in devices such as sensors, actuators and electronic devices. These devices utilize in some cases, the ability to switch the spontaneous electric fields either by applying a stress field, an electric field or by changing the temperature. A considerable amount of work is being carried out in fabricating miniature devices on a nanoscale since the ferroelectric effect exists not only in bulk, but also in films which are about 4 monolayers.[1, 7]

Examples of materials which demonstrate ferroelectricity are perovskites. Perovskites are materials which have the chemical formula ABO_3 where A is a di or monovalent metal and B is a tetra or pentavalent metal. Perovskites have complete cubic symmetry in the non-polar phase. The axis of polarization may be parallel to the cube edge, a phase diagonal or a body diagonal. Common examples of perovskite ferroelectrics are $BaTi0_3$, $PbTiO_3$ and $LiNbO_3$. The critical temperature's for know perovskites range from 400K to about 200K with spontaneous polarizations observed up to $71\mu Ccm^{-2}$ for $LiNbO_3$ [5] .

2 Devonshire-Landau Theory of Ferroelectric Phase Transitions

Ferroelectricity usually disappears above a certain temperature T_c. The substance is referred to as being paraelectric above the critical temperature. For ferroelectrics, the order parameter may be given as the displacement of a particular ion within a unit cell or the net polarization within a unit cell. The transition temperature is obtained theoretically by minimizing the D-L free energy. The Devonshire-Landau Free energy [4] is a function for temperature(T), Polarization(P) and the external field(E). The Landau free energy can be written as

$$F(P,T,E) = -EP + g_0 + g_2\frac{1}{2}P^2 + g_4\frac{1}{4}P^4 + g_6\frac{1}{6}P^6 + ...$$

where the coefficients g_n are functions of temperature. The expansion does not contain term in odd powers of P if the unpolarized crystal has a center of inversion symmetry. g_2 can be expressed as

$$g_0 = \gamma(T - T_c)$$

The equilibrium polarization in an applied field E is given by

$$\frac{\partial F}{\partial P} = 0 = -E + g_2P + g_4P^3 + g_6P^5 + ...$$

Slight distortions in the crystal symmetry would affect the overall polarization of the crystal. Close to the ferroelectric phase transition, the crystal undergoes a structural phase transition in which there is a change in the symmetry. The high symmetry phase is usually the high temperature one in which the spontaneous polarization disappears. The cause of the displasive transitions is the instability of a crystal towards a 'soft' vibrational mode in the high temperature phase[5]. If this change occurs in a smooth and continuous way, the transition is referred to as a Second Order Phase Transition.

In terms of the Landau expansion, if g_4 is positive we have a second order phase transition and we can neglect the g_6 term. In the case where $E = 0$ the spontaneous polarization P_s is found to be

$$P_s = \begin{cases} \frac{\gamma}{4}^{\frac{1}{2}}(T - T_c)^{\frac{1}{2}} & \text{if} \quad T > T_c; \\ 0 & \text{if} \quad T \geq T_c. \end{cases}$$

The polarization goes continuously to 0 at the critical temperature.

A first order transition occurs when $g_4 = -|g_4|$. From the equilibrium condition for zero field,

$$\gamma(T - T_c)P_s - |g_4|P_s^3 + |g_6|P_s^5 = 0$$

$$P_s = 0$$

or

$$\gamma(T - T_c) - |g_4|P_s^2 + |g_6|P_s^4 = 0$$

Thus, there is a discontinuous jump in the polarization at the transition temperature.

3 Coherent Bragg Rod Analysis

A recently developed experimental method to study ferroelectric thin films using synchrotron x-rays is the Coherent Bragg Rod Analysis procedure also known COBRA [6, 3]. COBRA involves measuring the diffraction intensities along substrate defined Bragg Rods to determine the complex scattering factors from which the electron density, and thus, the polarization, can be obtained directly by fourier transform. The complex scattering factor is vary continuously along the Bragg rods. Figure 1 shows the scattering geometry for COBRA experiments in real and reciprocal space. The incident beam with a wave vector k_i impinges on the sample surface.The scattered beam intensity with a wave vector k_s is measured by the detector. In the reciprocal space representation of the scattering geometry, the dots represent the reciprocal lattice points. The vertical lines represent Bragg rods. The circle represents the Eswald sphere. The three arrows represent incident k_i the scattered k_s and the crystal momentum transfer k.

The atomic structural factor is given as

$$T(\vec{q}) = \int \rho(\vec{q}) e^{i\vec{q}\cdot\vec{r}} d^3r$$

where ρ is the electron density, $\vec{r}$ is the position in real space and the integeral is over the whole volume. The general form for the electron density would be

$$\rho(\vec{r}) = \sum_{j_x,j_y=-\infty}^{\infty} \sum_{j_z=-\infty}^{N_{uc}} \sum_{j_{uc}=-\infty}^{n} f_{j_{uc}} \delta(\vec{R}_{j_x j_y j_z} + \vec{r}_{j_{uc}} - \vec{r}) g(\vec{r} \cdot \vec{e_z})$$

where $\vec{R}$ refers to a lattice vector and the subscript uc refers to the sum over the unit cells. The function $g(\vec{r} \cdot \vec{e_z})$ is included to account for roughness and $f_{j_{uc}}$ is the atomic scattering factor of the atom j_{uc} in the unit cell. In the case of epitaxial thin films, the measured atomic structural factor, T(q)

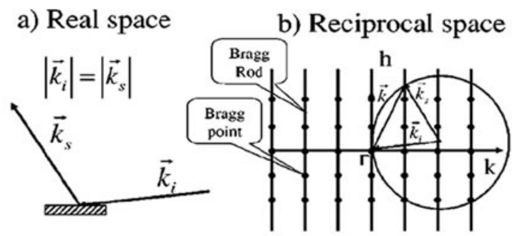

Figure 1: (a) Scattering geometry: (b) Reciprocal space

is a coherent combination of the structural factors of the bulk substrate, S(q) which is known and the film layer, U(q) which is unknown. [6, 2]

$$T(q) = S(q) + U(q)$$

By using the substrate as a reference, Bragg Rod measurements can be used to determine the unknown electron density distributions for the ferroelectric thin films. The films are assumed to have two dimensional periodicity within the plane of the film and aperiodicity in the perpendicular direction. Since the films studied in COBRA are epitaxial, the assumption can also be made that the first few monolayers of the film have 2D periodicity coherent with that of the underlying substrate. A system with 2D periodicity can be described as being infinite in the plane of the film and confined in the perpendicular direction.

COBRA can be used to study directly, the structural changes that occur in ferroelectrics epitaxial films at the phase transition by experimenting at various temperatures close to the transition temperature.

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