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Ginzburg soft mode conception and ferroelectricity in ultrathin films

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Abstract

It was shown recently that ferroelectricity and switching of the spontaneous polarization exist even in one monolayer (5–17 Å) of the ferroelectric copolymer P[VDF-TrFE]. Ferroelectric properties were found in the ultrathin perovskite-like PZT films with a thickness of 12 Å (three unit-cell parameters). Moreover, the simulation model, based on first principles, has shown that the critical size of perovskite ferroelectrics is three elementary cells. On the other hand the Ginzburg soft mode conception for displacive ferroelectrics supposed the existence of the low frequency vibration mode ω_0 (soft mode) and the corresponding long vibration wavelength λ_0 . Therefore the mechanism of the ferroelectric phase transition, connected with the soft mode, leads to the existence of a critical thickness of the film $l_{cr} \approx \lambda_0$. At $l_{cr} < \lambda_0$ the mechanism of the ferroelectricity is not caused by the soft mode. We show that in the ultrathin ferroelectric films the soft mode does not exist.

1. Introduction

1.1. The finite-size effect and soft mode

There are many experimental data about the influence of the film thickness and crystal size on the phase transition temperature and ferroelectric properties. The most recent data show that the ferroelectric copolymer P[VDF-TrFE], prepared by the Langmuir–Blodgett method, reveals ferroelectricity and ferroelectric switching in one monolayer (5–17 Å) [1–3]. Moreover, the simulation model, based on first principles, has shown that the critical size of perovskite ferroelectrics is three elementary cells [4]. In these films there is no critical thickness, predicted theoretically in many publications and summarized in [5]. Prepared by epitaxial growth, perovskite-like PZT films with thickness 12 Å (three unit cells) show ferroelectric properties [6]. Earlier the finite-size effect was investigated in sintered PbTiO₃ crystals [7]. The observation of an optical soft mode revealed (for particle size 250 Å) a transition to the ferroelectric at a point shifted to low temperature. The critical film thickness or crystal size,

compatible with ferroelectricity, is limited by two factors. The first factor is the surface energy; the second one is the depolarization field, which can suppress the phase transition, although this term can be largely compensated by the internal or external screening.

On the other hand, the finite-size effect is connected with the soft mode, because at film thickness $l \leq \lambda_0$ (λ_0 is the wavelength corresponding to the soft mode frequency ω_0) the soft mode disappears and the ferroelectric phase transition changes its mechanism.

1.2. Ginzburg soft mode conception

Considering the spontaneous polarization P in displacive ferroelectrics as the shift of some vibrating sublattice, we can write the equation of motion for the polar mode in the damped harmonic oscillator form:

$$\mu \ddot{P} + \nu \dot{P} = -\frac{\partial G}{\partial P} \quad (1)$$

$$G = \frac{\alpha}{2} P^2 - EP \quad (2)$$

where G is the Gibbs energy, E is the external field and $\alpha = \alpha'(T - T_0)$ is the well known Landau–Ginzburg coefficient. The equations (1), (2) are written for the small field and polarization. Substituting in (1) $P = P_s \exp(i\omega t)$, $E = E_0 \exp(i\omega t)$, we get the well known dielectric constant dispersion:

$$\varepsilon = \begin{cases} \frac{2\pi}{\alpha + i\omega\nu - \omega^2\mu}, & T > T_0 \\ \frac{2\pi}{2\alpha + i\omega\nu - \omega^2\mu}, & T < T_0 \end{cases} \quad (3)$$

with resonance frequency ω_0

$$\omega_0^2 = \frac{\alpha}{\mu}. \quad (4)$$

In the region of the phase transition ($T = T_1$) the frequency ω_0 decreases (it goes to zero for the second order phase transition) and the corresponding wavelength λ_0 increases. For BaTiO₃ the effective mass $\mu \approx 2 \times 10^{-24}$, $\alpha \approx 10^{-3}$ ($T = T_1$), $\omega_0 \approx 5 \times 10^{10}$ and $\lambda_0 = 2\pi c/\omega_0 \approx 1$ cm [8, 9].

This kind of dispersion $\varepsilon = \varepsilon(\omega)$ is very often called the resonance dispersion or soft mode dispersion. In the case of a big damping coefficient ν this kind of dispersion is not observed experimentally.

2. Dielectric resonance dispersion in the ultrathin films

Let us consider a uniaxial ferroelectric film between two electrodes, where the spontaneous polarization P is perpendicular to the film surfaces, located at positions $z = \pm l/2$. Let us also suppose that in the bulk this ferroelectric reveals the soft mode dispersion. For the small external electric field E and small polarization P the Gibbs free energy per unit area has the form [5, 10]

$$G = F_0 + \frac{1}{l} \int_{-l/2}^{l/2} dz \left[\frac{\alpha}{2} P^2 + \frac{\delta}{2} \left(\frac{dP}{dz} \right)^2 - P(z)E \right] + \frac{\delta}{2l\lambda} \left\{ \left[P \left(\frac{l}{2} \right) + P_m \right]^2 + \left[P \left(-\frac{l}{2} + P_m \right) \right]^2 \right\} \quad (5)$$

where $\alpha = \alpha'(T - T_0)$, T_0 is the Curie temperature, δ is the correlation factor, λ is the decay length, determining the strength of coupling in the surface layer, and P_m is the mismatch-induced polarization, caused by the mechanical tension due to the mismatch between film and electrode lattice constants and piezoelectric effect [10]. In [10] it was supposed that the mismatch effect is responsible for ferroelectricity in the ultrathin films. For simplicity we neglect here the depolarization field.

From (5) follows the equation of state in the form of the Euler–Lagrange equation:

$$\alpha P - \delta \frac{d^2 P}{dz^2} = E \quad (6)$$

with boundary conditions

$$\left(P + \lambda \frac{dP}{dz} \right)_{z=l/2} = -P_m, \quad \left(P - \lambda \frac{dP}{dz} \right)_{z=-l/2} = -P_m. \quad (7)$$

Integrating (6) at (7) gives

$$\alpha \bar{P} + \alpha \frac{2\delta}{l\lambda\alpha} \bar{P} \left(\frac{P + P_m}{\bar{P}} \right) = E \quad (8)$$

where \bar{P} denotes the average of P over the film thickness. Taking $\bar{P} \approx P$ (depolarization field is absent), we get from (8)

$$\alpha P \left[1 + \frac{2\delta}{l\lambda\alpha} \left(1 + \frac{P_m}{P} \right) \right] = E. \quad (9)$$

If we suppose [10] that for ultrathin film $P_m \gg P$, the equation of state (10) has the form

$$P \frac{2\delta}{\lambda l} \frac{P_m}{P} = E. \quad (10)$$

Comparing (10) with (1) and (2) we see that in the ultrathin ferroelectric film there is dielectric dispersion with resonance frequency ω_r :

$$\omega_r^2 = \frac{1}{\mu} \frac{2\delta}{\lambda l} \frac{P_m}{P}, \quad (11)$$

which does not depend on α and does not show soft mode nature. This means in turn that at the transition from the bulk ferroelectric to the ultrathin ferroelectric film there is a change of the ferroelectric phase transition nature. The corresponding critical thickness l_{cr} is given by

$$l_{cr} \approx \frac{2\delta}{\alpha\lambda} \frac{P_m}{P}. \quad (12)$$

The film thickness $l \leq l_{cr}$ is still compatible with ferroelectricity, but dielectric dispersion does not correspond to the soft mode. It is seen also from (9) that at $P_m < P$ the soft mode length $\lambda_0 \gg l$ ($\delta \ll l$, $\delta \ll \lambda$ [11]) and ferroelectricity cannot exist in the ultrathin films.

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