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Ferroelectric perovskite solid solutions in high magnetic fields; diagrams of the phase growth

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Abstract. Diagrams of the phase growth of ferroelectric perovskite solid solutions in strong magnetic fields are obtained by calculation. It is shown that high magnetic fields accelerate the growth of either paraelectric or ferroelectric phases. The width and velocity of the interphase boundary are calculated as functions of magnetic field and chemical composition of the perovskite solid solution.

The study of the physical properties of substances in a metastable state pertains to the general problem of phase transitions and is one of the most important problems in physics. Metastable states arise in first-order phase transformations in condensed matter, in nuclear matter, in a quark–gluon plasma, in the inflational expansion of the Universe at the early stages of its evolution, in the condensation and decomposition of an electron–hole liquid in semiconductors, and in biological and chemically reacting systems far from thermodynamic equilibrium near the threshold of self-organization [1–5]. It has been recently found that metastable states play an important role in the onset of high-temperature superconductivity in compounds of the 1–2–3 type, where the problem of oxygen stoichiometry is important [6]. Internal surfaces in solids, such as grain boundaries, coherent interphase interfaces and antiphase boundaries, are general nonequilibrium features of crystalline solids. A significant fraction of solid–solid phase transitions are purely structural, i.e. they occur at constant composition and are diffusionless [1]. Recently the field-induced dynamics of interphase boundaries have been studied in liquid crystals and some structural solid–solid phase transformations [7]. The influence of a magnetic field on ferroelectric perovskites was observed in BaTiO_3 and KTaO_3 and was due to the magnetoelectric effect [8–11]. The aim of this article is to consider the dynamics of a propagating interphase boundary during diffusionless first-order phase transitions in ferroelectric solid solutions under the influence of high magnetic fields. Thus, the work concerns the field of a magnetic effect on the kinetics of phase transformations in solid solutions in which phase transitions occur with composition changes but without diffusion.

We are interested in the influence of high magnetic fields on metastable states in ferroelectric phase transitions in mixed substances and in growth rates of paraelectric and ferroelectric phases at high magnetic fields. We propose a method for constructing diagrams of ferroelectric phase transformations and phase growth of the paraelectric and ferroelectric phases. The objects of our research are ferroelectric perovskite solid solutions in which composition changes strongly affect the mechanical, dielectric, piezoelectric, electro-optic

and superconducting properties [12–16]. Our calculations are based on the experimental data for $\text{Ba}_{1-\delta}\text{Sr}_\delta\text{TiO}_3$.

The dynamics of ferroelectric interphase boundaries are described in terms of the time evolution of the polarization P :

$$\frac{\partial P}{\partial t} = -\Gamma \frac{\delta F}{\delta P}. \quad (1)$$

Here Γ is the kinetic coefficient, which is assumed to depend noncritically on temperature, pressure, concentration and magnetic field. F is the bulk free energy:

$$F = \int [f + D(\nabla P)^2] dV. \quad (2)$$

f is the free-energy density. In the presence of an external magnetic field, f for perovskite ferroelectrics in the cubic phase can be described phenomenologically via

$$f = f_0 + \frac{1}{2}AP^2 - \frac{1}{4}BP^4 + \frac{1}{6}CP^6 + dX^2 + eXP^2 - \frac{1}{2}gP^2H^2 - \frac{1}{2}hP^2H^4 + iXH^2. \quad (3)$$

In this equation P is the polarization and X is the strain. f_0 is the free-energy density for the paraelectric phase, D is the positive coefficient of the gradient term. H is the magnetic field strength. For $B > 0$ and $C > 0$, equation (1) describes the first-order phase transition. $B < 0$ corresponds to the second-order phase transition taking place, and $B = 0$ to the tricritical point. $A = A'(T - T_0)$, where T_0 is the temperature of the stability limit of the paraelectric phase. It is known from experiment (see [17]) that T_0 and $T_c - T_0$ decrease with increasing Sr concentration δ , where T_c is the phase transition temperature. We can describe the coefficient B as follows: $B = b(\delta_t - \delta)$, where b does not depend on the Sr concentration δ (in the pure BaTiO_3 $\delta = 0$), i.e. $B_0 = b\delta_t$, where δ_t is the tricritical concentration. The terms $-\frac{1}{2}gP^2H^2$ and $-\frac{1}{2}hP^2H^4$ appear due to the magnetoelectric effect [18]. The magnetoelectric effect in nonferromagnetic ferroelectrics was first detected in the work of Wagner and Bäuerle [10]. In paramagnetic substances, if the symmetry allows, the magnetoelectric effect is a product of the piezomagnetic and electrostriction contributions and is a coupled electric and magnetic phenomenon in an elastic field. In diamagnetic materials such as perovskites magnetostriction does not exist and the magnetoelectric interaction is direct, being a relativistic effect. The possible microscopic origin is the effect of the magnetic field on the polarization through the Ti–O hybridization which plays an important role in the ferroelectricity of these materials [20]. The magnetic field weakens the Ti–O repulsion and ‘helps’ the ferroelectric state, leading to the shift of the phase transition to higher temperature. The solution of the kinetic equation (1) for the interface boundary conditions has the kink form [18]

$$P = \sqrt{\frac{B}{2C} (1 + \sqrt{1 - 4\alpha})} \left(\sqrt{1 + \exp\left(-\frac{s}{\Delta}\right)} \right)^{-1} \quad (4)$$

where $s = x - vt$, and x is one of the axes. Δ is the width of the interphase boundary, given by

$$\Delta = \frac{1}{B} \sqrt{\frac{3DC}{1 - 2\alpha + \sqrt{1 - 4\alpha}}} \quad (5)$$

which moves with the velocity v , given by

$$v = \frac{\Gamma B(8\alpha - 1 - \sqrt{1 - 4\alpha})}{3} \sqrt{\frac{2D}{C(1 - 2\alpha + \sqrt{1 - 4\alpha})}} \quad (6)$$

where $\alpha = (A - gH^2 - hH^4)C/B^2$, and A is the coefficient renormalized by the strain. The kink, described by equation (4), is the moving interphase boundary separating the paraelectric ($P = 0$ for $s \rightarrow +\infty$) and ferroelectric ($P = \sqrt{[(B/2C)(1 + \sqrt{1 - 4\alpha})]}$ for $s \rightarrow -\infty$) phases. The profile of the moving interphase boundary is shown in figure 1 (equation (4)). The interphase boundary moves in the direction of the ferroelectric phase with increasing magnetic field and decreasing Sr concentration in $\text{Ba}_{1-\delta}\text{Sr}_\delta\text{TiO}_3$. It moves in the direction of the paraelectric phase with decreasing magnetic field and increasing Sr concentration. The interphase boundary velocities v , which are shown in figures 2 and 3, as functions of Sr concentration, δ , and magnetic field, H , were obtained according to equation (6). The magnetic field dependence of the velocity, which is shown in figure 2(a), was calculated for pure barium titanate. The sign of the velocity v defines the direction in which one phase grows at the expense of the other, i.e. the sign depends on the direction in which the interphase boundary propagates thus leading to formation of paraelectric or ferroelectric phases. It is seen from figure 2 that a change of δ (see figure 2(a)) or H (figure 2(b)) up or down with respect to the phase transition point (δ_c and H_c for the concentration and the magnetic field respectively) induces motion of the interphase boundary. The front is in equilibrium at $\delta = \delta_c$ and $H = H_c$, where the free-energy densities of the two phases are equal.

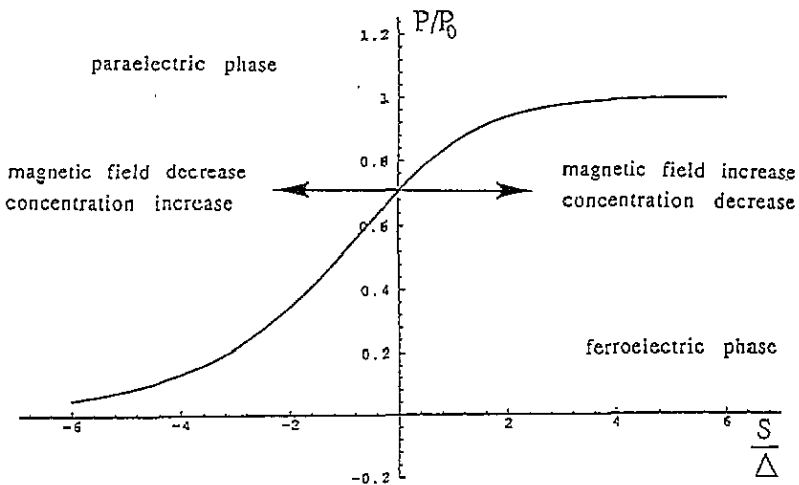
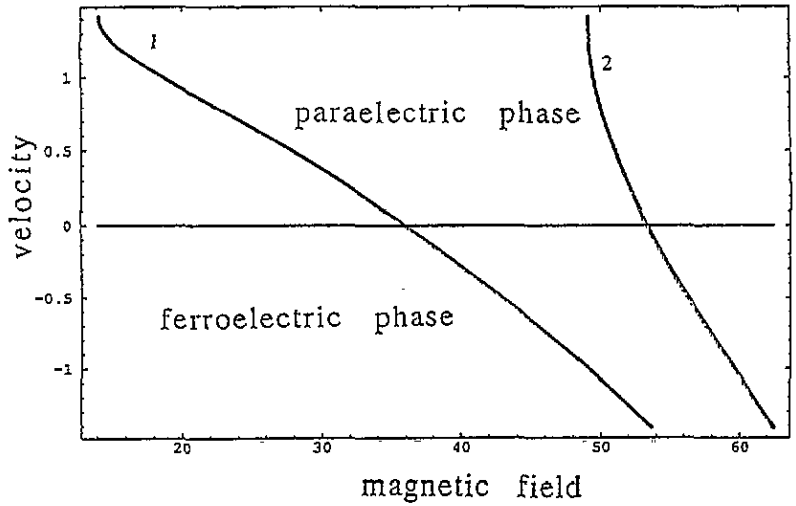
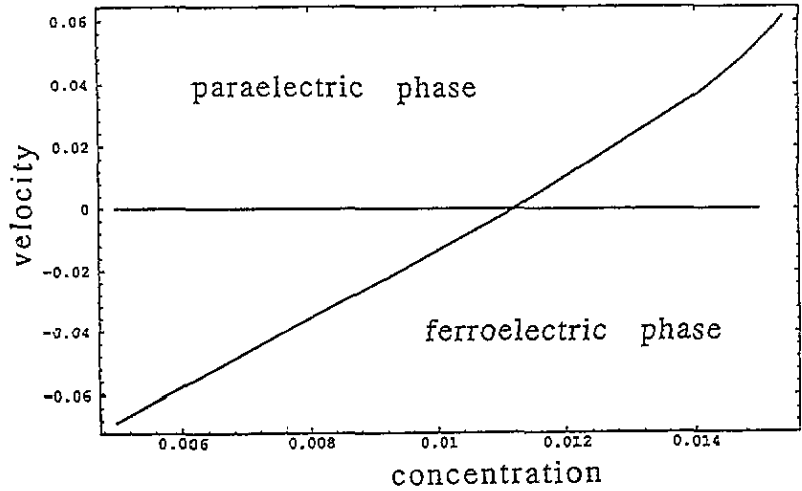


Figure 1. The profile of the moving interphase boundary (P/P_0 as a function of s/Δ).

In figures 3(a) and 3(b) the phase growth diagram is plotted for the solid solution $\text{Ba}_{1-\delta}\text{Sr}_\delta\text{TiO}_3$ in terms of coordinates δ and H . The interphase boundary velocity is shown here as a function of concentration and magnetic field at $T = 390$ K. The behaviour of the velocity, which is plotted in figures 3(a) and 3(b), results from the competition of the two opposite tendencies of change of the phase transition temperature. The phase transition temperature decreases when dopant concentration in the sample increases, and it increases with increasing magnetic field. The intersection of the two surfaces forms the curve of phase transitions at which the velocity is equal to zero and the minima of the free-energy density have the same depth (see figures 3(a) and 3(b), in which the phase growth diagrams are constructed for $T = 390$ K). The ends of the two velocity curves in terms of the coordinates δ and H designate the limits of the phase coexistence. The limits are determined from the conditions $\alpha_0 = 0$ and $\alpha^* = \frac{1}{4}$. The subscript '0' refers to the temperature T_0 and magnetic field strength H_0 , which determine the stability limit of the



a)



b)

Figure 2. (a) The velocity of the interphase boundary v as a function of magnetic field strength H (in T) in $\text{Ba}_{1-\delta}\text{Sr}_\delta\text{TiO}_3$. Plots 1 and 2 correspond to $\Delta T = 7$ K and $\Delta T = 12$ K respectively. (b) The velocity of the interphase boundary v as a function of the Sr concentration δ . The velocity is given in units of $(\Gamma B/3)[2D/C]^{0.5}$.

paraelectric phase. The superscript '*' refers to the temperature T^* and the magnetic field strength H^* , which determine the stability limit of the ferroelectric phase. Through change of the magnetic field and the concentration we arrive at a state in which only one phase (paraelectric or ferroelectric) is stable. We see from figure 2(a) that the curve of the velocity for higher magnetic fields (curve 2, $T - T_0^0 = \Delta T = 12$ K, where T_0^0 is the stability limit temperature for pure BaTiO_3 at $H = 0$) is steeper than one for lower magnetic fields (curve 1, $\Delta T = 7$ K). The field decrease, which is equal to 1 T, leads to the 200% decrease of the velocity of the paraelectric phase, while the same change of the velocity for low fields

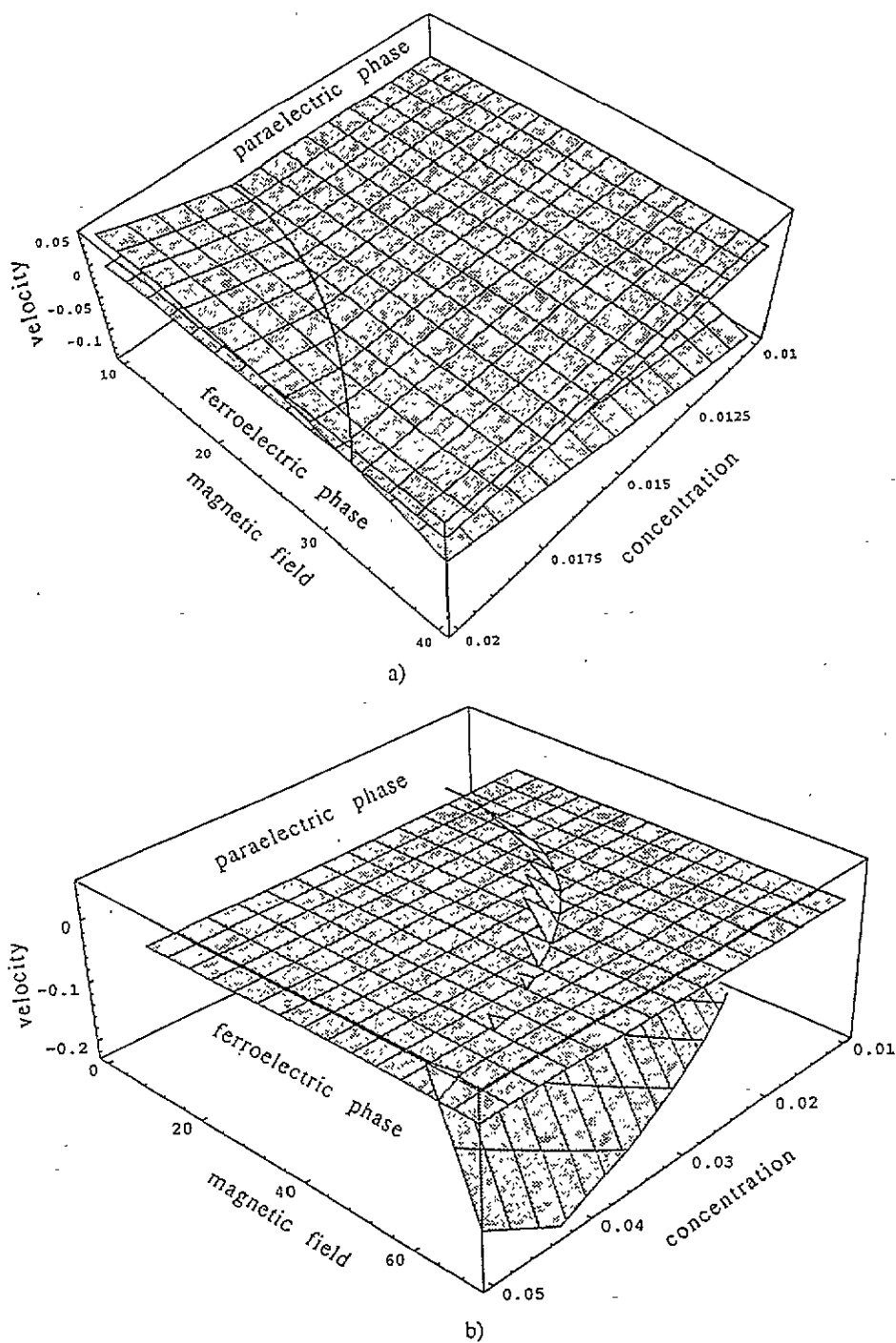


Figure 3. The diagram showing the phase growth in terms of the coordinates H and δ in $\text{Ba}_{1-\delta}\text{Sr}_\delta\text{TiO}_3$ at $T = 390$ K, with H in T: (a) for compositions with $\delta = 0.01-0.02$, and (b) for compositions with $\delta = 0.01-0.05$. The velocity is given in units of $(\Gamma B/3)[2D/C]^{0.5}$.

is reached by the field increase which is equal to 10 T. On the other hand, the ferroelectric phase growth proceeds more slowly: the 200% velocity change is obtained via the field change which is equal to 4 T at $\Delta T = 12$ K and $\Delta T = 7$ K. At higher magnetic fields the slope of the phase transition curve is substantially changed (figures 3(a) and 3(b)). The 'teeth' above the phase transition curve in figure 3(b) denote the allowed concentration and field ranges for existence of the interphase boundary and they describe its motion towards the paraelectric phase. Thus, the diagram in figure 3(a) is part of the more general diagram given in figure 3(b), which describes a wider region of fields and concentrations.

The experimental data used here for calculations are: $A'_0(\delta = 0) = 7.41 \times 10^{-5} \text{ K}^{-1}$ [19] ($A'_0(\delta = 0)$ denotes the coefficient A'_0 for pure barium titanate, i.e. when the Sr concentration δ is equal to zero), $B_0 = 6.8 \times 10^{-13} \text{ cm s}^2 \text{ g}^{-1}$ [19], $n_t = 0.6$ [17], $C = 2.28 \times 10^{-22} \text{ cm}^2 \text{ s}^4 \text{ g}^{-2}$ [19], $dT_0/dn = -358 \text{ K}/n_{Sr}$ [17], $(A'C/B^2)g = 6.27 \times 10^{-4} \text{ K T}^{-2}$ [10], $(A'C/B^2)h = 6.28 \times 10^{-7} \text{ K T}^{-4}$ [10]. The dependence $D = D(\delta)$ determined from the square of the lattice parameter [18] turns out to be negligible compared to the dependence of v on δ , which follows from $T_0(\delta)$ and $B(\delta)$. We see that high magnetic fields accelerate the formation of the two phases. Despite small shifts of the phase transition temperature under the influence of magnetic fields (the shift is about 0.3 K for $H = 20$ T in BaTiO_3 [10]) the effect of the magnetic field on the interphase boundary velocity is very large. Therefore the use of high magnetic fields results in larger shifts of ferroelectric phase transitions and in a considerable increase of the rate of phase growth. This large magnetic field effect is found close to the phase transition point even for relatively small fields within the range of coexistence of metastable and stable phases. It occurs because each slight change of the external magnetic field leads to a substantial change of the hyperspace curvature of the free-energy density in the region of coexistence of ferroelectric and paraelectric phases. In figures 2 and 3 we see the effect of the slowing down of the interphase boundary motion at the phase transition point. The interphase boundary changes the direction of its motion, although the direction of the magnetic field is not changed. The strong dynamic effect is therefore caused by the first-order origin of the phase transition. Thus, the influence of magnetic fields on the interphase boundary dynamics in the metastable region is large, although the magnetic field shift of the ferroelectric phase transition point is relatively small. The dynamics of interphase boundaries differs for the two limits of stability of paraelectric and ferroelectric phases. For the metastable paraelectric phase close to its stability limit, $\alpha \ll 1/4$, we obtain $v \sim (\delta_t - \delta)$ (see equation (6)). The interphase boundary velocity for the metastable ferroelectric phase is $v \sim (\delta_t - \delta)\alpha^{0.5}$, near to the ferroelectric stability limit, $\alpha \sim 1/4$.

It should be noted that the diagrams for the phase growth constructed here substantially reflect the peculiarities of the solid solution under consideration and its response to the external magnetic field. The slopes of the dependences on T , δ , and H of the velocity are very sensitive functions of composition. Thus, the magnetic field-concentration diagrams can serve as indicators of the properties of ferroelectric solid solutions.

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