Pressure-induced kinetics of ferroelectric phase transitions

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The hydrostatic-pressure-induced kinetics of paraelectric-ferroelectric phase transitions is considered on the basis of the time-dependent Ginzburg-Landau theory. The exact solution describing the interphase boundary at first-order ferroelectric phase transitions is used for analyzing the movement of the interphase boundary under the influence of hydrostatic pressure. Temperature and pressure dependences of the interphase boundary width and velocity are calculated by using the experimental data in BaTiO$_3$. Power laws of the temperature and pressure behavior of the interface velocity $v = v(|T - T_c|)$ and $v = v(|p - p_c|)$ are found. The pressure hysteresis is calculated.

In the last few years the problem of interphase boundary propagation at first-order phase transitions has received renewed experimental and theoretical interest.[1–16] The growth and kinetics processes at symmetry-breaking first-order phase transitions are associated with the migration of interphase boundaries separating the two coexisting phases. Recently the influence of electric and magnetic fields on the phase-transition kinetics has been extensively studied at first-order diffusionless phase transitions in solids.[17,18] As is well known, a great part of diffusionless solid-solid phase transitions is turned out to be a first-order type. Hydrostatic pressure can be a powerful tool of governing the phase-transition order: first-order phase transitions can be transformed into second-order ones with increasing pressure.[19] To the best of our knowledge, the majority of hydrostatic pressure researches of ferroelectric phase transitions has been carried out for studying the static properties of ferroelectrics.[20] The efficiency of the pressure investigations in ferroelectrics is caused by the sensibility of short-range and Coulomb forces, determining the nature of ferroelectric phase transitions, to pressure. One of the most pronounced pressure effects on the ferroelectric properties is large shifts of phase-transition temperatures.[20] For this reason, we assume that pressure may also essentially influence the phase-transition kinetics which depends strongly on the phase-transition temperature. The picture of the temperature-induced phase-transition kinetics at ferroelectric phase transitions should be complemented by investigating the pressure effect on the interphase boundary propagation. This paper concerns the hydrostatic pressure effect on the phase-transition kinetics in ferroelectrics. We discuss the interfacial kinetics within an exactly soluble model which is the time-dependent Ginzburg-Landau theory. It has been used for temperature, electric, and magnetic field effects on the phase-transition kinetics in ferroelectrics in (Refs. 1, 3–5, 7, 10, 17, 18, 21, and 22). We propose here to use this model for studying the pressure-induced kinetics of ferroelectric phase transitions. We also calculate the hydrostatic-pressure hysteresis.

The most common approach for the ferroelectric phase transitions involves the use of the time-dependent Ginzburg-Landau theory which associates a thermodynamic force with an approach to equilibrium governed by a damping term. The model assumes that the interfacial dynamics is entirely governed by the evolution of the order parameter which is polarization P:

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

where Γ is the Landau-Khalatnikov transport coefficient which sets the time scale of the relaxation process and is assumed to depend noncritically on a temperature and pressure, F is the free energy given by the Landau's thermodynamic theory of phase transitions. The theory is based on the expansion of the free energy in a power series of the polarization which serves as the order parameter of the system. For the simple case of a free ferroelectric crystal which is nonpiezoelectric in the paraelectric phase, like ferroelectric perovskites, the free energy takes the form

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

where f is the free-energy density given by

$$f(p,T,P) = f_0(p,T) + \tfrac{1}{2} A P^2 - \tfrac{1}{4} B P^4 + \tfrac{1}{6} C P^6 , \qquad (3)$$

where p is a pressure, T is a temperature, f_0 is the free-energy density for the paraelectric phase. A, B, and C are coefficients which can be functions of temperature and hydrostatic pressure. For B and $C > 0$, Eq. (3) describes a first-order phase transition. For $B < 0$, a second-order phase transition takes place. If $B = 0$, a tricritical point (p_t, T_t) is reached; this is the point in which a line of first-order phase transition goes continuously into a line of second-order phase transition. D is the positive coefficient of the gradient, inhomogeneity term. The

functional derivative $\partial F/\partial P$ is a term tending to restore the value P to its thermal equilibrium value.

When hydrostatic pressure is applied to a crystal with a centrosymmetric paraelectric phase and a polarization along one of the crystallographic axes in the ferroelectric phase, the lowest-order interaction is[20]

$$f(P,p)=\Omega p P^2 , \qquad (4)$$

where Ω is a function of the electrostrictive compliances. Then Eq. (3) taking into account the term depending on mechanical strains f_s can be presented as follows:

$$f=f_s+\{\tfrac{1}{2}\beta(T-T_0)+\Omega p\}P^2-\frac{B}{4}P^4+\frac{C}{6}P^6 , \qquad (5)$$

where $A=\beta(T-T_0)+2\Omega p$. T_0 is the stability limit of the paraelectric phase, coefficient β does not depend on a temperature and pressure; this statement is confirmed by the absence of a temperature and pressure dependence of the Curie-Weiss constant, for example, in perovskites.[20,23] The present form of the coefficient A in Eq. (5) is correct in ferroelectrics for which the temperature of stability limit of the paraelectric phase decreases linearly with increasing pressure, for example, in perovskites:[20,23]

$$T_0(p)=T_0(0)-\frac{2\Omega p}{\beta} . \qquad (6)$$

It follows from Eq. (5) that dielectric susceptibility ϵ obeys the Curie-Weiss law. At a constant temperature the Curie-Weiss law can be written as follows:[24]

$$\frac{1}{\epsilon}=2\Omega(p-p_0) , \qquad (7)$$

$$p_0=-\frac{1}{2}\frac{\beta[T-T_0(0)]}{\Omega} . \qquad (8)$$

In perovskites the crystal obeys the Curie-Weiss law both with respect to pressure and temperature:[24]

$$\epsilon=\frac{c}{T-T_0(p)} , \qquad (9)$$

$$\epsilon=\frac{c^*}{p-p_0(T)} , \qquad (10)$$

where c is the temperature Curie-Weiss constant and c^* is the pressure Curie-Weiss constant; $c=1/2\beta$ and $c^*=1/2\Omega$.

At a constant pressure the interphase boundary exists at the temperature range $T_0<T<T^*$, where T^* is the stability limit of the ferroelectric phase. Analogously, we state that the interphase boundary exists at the pressure range $p_0<p<p^*$; p_0, p_c, and p^* correspond to T_0, T_c, and T^*. Temperature T_c and pressure p_c at which the phase transition occurs are determined from $\partial f/\partial P=0$ and $f=f_0$: $(AC/B^2)_c=\frac{3}{16}$ and $(AC/B^2)^*=\frac{1}{4}$. Temperature T^* and pressure p^* are determined from $\partial f/\partial P=0$ and $\partial^2 f/\partial P^2=0$. Thus, we have the ranges of supercooling and superheating and corresponding pressure ranges.

$$T_0=T_c-\frac{3B^2c}{8C}, \quad T^*=T_0+\frac{B^2c}{2C} , \qquad (11)$$

$$p_c=p_t+\frac{1}{2Q}-\sqrt{(1/Q)(p_t-p_0+1/4Q)} ,$$
$$p^*=p_t+\frac{3}{8Q}-\sqrt{(3/4Q)(p_t-p_0+3/16Q)} , \qquad (12)$$

$$Q=\frac{3b^2c^*}{16C} , \qquad (13)$$

$$B=b(p_t-p) , \qquad (14)$$

where the coefficient b does not depend on a pressure. The pressure dependence in Eq. (14) is explained as follows. This interphase boundary may remain quite sharp unless the temperature or pressure get sufficiently near the tricritical point, when it becomes dispersed by fluctuations that are large in spatial extent. The temperature difference between the phase-transition temperature T_c and the temperature corresponding to the stability limit of the paraelectric phase T_0 decreases with increasing pressure and this is a manifestation of the fact that the character of the phase transition changes from first order to second order with pressure, as seen in perovskites.[20,23-26] The tricritical point is characterized by the temperature T_t at which $T_0=T_c=T^*=T_t$ and the pressure p_t at which $p_0=p_c=p^*=p_t$. In many cases the tricritical pressure is much larger than the atmosphere one. Thus, $B_0\approx bp_t$ ($p_t\gg1$ bar), where $B_0=B$ (at $p=1$ bar). Therefore, the phase transition is accompanied by pressure hysteresis (p^*-p_0) determined by Eqs. (12) and (13).

Using the above pressure dependences we consider the pressure-controlled interfacial dynamics at ferroelectric phase transitions. Variating the functionals (2) and (3) and substituting the result into Eq. (1), we obtain for the uniaxial case

$$\frac{\partial P}{\partial t}+\Gamma(AP-BP^3+CP^5)-2\Gamma D\frac{\partial^2 P}{\partial x^2}=0 . \qquad (15)$$

Equation (15) is therefore the equation of motion for the polarization and it is mean-field representation of the nonequilibrium interphase boundary kinetics. Now we look for a steady-state solution of Eq. (15) for which, in the moving reference frame of the interphase boundary, the profile of polarization P is time independent, i.e., letting $s=x-vt$:

$$2\Gamma D\frac{d^2P}{ds^2}+v\frac{dP}{ds}-\Gamma(AP-BP^3+CP^5)=0 . \qquad (16)$$

Equation (16) was solved and studied in Refs. 21, 3, and 9. The solution of Eq. (16) for the interface boundary conditions has the kink form

$$P=\frac{P_0}{\sqrt{1+\exp(s/\Delta)}} , \qquad (17)$$

where P_0 is the equilibrium value of polarization

$$P_0^2=\frac{B}{2C}(1+\sqrt{1-4AC/B^2}) , \qquad (18)$$

and Δ is the width of the interphase boundary given by

$$\Delta = \frac{(3DC)^{1/2}}{B\sqrt{1-2\alpha+\sqrt{1-4\alpha}}} , \qquad (19)$$

where $\alpha = AC/B^2$, which moves with the velocity v, given by

$$v = \frac{\sqrt{2}}{3} \frac{\Gamma DB}{\sqrt{C}} \frac{(8\alpha-1-\sqrt{1-4\alpha})}{\sqrt{1-2\alpha\sqrt{1-4\alpha}}} , \qquad (20)$$

$$\alpha = \frac{16Q}{3} \frac{p^-p_0}{(p_t-p)^2} . \qquad (21)$$

The driving force of the interphase boundary movement is the tendency of the system to diminish its free energy through a kinetic relaxation towards equilibrium. The meaning of Eq. (17), as the moving interphase boundary, can be understood as follows. For $s \to \infty$, $P \to P_0$ and the ferroelectric phase is obtained, for $s \to +\infty$ the paraelectric phase $P=0$ is obtained. Since $x \to -x$, $v \to -v$ is a symmetry problem, for the kink solution there is an antikink solution with the opposite velocity, i.e., for the antikink we obtain $\exp(-S/\Delta)$ in (17). Consequently, the kink described by Eq. (17) is the moving interphase boundary separating between the paraelectric and ferroelectric phases. According to Eq. (17) the paraelectric phase is located at the right, and the ferroelectric phase is situated at the left. The negative sign reverses this situation and puts the paraelectric phase at the left. Strictly speaking, Eq. (15) admits a multitude of particular solutions. We restricted ourselves to steady-state solutions, where the interphase boundary moves with a constant velocity v given by (20), but does not change its shape. The fixed interphase boundary shape is expected for a nonconserved order parameter. The interphase boundary preserves its shape (17) during the propagation because of the competition of the two terms: the homogeneous part of the free-energy density tends to bring the system to a stable state, while the inhomogeneous part of Eq. (2) has the opposite tendency. The ferroelectric phase transition proceeds at a finite rate by means of the phase transition front which separates

stable and metastable regions of the crystal specimen. Under isobaric conditions, we can rewrite Eq. (20) as follows:[9]

$$v = 2\Gamma[D\beta(T_c-T_0)^{1/2}]\frac{\{\delta-(2/3)[1+\sqrt{1-(3/4)\delta}]\}}{\sqrt{1-(3/8)\delta}+\sqrt{1-(3/4)\delta}} , \qquad (22)$$

$$\delta = \frac{T-T_0}{T_c-T_0} . \qquad (23)$$

It is seen that the interphase boundary velocity may be positive or negative depending on whether $T < T_c$ or $T > T_c$. The velocity v is therefore a function of supercooling and superheating. In Fig. 1, the interphase boundary velocity v [Eq. (20)] is shown as a function of temperature in BaTiO$_3$ at atmosphere pressure, where $T_c = 406$ K,[27] $T_0 = 391$ K,[27] $T^* = 411$ K. Analyzing the temperature dependence of the interface velocity we obtain for $T > T_c$, $v \propto (T-T_c)^n$, where $n = 1.49\pm0.02$, and for $T < T_c$ $v \propto (T_c-T)^m$, where $m = 0.82\pm0.02$. Thus, the interphase boundary velocity is expressed in terms of the superheating and supercooling with the help of simple power laws. We can justify the application of the theory in ferroelectric perovskites by three following experimental facts.

(a) The experiment in BaTiO$_3$ (Ref. 33) shows that the interphase boundary velocity is an increasing function of temperature of the type demonstrated in Fig. 1 for the superheating part of the curve, i.e., it does not reach a saturation: $n > 1$; the experimental data in Ref. 33 are concentrated in a very narrow temperature range, $\Delta T = 0.9-0.2$ K, and for this reason it is difficult to compare quantitatively between the theory and the experiment. However, it is clear that $n > 1$ implies that the case under consideration describes the overdamped motion of the interphase boundary.[28]

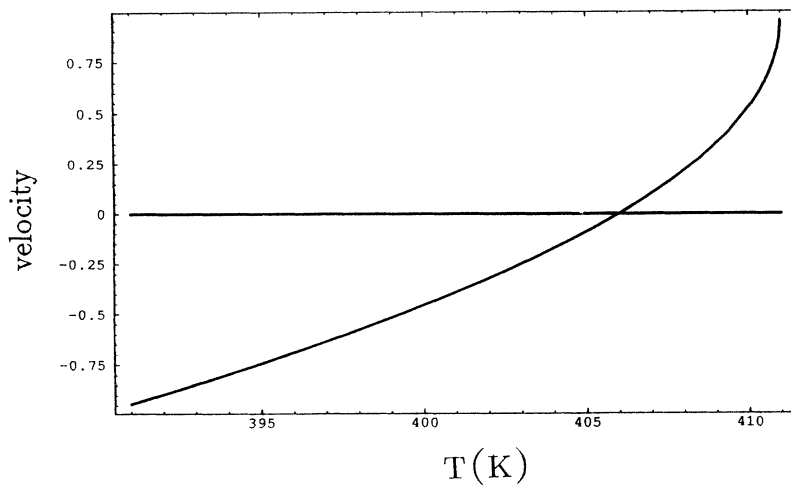(b) The experiment in PbTiO$_3$ (Ref. 7) shows that for

FIG. 1. The interphase boundary velocity v as a function of temperature T in BaTiO$_3$. The velocity is given in units of $(2^{1/2}/3)(\Gamma DB/C^{1/2})$.

the same value of supercooling and superheating the interphase boundary velocity in the heating process is larger than in the cooling one, as is seen from Fig. 1.

(c) The calculated velocities are in agreement with measured ones for reasonable values of Γ and D.[3,7]

In the same spirit we can analyze the pressure dependences of the width and velocity of the interphase boundary under isothermal conditions. We use experimental data for the ferroelectric BaTiO$_3$ which is a well-studied substance. It is seen from (19) that at $p = p_t$ the interphase boundary width Δ tends to infinity and thus at this pressure the first-order phase transition is transformed into a second-order one as it should take place at tricritical point. In Fig. 2, the pressure dependence of the width Δ is shown [Eq. (19)]. This is an increasing function of pressure. It is seen that the maximal increase of the width is approximately equal to 2. This means that the interphase boundary remains well defined under the hydrostatic pressure influence. In Fig. 3(a) the pressure dependence of the velocity v is demonstrated [Eq. (20)]. 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 the paraelectric or ferroelectric phase. At $p = p_c$ the interphase boundary stops because the difference between the free-energy densities of the two phases being the driving force of the phase transition is equal to zero. True equilibrium between the two phases is possible only at $p = p_c$. The above-mentioned interfacial broadening results from the increase in the interphase boundary velocity. We can clarify the above pressure-controlled dynamics of the interphase boundary by using Fig. 3(b), in which the free-energy density f is demonstrated as a function of pressure p. The free-energy density is presented for three pressures: $p = 20$ kbar ($p_0 < p \leq p_c$-curve 1); $p = 20.24$ kbar ($p = p_c$-curve 2), and $p = 20.5$ kbar ($p_c < p \leq p^*$-curve 3). Below p_0 two minima of the ferroelectric phase exist. At pressures above p_0 a third, local minimum of the paraelectric phase appears ($P = 0$). The paraelectric phase is here metastable, whereas the ferroelectric one is

stable (curve 1). At the phase-transition pressure $p = p_c$, the central minimum has the same depth as the two other minima (curve 2). At $p = p_c$ the free-energy densities of the paraelectric and the ferroelectric phases are equal. At pressures above p_c but below p^* the central minimum is deeper than the two outside minima (curve 3); the ferroelectric phase is metastable, whereas the paraelectric phase is stable. The two outside minima finally disappear at pressures above p^*, and only the central minimum at $p = 0$ remains. Therefore, the interphase boundary exists at the pressure range $p_0 \leq p \leq p^*$. The increase in pressure leads to the interphase boundary motion such that the paraelectric phase grows at the expense of the ferroelectric one. The decrease in pressure leads to the interface motion such that the ferroelectric phase grows at the expense of the paraelectric one.

For our calculations we used the following experimental data for BaTiO$_3$ at room temperature: $p_t = 34$ kbar,[26] $p_0 = 18.5$ kbar,[24] $C^* = 2.8 \times 10^4$ kbar,[24] C ($p = 1$ bar-atmosphere pressure) $= 2.28 \times 10^{-22}$ CGSE,[29] $B_0 = 6.8 \times 10^{-13}$ CGSE.[29] We can estimate the coefficient D according to Ref. 30: $D = (\pi/15)d^2$, where d is the lattice parameter. Using $d(p)$ from Ref. 31 we see that at the pressure range of the interphase boundary existence (18.5 kbar $< p <$ 20.65 kbar) the largest pressure change of the length of the unit cell in BaTiO$_3$ (along the c axis) is about 4%. This change is negligible in comparison with the pressure effects presented in Figs. 2 and 3. For this reason we do not include $d(p)$ in Eqs. (19) and (20). Analyzing the pressure dependence of the interface velocity for $p > p_c$ we obtain that $v \propto (p - p_c)^n$, where $n = 1.38 \pm 0.02$ and for $p < p_c$ we have $v \propto (p_c - p)^m$, where $m = 0.78 \pm 0.02$.

Experimental investigations of the temperature dynamics of interphase boundaries were carried out in ferroelectric[1,4,7,32−36] and antiferroelectric perovskites[37] under isobaric conditions. As was shown in Ref. 37, the interphase boundary of the Kittel antiferroelectric may also be expressed by the kink solution (17). Consequently, the results presented here for the ferroelectric interphase boundary kinetics may be also applied for the pressure-
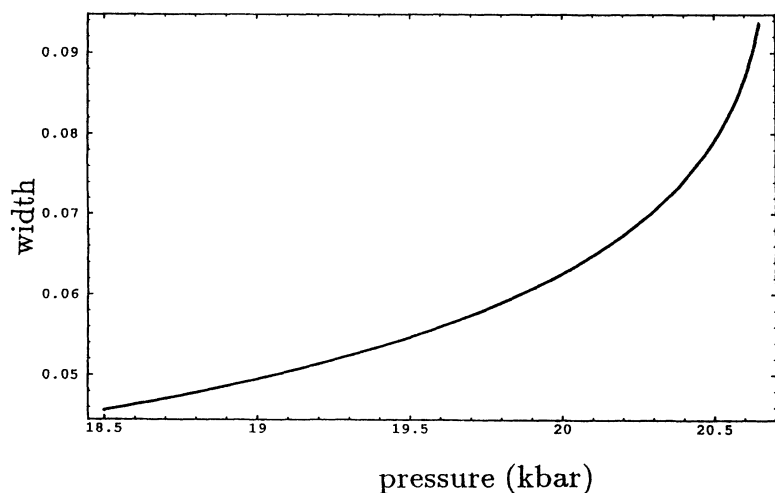

FIG. 2. The interphase boundary width Δ as a function of pressure p in BaTiO$_3$. The width is given in units of $(3DC)^{1/2}/B$.
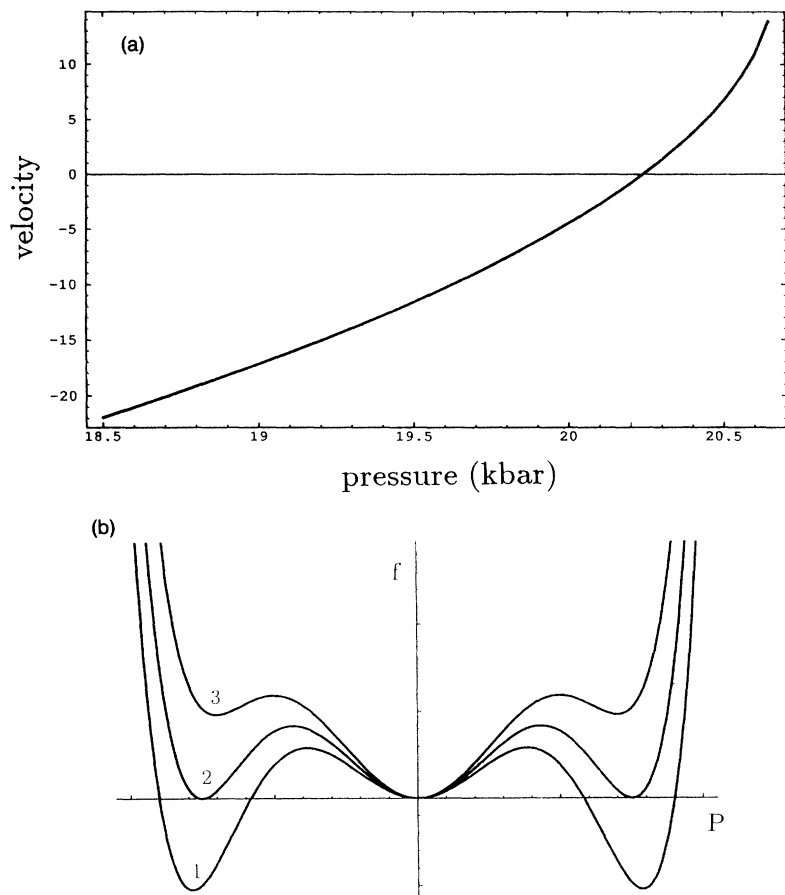
pressure (kbar)

FIG. 3. (a) The interphase boundary velocity v as a function of pressure p in BaTiO$_3$. The velocity is given in units of $(2^{1/2}/3)(\Gamma DB/C^{1/2})$. (b) The free-energy density f as a function of polarization p for three values of hydrostatic pressure p; $p = 20$ kbar (curve 1), $p = p_c = 20.24$ kbar (curve 2), and $p = 20.5$ kbar (curve 3). For the present temperature the interphase boundary exists at 18.5 kbar $< p < 20.65$ kbar.

controlled kinetics of antiferroelectric interphase boundaries.

In conclusion, we have presented a study of the pressure-induced kinetics of ferroelectric phase transitions. Our research is based on the exact solution of the time-dependent Ginzburg-Landau equation taking into account the hydrostatic pressure influence. The mean-field approximation describes well many static and dynamic phenomena in ferroelectrics, for example, in perovskites discussed here.[19,20] For this reason, the temperature-induced kinetics of perovskite ferroelectrics has been successfully used for the interpretation of experiments on the interphase boundary motion under isobaric conditions.[7,37] Therefore, the application of the pressure-induced kinetics of ferroelectric phase transitions can be also useful for the interpretation of corresponding hydrostatic pressure measurements. We have also calculated the pressure hysteresis.

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