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Dependence of interface motion on pressure in ferroelectrics*

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The motion of the paraelectric–ferroelectric interface in $KNbO_3$ at a hydrostatic pressure is studied in the framework of the mean-field theory. The kink solution is applied to the calculations of the width and velocity of the interface at different pressures. The calculations are based on the experimental data for the Curie–Weiss constant and the parameter of the Ginzburg-Landau expression for the free energy. The response of the interface motion to the hydrostatic pressure and the tricritical point is investigated nonempirically.

Keywords: interface, pressure, ferroelectrics, Ginzburg–Landau equation
PACC: 7780, 7780B, 0570F, 0520D

1. Introduction

In recent years, the motion of interface in ferroelectrics in a first-order phase transition has been a subject of experimental and theoretical studies.[1−13] The dynamics of a first-order paraelectric–ferroelectric phase transition has been well described. A kink solution of the time-dependent Ginzburg–Landau equation for the evolution of the order parameter (spontaneous polarization) $\boldsymbol{P}$ can describe the profile and motion of the interface,[4,5] which has been verified experimentally.[9,10] The dynamics of a phase transition may be influenced by the external thermodynamic parameters, such as temperature, external field, and composition (or concentration of one element). In the above research, only temperature is considered. Here, we describe the dynamics of a first-order paraelectric–ferroelectric phase transition with the pressure taken into account.

2. Theoretical model

For ferroelectrics, the evolution of the order parameter $\boldsymbol{P}$ can be described by the generalized Ginzburg–Landau equation[4−6]

$$\frac{\partial P}{\partial t} = -\Gamma \frac{\delta F}{\delta P}, \tag{1}$$

where t is the time, Γ is the Landau–Khalatnikov damping coefficient, which is assumed to depend noncritically on temperature, pressure, and concentration, and F is the free energy. The expansion of the free energy F is in the following form:

$$F = F_0 + \frac{1}{2}AP^2 - \frac{1}{4}BP^4 + \frac{1}{6}CP^6 + D\left(\frac{\partial P}{\partial x}\right)^2, \tag{2}$$

where F_0 is the free energy for the paraelectric phase, and D is the positive coefficient of the inhomogeneity term. For $B > 0$ and $C > 0$, Eq.(2) describes a first-order phase transition. For $B < 0$, a second-order phase transition takes place. If $B = 0$, a tricritical point is reached. If we do not consider pressure, the coefficient A can be expressed as

$$A = A'(T - T_0), \tag{3}$$

where T_0 is the temperature of the stability limit of the paraelectric phase. Considering low pressures, we can express the coefficient A as follows according to Ref.[14]:

$$A = A'(T - T_0) + 2\xi p, \tag{4}$$

where ξ is a function of the elastic and electrostrictive coefficients. Coefficient $A = 1/2c$, where c is the Curie–Weiss constant and depends on neither temperature nor pressure.[15]

It is well known that there exists a temperature hysteresis in the case of a first-order phase transition. The paraelectric phase may exist at high temperatures and becomes unstable below T_0. The ferroelectric phase may exist at low temperatures and becomes

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unstable above T^*. These two temperature regions overlap: $T_0 < T^*$. Only at the Curie temperature T_C can the free energies of the two phases be equal. There appears an equilibrium between the two phases. Similarly, upper and lower critical values and hysteresis exist with respect to pressure. At a given temperature, the pressure p_C that induces the phase transition ranges between the two critical values: $p_0 < p_C < p^*$, where p_0 is the lower critical pressure for the stability of the paraelectric phase, and p^* is the higher critical pressure for the stability of the ferroelectric phase. At a pressure of p in the range $p_0 < p < p_C$, the paraelectric phase is metastable whereas the ferroelectric phase is stable. At a pressure of p in the range $p_C < p < p^*$, the paraelectric phase is stable and the ferroelectric phase is metastable.

The tricritical point (p_t, T_t): $p_0 \to p_C = p_t \leftarrow p^*$, $T_0 \to T_C = T_t \leftarrow T^*$ is determined at $B = 0$. This means that the phase transition changes from the first-order to the second-order. The temperature difference between T_C and T_0 decreases with the increasing pressure. As a matter of fact, this is a demonstration of the fact that the phase transition changes from the first-order to the second-order with pressure. The case may be described with the following pressure dependence of B apart from the tricritical point:

$$B = B'(p_t - p). \tag{5}$$

This linear dependence is analogous to the temperature dependence of the coefficient A in the Ginzburg-Landau theory of phase transition.

Making variation of Eq.(2) and substituting the result into Eq.(1), we obtain the equation of evolution for the polarization

$$\frac{\partial P}{\partial t} + \Gamma\left(AP - BP^3 + CP^5\right) - 2\Gamma D\frac{\partial^2 P}{\partial x^2} = 0. \tag{6}$$

According to Refs.[4–6], we make a transformation $s = x - vt$, where v is the velocity in the x-direction, then obtain an ordinary differential equation with a variable s

$$2\Gamma D\frac{\mathrm{d}^2 P}{\mathrm{d}s^2} + v\frac{\mathrm{d}P}{\mathrm{d}s} - \Gamma\left(AP - BP^3 + CP^5\right) = 0. \tag{7}$$

A kink solution can be obtained

$$P = P_0\left[1 + \exp\left(\frac{s}{\Delta}\right)\right]^{-1/2}. \tag{8}$$

The boundary conditions are $P \to 0$ for $s \to -\infty$, and $P \to P_0$ for $s \to +\infty$. Here P_0, the equilibrium value of polarization, is given by

$$P_0^2 = \frac{B}{2C}\left[1 + \left(1 - \frac{4AC}{B^2}\right)^{1/2}\right] \tag{9}$$

and Δ, the width of the interface, is given by

$$\Delta^2 = \frac{3DC}{B^2}\left[1 - 2\alpha + \sqrt{1 - 4\alpha}\right]^{-1}, \tag{10}$$

where

$$\alpha = \frac{AC}{B^2} = \frac{p - p_0}{(p_t - p)^2}\frac{b^2}{2\xi C}. \tag{11}$$

The interface moves at a velocity of v:

$$v = \left(\frac{2D}{C}\right)^{1/2}\frac{\Gamma B}{3}\frac{\left(8\alpha - 1 - \sqrt{1 - 4\alpha}\right)}{\left(1 - 2\alpha + \sqrt{1 - 4\alpha}\right)^{1/2}}. \tag{12}$$

Equation (8) describes the kink profile of the moving interface separating the paraelectric phase from the ferroelectric phase. The interface preserves its shape (8) during the propagation because of the competition between the two terms: the homogeneous part in the free energy tends to make the interface infinitely sharp, while the inhomogeneous part in Eq.(2) has an opposite tendency. The ferroelectric phase transition proceeds at a finite rate by means of the phase transition front, which separates a stable region of the crystal from a metastable one.

3. Dependence of the interface width and velocity on pressure

As an example of $KNbO_3$, we analyse the dependence of the width and velocity of the interface on pressure under isothermal condition. In calculation we use the following experimental data for $KNbO_3$ at room temperature:[16] $c = 2.4 \times 10^5$K, T_0=377°C, $C = 5.4 \times 10^{-22}$ CGSE (ambient pressure p=100kPa), and $B = 10^{-12}$ CGSE.

The calculations of the coefficient ξ and the tricritical point for $KNbO_3$ have been performed based on full-potential LMTO (linear muffin-tin orbital) calculation using Methfessel's code.[17] With the choice of the basis set as indicated in Ref.[18] we have carried out the calculations of the total energies at the set of different volumes for the paraelectric phase (Fig.1(a)) and three ferroelectric phases. The differences in total energy between the paraelectric phase and the three ferroelectric phases each are shown in Fig1(b). In these calculations, we concentrate on the off-centre displacement of Nb atoms as the primary feature of a ferroelectric transition. First, we have found the equilibrium off-centre displacements for tetragonal, orthorhombic, and rhombohedral ferroelectric phase

to be 0.022, 0.028 and 0.033 times the "theoretical" lattice constant, respectively. We then scale this displacement along with the unit cell dimensions while fitting the total energy versus volume dependence, in order to obtain the coefficient ξ

$$\xi = \left[-\frac{1}{V} \left(\frac{\mathrm{d}^2 E}{\mathrm{d}V^2} \right)^{-1} \right],$$

where [ ] stands for the averaging over a set of volumes. For the paraelectric phase, we obtained $\xi = 4.70 \times 10^{-8} \mathrm{kPa}^{-1}$. The measurement of this parameter is expected to be rather difficult. Therefore, nonempirical calculation of this value is crucially important for our high-pressure interface simulation.

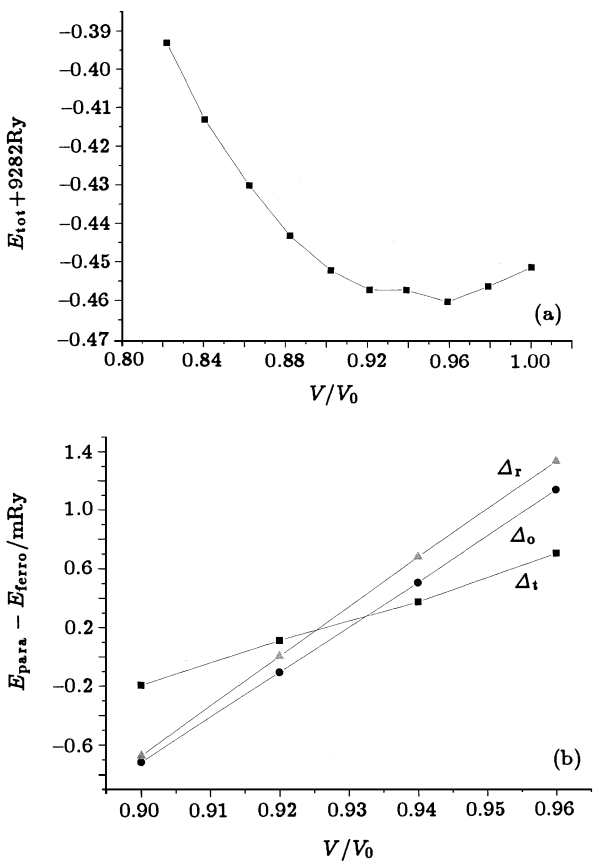


Fig.1. (a) Total energy of the paraelectric phase in $KNbO_3$ as a function of the relative volume V/V_0, where V_0 is the measured equilibrium volume of the paraelectric phase with the lattice parameter 0.3997nm.(b) Differences in total energy between the paraelectric and the three ferroelectric phases: $\Delta_t = E_{\mathrm{para}} - E_{\mathrm{tetra}}$; $\Delta_{\mathrm{o}} = E_{\mathrm{para}} - E_{\mathrm{orthor}}$; $\Delta_r = E_{\mathrm{para}} - E_{r\mathrm{hom\ bo}}$.

As seen from Fig.1(b), the cubic phase remains stable against any ferroelectric transformation for $V/V_0 < 0.9135$. Larger volume favours ferroelectric transitions first into the tetragonal phase, and then, for $V/V_0 > 0.9253$, the rhombohedral phase becomes energetically favourable for both the tetragonal and orthorhombic phases. For $V/V_0 > 0.9326$, i.e. the region of both "theoretical" and "experimental" lattice volumes is covered, the well-known hierarchy of stabilities of three ferroelectric phases is established. As temperature increases, the substance is expected to undergo a transition from the rhombohedral phase to the orthorhombic phase, then to the tetragonal phase, and finally to the cubic paraelectric phase. When an external pressure is applied, the sequence of transitions initially remains the same, but the temperature interval which is required to pass the system through the sequence of transitions gradually decreases, as is qualitatively evident from the difference in ever shrinking energy between phases.

For $V/V_0 < 0.9326$ our calculations show that the sequence of phases is changed: the rhombohedral phase tends to undergo, as temperature increases, a transition first to the tetragonal and then to the orthorhombic phase. For pressures corresponding to this volume region, it is possible to determine the interface as the one between the cubic (paraelectric) and orthorhombic (ferroelectric) phases. When pressure further increases and reaches a value corresponding to $V/V_0 = 0.9232$,the total energy of the orthorhombic phase becomes equal to that of the cubic phase at zero temperature, and the cubic-to-orthorhombic phase no longer exists. The pressure related to this critical volume is therefore termed the tricritical pressure p_t. From the pressure–volume relation

$$p = -\frac{\mathrm{d}E}{\mathrm{d}V}$$

which is shown in Fig.2 for the cubic phase (corresponding curves for all phases are indistinguishable in this scale) and on the assumption that the thermal expansion coefficients for both phases are equal, the pressure is found to be $p_t = 5.85 \times 10^6 \mathrm{kPa}$.

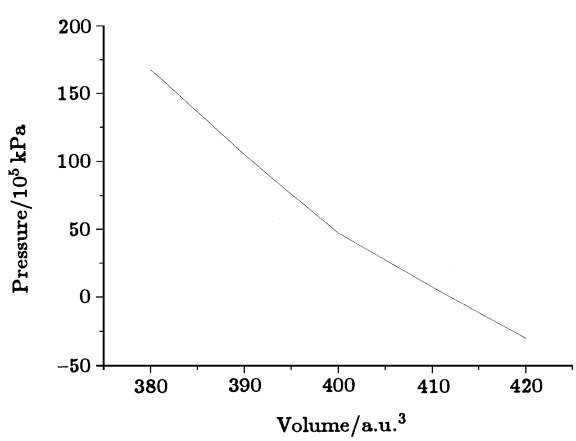


Fig.2. Equation of state for the paraelectric phase in $KNbO_3$.

According to Ref.[19], $D = \frac{\pi}{15}d^2$, and the coefficient D is estimated, where d is the lattice parameter. The $d(p)$ dependence is also extracted from the data of the full potential calculations by solving the equation of state. Using the calculated $d(p)$, we see that within the pressure limit where both the paraelectric and the ferroelectric phases and hence the interface exist, the maximum of change in the unit cell size induced by pressure is about 6%.

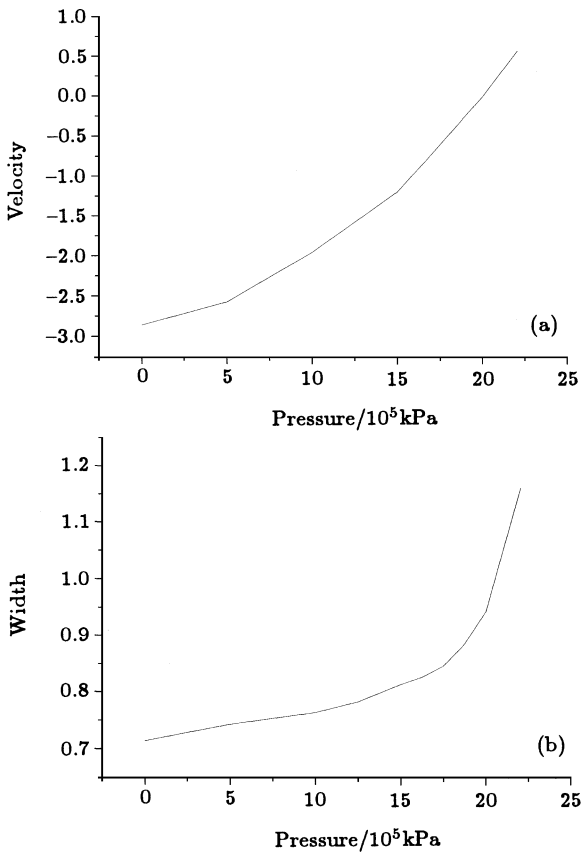


Fig.3. (a) Interface velocity v (in units of $(2D/C)^{0.5}\,\Gamma B/3$) as a function of pressure in $KNbO_3$. (b) Width Δ (in units of $(3DC)^{0.5}/B$) as a function of pressure in $KNbO_3$.

It is seen from Eq.(10) that at $p = p_t$ the interface width Δ tends to be infinite and thus at this pressure the first-order phase transition is transformed into the second-order one as it should take place at a tricritical point. In Fig.3 the pressure dependences of the width Δ (calculated from Eq.(10)) and velocity v (calculated from Eq.(12)) are shown in the whole range of pressure where two phases may coincide, which is found to be $1.50 \times 10^5\text{kPa} < p < 2.26 \times 10^6\text{kPa}$. Both Δ and v are ever increasing functions of pressure. Since the width increases merely by a factor of 2, the interface remains well defined under typical hydrostatic pressures. The sign of the velocity specifies the direction in which the interface propagates, i.e. in which one of two phases (paraelectric or ferroelectric) grows at the expense of the other. At $p = p_C = 1.99 \times 10^6\text{kPa}$, the interface stops because the difference in the free energy between the two phases that is the driving force of the phase transition becomes 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 interface velocity.

4. Conclusion

A study of the pressure-induced movement of the ferroelectric phase transition interface in the example of $KNbO_3$ is presented here, which is based on the exact solution of the time-dependent Ginzburg–Landau equation with the hydrostatic pressure influence taken into account. The theoretical results in the temperature-induced dynamics of ferroelectrics have been successfully used for the interpretation of experimental results about the interface motion under isobaric condition.[9,10] The pressure-induced dynamics of the ferroelectric phase transitions is useful to interpret the corresponding hydrostatic pressure measurements. Data for the tricritical pressure in $KNbO_3$ are extracted from the nonempirical calculation.

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