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Paraelectric–ferroelectric interface dynamics induced by latent heat transfer and irreversibility of ferroelectric phase transitions*

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The temperature gradients that arise in the paraelectric–ferroelectric interface dynamics induced by the latent heat transfer are studied from the point of view that a ferroelectric phase transition is a stationary, thermal-electric coupled transport process. The local entropy production is derived for a ferroelectric phase transition system from the Gibbs equation. Three types of regions in the system are described well by using the Onsager relations and the principle of minimum entropy production. The theoretical results coincides with the experimental ones.

Keywords: ferroelectric phase transition, interface dynamics, irreversible thermodynamics
PACC: 7780, 7780B, 4430, 0547

1. Introduction

The interface dynamics of first-order phase transitions is an active branch of research. There have been a lot of theoretical and experimental work about interface (phase boundary) motion in ferroelectrics and antiferroelectrics.[1−17] The most common approach to interface motion is confined in the framework of the time-dependent Ginzburg–Landau theory for first-order phase transitions.[18] The kink solution of the Ginzburg–Landau equation characterizes the moving interface between ferroelectric and paraelectric phase.[1] This type of motion is due to the relaxation of polarization and is relatively slow. In the experiments, a fast motion of interface has been observed.[5,19,20] And according to this, a mechanism due to the latent heat transfer has been introduced.[14,15] The interface dynamics induced by the latent heat transfer might be a vigorous one just like that induced by the relaxation of polarization. We think that the thermodynamics, especially the irreversible thermodynamics with the evolving characteristics, may be beneficial to it since it involves the heat conduction. In fact, the details of evolution of a phase transition can be described not only by dynamics but by thermodynamics. The supplements to the interface dynamics induced by the latent heat transfer will be made as the results of some necessary related thermodynamic considerations. And we will verify it through the comparison with the experiments.

2. Interface dynamics induced by latent heat transfer[14,15]

The moving interface in a system is a source or sink of heat if a first-order phase transition arises in it. When the temperature decreases from above to the phase transition temperature (Curie temperature), the latent heat is released. It heats and accelerates the motion of the interface. On the other hand, the acceleration of the interface can increase the amount of heat released per unit time. This avalanche-

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like process is stabilized eventually by heat removal via heat conduction and heat exchange with the thermal bath. Obviously, the interface velocity is controlled by heat flow and determined by the rate at which the latent heat is removed from the interface.

Assume n the axis perpendicular to the interface and pointing from the ferroelectric phase part to the paraelectric phase part. In the ferroelectric phase part, a plane is parallel to the interface, whose area is S. Then, the heat flowing across the plane in time Δt is

$$Q = k_{\mathrm{fer}} \left(\frac{\mathrm{d}T}{\mathrm{d}n}\right)_{\mathrm{fer}} S\Delta t, \tag{1}$$

where k_{fer} is the thermal conductivity coefficient of the ferroelectric phase, $\left(\frac{\mathrm{d}T}{\mathrm{d}n}\right)_{\mathrm{fer}}$ is the component of the temperature gradient in the ferroelectric phase part $(\boldsymbol{\nabla}T)_{\mathrm{fer}}$ in the n direction. Similarly, the heat flowing across a plane in time Δt, in the paraelectric phase part and parallel to the interface, is

$$Q' = k_{\mathrm{par}} \left(\frac{\mathrm{d}T}{\mathrm{d}n}\right)_{\mathrm{par}} S\Delta t, \tag{2}$$

where k_{par} is the thermal conductivity coefficient of the paraelectric phase, $\left(\frac{\mathrm{d}T}{\mathrm{d}n}\right)_{\mathrm{par}}$ is the component of the temperature gradient in the paraelectric phase part $(\boldsymbol{\nabla}T)_{\mathrm{par}}$ in the n direction. The difference between Q and Q' should be the latent heat generated during the phase transition in the volume considered, which is $l\rho S v_n \Delta t$, where l is the latent heat (per unit mass), ρ is the density of the metastable phase (paraelectric phase), v_n is the normal velocity of the interface. So, we have

$$k_{\mathrm{fer}} \left(\frac{\mathrm{d}T}{\mathrm{d}n}\right)_{\mathrm{fer}} - k_{\mathrm{par}} \left(\frac{\mathrm{d}T}{\mathrm{d}n}\right)_{\mathrm{par}} = l\rho v_n. \tag{3}$$

Then

$$\begin{aligned} v_n =& \frac{1}{l\rho}\left[k_{\mathrm{fer}} \left(\frac{\mathrm{d}T}{\mathrm{d}n}\right)_{\mathrm{fer}} - k_{\mathrm{par}} \left(\frac{\mathrm{d}T}{\mathrm{d}n}\right)_{\mathrm{par}}\right] \\ =& \frac{1}{l\rho}\left[k_{\mathrm{fer}} \left(\boldsymbol{\nabla}T\right)_{\mathrm{fer}} - k_{\mathrm{par}} \left(\boldsymbol{\nabla}T\right)_{\mathrm{par}}\right] \cdot \boldsymbol{n}, \end{aligned} \tag{4}$$

where $\boldsymbol{n}$ is the unit vector in the n direction. The normal velocity of the interface v_n is also the rate at which the latent heat is carried away by conduction.

In Ref.[14], the author made such an approximation as the following when he verified the above theory by comparing it with the experiments:

$$\left[k_{\mathrm{fer}} \left(\boldsymbol{\nabla}T\right)_{\mathrm{fer}} - k_{\mathrm{par}} \left(\boldsymbol{\nabla}T\right)_{\mathrm{par}}\right] \cdot \boldsymbol{n} \approx k_{\mathrm{fer}} \frac{\Delta T}{\Delta},$$

where ΔT stands for the temperature change within the interface and Δ stands for the interface width, which is given by $\Delta = \frac{1}{2}\left(\frac{3K}{BP_0^2 - A}\right)^{1/2}$. We think the above approximation maybe very wrong. The reason is simple. $\frac{\Delta T}{\Delta}$ stands for the temperature gradient within the interface. It cannot be determined by the difference of the temperature gradients within the adjacent regions. The case is just like that of an electric field for the field intensity is the negative potential gradient. Yet, the field intensity at one site is not related to that at an adjacent site directly.

Though the above approximation is wrong, the interface dynamics induced by the latent heat transfer seems to be rational. Since in the theory temperature gradients are included, the crystal system where a ferroelectric–paraelectric phase transition occurs must be in non-equilibrium states, i.e. the process of phase transition are irreversible. In order to deal with this problem, we have to consider the factor of time, which is a symbol of irreversible thermodynamics, and not considered in the equilibrium thermodynamics. The temperature gradients may be studied in the following irreversible thermodynamic considerations.

3. Irreversibility of ferroelectric phase transitions

By now, the thermodynamics of ferroelectric phase transitions is still equilibrium thermodynamics—the well-known Ginzburg–Devonshire theory,[21] which is based on the Landau theory of phase transitions. But we have to consider the irreversibility. As a rational assumption, the processes of phase transitions are considered to be not far from equilibrium.

3.1. Local entropy production

For some local thermodynamic quantities, the Gibbs equation must be satisfied

$$T\mathrm{d}s = \mathrm{d}u - \boldsymbol{E} \cdot \mathrm{d}\boldsymbol{D} - \sum_i \mu_i \mathrm{d}n_i, \tag{5}$$

where $T, \boldsymbol{E}, \boldsymbol{D}$ is the temperature, the electric field intensity and the electric displacement within an arbitrary small volume, respectively; s, u, μ_i, n_i is the entropy density, the internal energy density, the chemical potential and the molar number of the component in the small volume, respectively. And, we assume that the crystal system is mechanically-free, i.e. no force is exerted on it.

Differentiating Eq.(5) yields

$$T\frac{\partial s}{\partial t}=\frac{\partial u}{\partial t}-\boldsymbol{E}\cdot\frac{\partial \boldsymbol{D}}{\partial t}-\sum_i \mu_i\frac{\partial n_i}{\partial t}. \tag{6}$$

It can be re-written as

$$\begin{aligned}\frac{\partial s}{\partial t}=&\frac{1}{T}\left[\frac{\partial u}{\partial t}-\boldsymbol{E}\cdot\frac{\partial \boldsymbol{D}}{\partial t}-\sum_i \mu_i\frac{\partial n_i}{\partial t}\right]\\ =&-\frac{1}{T}\boldsymbol{\nabla}\cdot\boldsymbol{J}_u-\frac{\boldsymbol{E}}{T}\cdot\boldsymbol{J}_P+\sum_i\frac{\mu_i}{T}\boldsymbol{\nabla}\cdot\boldsymbol{J}_{ni},\end{aligned} \tag{7}$$

where $\boldsymbol{J}_u,\boldsymbol{J}_P,\boldsymbol{J}_{ni}$ are the energy flux, the polarization current and the matter flux, respectively. Here the following relations are used:

$$\frac{\partial u}{\partial t}+\boldsymbol{\nabla}\cdot\boldsymbol{J}_u=0, \tag{8}$$

$$\frac{\partial \boldsymbol{D}}{\partial t}=\frac{\partial\left(\varepsilon_0\boldsymbol{E}+\boldsymbol{P}\right)}{\partial t}=\boldsymbol{J}_P, \tag{9}$$

$$\frac{\partial n_i}{\partial t}+\boldsymbol{\nabla}\cdot\boldsymbol{J}_{ni}=0, \tag{10}$$

where $\boldsymbol{P}$ is the polarization. The above equations stand for the energy conservation, the charge conservation and the matter conservation. $\boldsymbol{J}_u$ consists of three parts: the energy flux caused by the heat conduction, the energy flux caused by the charge transport, the energy flux caused by the matter transport, expressed as

$$\boldsymbol{J}_u=\boldsymbol{J}_q+\phi\boldsymbol{J}_P+\sum_i\mu_i\boldsymbol{J}_{ni}, \tag{11}$$

where $\boldsymbol{J}_q$ is the heat flux, ϕ is the electrical potential and satisfies

$$\boldsymbol{E}=-\boldsymbol{\nabla}\phi. \tag{12}$$

Then we can deduce the following expression:

$$\begin{aligned}\frac{\partial s}{\partial t}=&-\frac{1}{T}\left[\boldsymbol{\nabla}\cdot\boldsymbol{J}_q+\boldsymbol{\nabla}\cdot(\phi\boldsymbol{J}_P)+\sum_i\boldsymbol{\nabla}\cdot(\mu_i\boldsymbol{J}_{ni})\right]-\frac{\boldsymbol{E}}{T}\cdot\boldsymbol{J}_P+\sum_i\frac{\mu_i}{T}\boldsymbol{\nabla}\cdot\boldsymbol{J}_{ni}\\ =&-\boldsymbol{\nabla}\cdot\left(\frac{\boldsymbol{J}_q}{T}\right)+\boldsymbol{J}_q\cdot\boldsymbol{\nabla}\left(\frac{1}{T}\right)-\boldsymbol{\nabla}\cdot\left(\frac{\phi}{T}\boldsymbol{J}_P\right)+\phi\boldsymbol{J}_P\cdot\boldsymbol{\nabla}\left(\frac{1}{T}\right)-\sum_i\boldsymbol{\nabla}\cdot\left(\frac{\mu_i}{T}\boldsymbol{J}_{ni}\right)\\ &+\sum_i\mu_i\boldsymbol{J}_{ni}\cdot\boldsymbol{\nabla}\left(\frac{1}{T}\right)+\boldsymbol{J}_P\cdot\frac{\boldsymbol{\nabla}\phi}{T}+\sum_i\frac{\mu_i}{T}\boldsymbol{\nabla}\cdot\boldsymbol{J}_{ni}\\ =&-\boldsymbol{\nabla}\cdot\left(\frac{\boldsymbol{J}_q+\phi\boldsymbol{J}_P}{T}\right)+\boldsymbol{J}_q\cdot\boldsymbol{\nabla}\left(\frac{1}{T}\right)-\sum_i\boldsymbol{J}_{ni}\cdot\boldsymbol{\nabla}\left(\frac{\mu_i}{T}\right)+\sum_i\mu_i\boldsymbol{J}_{ni}\cdot\boldsymbol{\nabla}\left(\frac{1}{T}\right)+\boldsymbol{J}_P\cdot\boldsymbol{\nabla}\left(\frac{\phi}{T}\right)\\ =&-\boldsymbol{\nabla}\cdot\left(\frac{\boldsymbol{J}_q+\phi\boldsymbol{J}_P}{T}\right)+\boldsymbol{J}_q\cdot\boldsymbol{\nabla}\left(\frac{1}{T}\right)+\boldsymbol{J}_P\cdot\boldsymbol{\nabla}\left(\frac{\phi}{T}\right)-\sum_i\frac{\boldsymbol{J}_{ni}}{T}\cdot\boldsymbol{\nabla}\mu_i.\end{aligned} \tag{13}$$

If we define the entropy flux and the rate of local entropy production as

$$\boldsymbol{J}_s=\frac{\boldsymbol{J}_q+\phi\boldsymbol{J}_P}{T}, \tag{14}$$

$$\sigma_s=\boldsymbol{J}_q\cdot\boldsymbol{\nabla}\left(\frac{1}{T}\right)+\boldsymbol{J}_P\cdot\boldsymbol{\nabla}\left(\frac{\phi}{T}\right)-\sum_i\frac{\boldsymbol{J}_{ni}}{T}\cdot\boldsymbol{\nabla}\mu_i, \tag{15}$$

Eq.(13) can be re-written as

$$\frac{\partial s}{\partial t}+\boldsymbol{\nabla}\cdot\boldsymbol{J}_s=\sigma_s. \tag{16}$$

This is called the local entropy balance equation. We know that the system is in the crystalline states before and after a phase transition so that there is no diffusion of any kind of particles in the system. So, $\boldsymbol{J}_{ni}=0$. The local entropy production can be reduced as

$$\sigma_s=\boldsymbol{J}_q\cdot\boldsymbol{\nabla}\left(\frac{1}{T}\right)+\boldsymbol{J}_P\cdot\boldsymbol{\nabla}\left(\frac{\phi}{T}\right). \tag{17}$$

We know that the existence of ferroics (including ferromagnetics, ferroelectrics, ferroelastics, etc.) is due to the molecular field, which is an inner field. So we must take it into account. Here, the electric field should be the sum of the outer electric field and the inner electric field

$$\boldsymbol{E}=\boldsymbol{E}_{\mathrm{o}}+\boldsymbol{E}_{\mathrm{i}}. \tag{18}$$

Correspondingly, there are the outer electrical potential and the inner electrical potential and they should satisfy

$$\boldsymbol{E}_{\mathrm{o}}=-\boldsymbol{\nabla}\phi_0, \tag{19}$$

$$\boldsymbol{E}_i=-\boldsymbol{\nabla}\phi_i, \tag{20}$$

respectively. We can find the relation

$$\boldsymbol{E}=-\boldsymbol{\nabla}\left(\phi_0+\phi_i\right)=-\boldsymbol{\nabla}\phi. \tag{21}$$

If the outer electric field is absent, ϕ_0 can be an arbitrary constant. There is no harm in letting the constant equal to zero. Then the entropy production will be

$$\sigma_s=\boldsymbol{J}_q\cdot\boldsymbol{\nabla}\left(\frac{1}{T}\right)+\boldsymbol{J}_P\cdot\boldsymbol{\nabla}\left(\frac{\phi_i}{T}\right). \tag{22}$$

From this, we may find that the entropy production due to the change of charge distribution in a phase transition cannot be obtained if the inner electric field is not taken into consideration. Since ferroelectric phase transitions are displacive or order–disorder,[21] the polarization current $\boldsymbol{J}_P$ should originate from the displacement or ordering of ions in the ferroelectrics. We may consider it as the transport of charges influenced by the inner electric field.

3.2. Thermodynamic description of ferroelectric phase transitions

The thermal–electric coupled transport phenomena are not strange to scientists, e.g. thermoelectricity is the familiar one. Since we have regarded the change of polarization with temperature as the transport of charges influenced by the inner electric field, ferroelectric phase transition is also a thermal–electric coupled transport process. However, this type of transport of charges cannot convey the energy but stores it in terms of polarization.

The capable tool used to deal with the multi-coupled transport is the Onsager relations, which are also called the Onsager reciprocal relations.[22] They are the relations between the transport coefficients of different-coupled transport and are the reflection of microscopic reversibility.

Assume the outer electric field is absent. There are the thermodynamic fluxes $\boldsymbol{J}_q, \boldsymbol{J}_P$ and the corresponding thermodynamic forces $\boldsymbol{X}_q$ and $\boldsymbol{X}_P$ which are given by

$$\boldsymbol{X}_q = \boldsymbol{\nabla}\left(\frac{1}{T}\right), \tag{23}$$

$$\boldsymbol{X}_P = \boldsymbol{\nabla}\left(\frac{\phi_i}{T}\right). \tag{24}$$

$\boldsymbol{J}_i$ can be expanded linearly with respect to $\boldsymbol{X}_j \quad (i,j = q,P)$

$$\boldsymbol{J}_q = L_{qq}\boldsymbol{X}_q + L_{qP}\boldsymbol{X}_P, \tag{25}$$

$$\boldsymbol{J}_P = L_{Pq}\boldsymbol{X}_P + L_{PP}\boldsymbol{X}_P. \tag{26}$$

The Onsager relations read

$$L_{qP} = L_{Pq}, \quad L_{qq} > 0, \quad L_{PP} > 0,$$
$$L_{qq}L_{PP} > L_{qP}^2, \tag{27}$$

i.e. L is a positive definite symmetric matrix, whose elements are the above transport coefficients.

The inner electrical potential ϕ_i, generally depends on the factors such as the temperature, the stress, etc. According to Eqs.(24) and (25), $\boldsymbol{J}_q$ cannot be determined by $\boldsymbol{\nabla}T$ only. This is a feature of multi-coupled transports. In the problem under discussion, the temperature is the main factor. So as a simplified process, we assume ϕ_i is a function of the temperature only $\phi_i(T)$. We may assume empirically

$$\phi_i = \begin{cases} \phi_i(T), & T < T_{\mathrm{C}}, \\ 0, & T > T_{\mathrm{C}}, \end{cases} \tag{28}$$

where T_{C} is the Curie temperature. For a first-order ferroelectric phase transition, the force $\boldsymbol{X}_P$ in the region where the phase transition is occurring can be regarded roughly as a large constant in the characteristic time of phase transition.

According to the Ginzburg–Devonshire theory, the 'thermal hysteresis' of a first-order ferroelectric phase transition is due to a series of metastable states existing around the Curie temperature T_{C}.[21] In fact, these metastable states and equilibrium states can be regarded as the so-called stationary states in irreversible thermodynamics. Stationary states are important in irreversible thermodynamics as are equilibrium states in reversible thermodynamics. When a system reaches a stationary state, the local entropy production is a minimum–the so-called principle of minimum entropy production.[22] Ferroelectric phase transition may be regarded as a stationary state process.

According to Eqs.(22),(25) and (26), we have

$$\sigma_s = L_{qq}\boldsymbol{X}_q^2 + 2L_{qP}\boldsymbol{X}_q\boldsymbol{X}_P + L_{PP}\boldsymbol{X}_P^2. \tag{29}$$

If there is no restriction on $\boldsymbol{X}_q$ and $\boldsymbol{X}_P$, according to the conditions that the entropy production is a minimum,

$$\left(\frac{\partial\sigma_s}{\partial\boldsymbol{X}_q}\right)_{X_P} = 2L_{qq}\boldsymbol{X}_q + 2L_{qP}\boldsymbol{X}_P = 2\boldsymbol{J}_q = 0, \tag{30}$$

$$\left(\frac{\partial\sigma_s}{\partial\boldsymbol{X}_P}\right)_{X_q} = 2L_{Pq}\boldsymbol{X}_q + 2L_{PP}\boldsymbol{X}_P = 2\boldsymbol{J}_P = 0, \tag{31}$$

we know that the stationary states are equilibrium states actually. If we let $\boldsymbol{X}_q$ (or $\boldsymbol{X}_P$) be a constant, according to Eq.(31)(or (30)) we know $\boldsymbol{J}_P$ (or $\boldsymbol{J}_q$), which corresponds to the force $\boldsymbol{X}_P$ (or $\boldsymbol{X}_q$), should be zero.

Then, a first-order ferroelectric phase transition can be described by the second paradigm. Since the force $\boldsymbol{X}_P$ in the region where the phase transition is occurring is a large constant, the flux $\boldsymbol{J}_q$ in the region should be zero (but $\boldsymbol{J}_P \neq 0$). This states clearly

that the pure heat conduction and the heat conduction induced by the thermal-electric coupling cancel out each other so as to release or absorb the latent heat. It is certain that the latent heat passes through the region where the phase transition has occurred (at the outside of the region where the phase transition is occurring) and exchanges itself with the thermal bath. Accompanied by the continuous change of the surface's temperature and the unceasing moving of the region where the phase transition is occurring, a constant temperature gradient is kept in the region where the phase transition has occurred, i.e. the force $\boldsymbol{X}_q$ is a constant. So, the flux $\boldsymbol{J}_P = 0$ (but $\boldsymbol{J}_q \neq 0$). This states clearly that the spontaneous polarization of the region where the phase transition has occurred will not change but keep the value at the Curie temperature or zero until the phase transition finishes. On the other hand, the region where the phase transition will occur should be described by the first paradigm for there is no restriction on the two forces $\boldsymbol{X}_P$ and $\boldsymbol{X}_q$ (especially when $T > T_{\rm C}$, there is no transport of charges but only the heat conduction). The states of this region are equilibrium states. So the temperature gradient $\boldsymbol{\nabla} T$ should be zero.

3.3. Verification of interface dynamics

The normal velocity of the interface v_n is determined by Eq.(4). Considering that the region having $(\boldsymbol{\nabla} T)_{\rm par} \approx 0$ where the phase transition will occur (i.e. the paraelectric phase part) can be regarded as an equilibrium system, we modify Eq.(4) as

$$v_n = \frac{k_{\rm fer}\,(\boldsymbol{\nabla} T)_{\rm fer} \cdot \boldsymbol{n}}{l\rho}. \tag{32}$$

In order to compare it with experiments, we make use of the following values which are for the $PbTiO_3$ crystal: ρ=7.1g/cm^3,[23] l=3762J/mol,[24] $k_{\rm fer}$=8.8×10^{-2}J/cm s K.[25] The value of the velocity of the interface's fast motion, which has been measured by experiments, is 0.5mm/s.[5] Using Eq.(32), we obtain the corresponding temperature gradient 57.35K/cm. However, Ref.[6] reported that the experimental temperature gradient varies from 1.5 to 3.5K/mm while the experimental velocity of interface's motion varies from 732 to 843 μm/s. Considering the model is rather rough, we may conclude that the theory coincides with the experiments.

4. Conclusion

The irreversibility of a ferroelectric phase transition has been studied for the paraelectric–ferroelectric interface dynamics induced by the latent heat transfer which includes heat conduction. The ferroelectric phase transition can be regarded as a stationary, thermal–electric coupled transport process. To a first-order ferroelectric phase transition, the situations differ radically among the region where the phase transition has occurred, the region where the phase transition is occurring and the region where the phase transition will occur. In the region where the phase transition has occurred, the temperature gradient is a constant and the spontaneous polarization will not change until the phase transition finishes; the region where the phase transition is occurring is a complete source or sink of heat, where the spontaneous polarization changes suddenly; the region where the phase transition will occur can be regarded as an equilibrium system so the temperature gradient should be zero. Based on the above facts, the interface dynamics induced by the latent heat transfer is reduced (see Eqs.(4) and (32)). Comparison shows that the theory coincides with the experiments.

The interface dynamics and the thermodynamics of phase transitions are two relatively independent fields and they are used for studying phase transitions from two different points of view. Since the two both involve the 'thermal' factor, they can be combined together. We expect that this will bring about abundant results.

References

[1] Gordon A 1983 *Phys. Lett.* A **99** 329

[2] Soboleva T K, Stepanovskii E P and Sukstanskii A L 1985 *JETP Lett.* **42** 68

[3] Dec J 1986 *Ferroelectrics* **69** 181

[4] Gordon A 1986 *Physica* B **138** 239

[5] Dec J 1988 *J. Phys.* C **21** 1257

[6] Dec J 1989 *Ferroelectrics* **89** 193

[7] Tuszynskii J A, Otwinovski M and Dixon J M 1991 *Phys. Rev.* B **44** 9201

[8] Gordon A 1991 *Phys. Lett.* A **154** 79

[9] Mamin R F 1994 *JETP Lett.* **60** 52

[10] Bornarel J and Cach R 1994 *J. Phys. Cond. Matter* **6** 1663

[11] Gordon A and Dorfman S 1995 *Phys. Rev.* B **51** 9306

[12] Dorfman S, Felsteiner J and Fuks D 1996 *Surface Science* **352-354** 879
[13] Gordon A, Dorfman S and Fuks D 1997 *Journal de Physique* IV-C **57** 53
[14] Gordon A 2001*Phys. Lett.* A **281** 357
[15] Fuks D, Dorfman S and Gordon A 2002 *Philosophical Magazine* B **82** 63
[16] Ai S T 2005 *Chin. Phys.* **14** 1246
[17] Ai S T and Cai Y Z *Acta Phys. Sin.* (in Chinese) (in press)
[18] Blinc R and Zeks B 1974 *Soft Modes in Ferroelectrics and Antiferroelectrics* (Amsterdam: North-Holland)
[19] Surowiak Z, Skulski R, Gavriyatchenko V G, Semenchev A F and Fesenko E G 1978 *Sov. Phys. Solid State* **20** 1411
[20] Yufatova S M, Sindeyev Y G, Gavrilyatchenko V G and Fesenko E G 1980 *Ferroelectrics* **26** 809
[21] Lines M E and Glass A M 1977 *Principles and Applications of Ferroelectrics and Related Materials* (Oxford: Oxford University Press)
[22] Lavenda B H 1978 *Thermodynamics of Irreversible Processes* (London: Macmillan Press)
[23] Chewasatn S and Milne S J 1994 *J. Mat. Sci.* **29** 3621
[24] Nomura S and Sawada S 1955 *J. Phys. Soc. Japan* **10** 108
[25] Mante A J H and Volger J 1967 *Phys. Lett.* A **24** 139