

## Constructing Landau-Ginzburg-Devonshire Type Models for Ferroelectric Systems Based on Symmetry

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*Landau-Ginzburg-Devonshire type phenomenological models have been widely used to study ferroelectric phase transitions and domain pattern formation. By including time variation, such models become the time dependent Ginzburg-Landau (TDGL) theory, which may be used to study the kinetics of domains and predicting time variation of material properties. The model construction is straightforward for one-dimensional systems, but for multiple dimensions, more rigorous group theoretical analysis based on crystal symmetry must be used to derive the proper form of the free energy. This paper illustrates the basic procedure for the model construction and provides free energy densities for a few commonly encountered crystal symmetries in ferroelectric systems. An example is also given to illustrate how to deal with phase transitions involving unit cell change using phenomenological theory.*

**Keywords** Landau-Ginsburg theory; phenomenology; ferroelectric phase transition; crystal symmetry; group theory.

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### I. Introduction

The original work of Landau [1] was developed to describe a second order phase transition. The key in the Landau theory is to introduce an order parameter whose non-zero value will signature the low temperature phase, while it is zero in the high temperature phase. For describing structural phase transitions in crystals, the order parameter is directly related to the lattice mode that will be frozen-in at the phase transition. The physical picture can be better explained by the “soft mode” concept. The restoring force of a particular lattice mode becomes “soft” at the phase transition temperature so that the amplitude of this mode becomes much much larger than all other modes near the phase transition temperature. The total energy, which is supposed to be the sum of all lattice modes, now can be approximated by the series expansion of the amplitude of this mode only [2, 3].

In 1949, Devonshire independently derived a phenomenological theory that has the same nature as the Landau theory and used it to successfully describe ferroelectric phase transitions and the temperature dependence of dielectric properties for BaTiO<sub>3</sub> [4]. His work

showed that such free energy expansion treatment could be extended to a first order system, although physically, such treatment for a first order phase transition is not as rigorous as for a second order phase transition because the “weakened mode” does not totally become “soft” so that the total energy cannot be accurately represented by the amplitude of the dominant mode alone. However, experimentalists found that such theoretical treatment is more accurate than other theories even for first order systems. More surprisingly, a normalized plot showed that prediction of phenomenological theory matches well with experimental results for many systems in a very broad temperature range, i.e., for temperatures far away from T<sub>c</sub> where the dominant mode is not so dominant anymore even for a second order phase transition [5]. Therefore, some of the original rigorous rules of the Landau theory have been loosened so that the theory may be used to describe both first and second order phase transitions as well as many other phase changes. The continuum theory originated from Landau’s one dimensional treatment now becomes a true phenomenological theory (also called phase field model in engineering communities) with the order parameter not always proportional to the amplitude of the “soft mode” but a convenient and signature quantity that can uniquely specify the phase transition, i.e., its value is zero above and nonzero below the phase transition temperature T<sub>c</sub>. For crystalline systems, such as ferroelectric materials, one important aspect of the original Landau theory must be preserved, i.e., the free energy must be invariant under the operations of the symmetry group of the parent phase. In other words, so long as the symmetry constraints are preserved, one could add different terms involving quantities that may not even have anything to do with the soft mode, including mutual coupling terms, to the free energy expansion. For example, in a ferroelectric system, polarization formation is associated with the softening of a transverse zone center optical mode, but the elastic strain, which is associated with a zone center acoustic mode, also changes at the phase transition, which is not proportional to the soft mode amplitude. One can add the expansion terms of strains as well as their coupling to the order parameter in the free energy expansion so that the theory can also describe the transformation strain and piezoelectric behavior. In such cases, the elastic strain is often called the secondary order parameter, which is independent from the primary order parameter. For the same argument, other quantities, such as rotational angles of octahedral in perovskite structure, etc. may all be included in the free energy expansion so long as they are related to the phase transition and the crystal symmetry of the prototype phase are preserved [6, 7].

By adding a relaxation type (or diffusion type in phase mixing language) of time dependence in the energy minimization process, the theory becomes the popular time dependent Ginzburg-Landau (TDGL) models that can be used to describe the kinetic process of domains associated with the phase transition [8–10].

The addition of the order parameter gradient terms was first introduced by Ginzburg and Landau [11] for describing superconductivity. For a ferroelectric system, such gradient energy terms are important for describing inhomogeneous structures, such as domain walls and interfaces.

Nowadays, phenomenological modeling has already evolved into a standard theoretical treatment and has been used to explain a wide spectrum of physical phenomena in many different systems. Such generalization of the Landau theory sometimes may create confusions. The basic principle of symmetry invariance originally introduced by Landau is not always strictly followed in the literature, particularly when the model is multi-dimensional. It is even more confusing when dealing with phase transitions that involve the softening or weakening of a mode on the Brillouin zone boundaries, for which the unit cell size will change before and after the phase transition. Such unit cell changes were not generally included in the phenomenological modeling [12].

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The preservation of symmetry is an intrinsic nature of structural phase transitions in solids. Based on the symmetry argument, one can predict and/or understand crystal structure changes resulting from the softening of a particular lattice mode. The essence of the Landau theory is the so called group-subgroup relationship between the parent and product phases. In 1966, Aizu [13] systematically characterized symmetry allowed ferroelectric species based on the group-subgroup relationship between paraelectric and ferroelectric phases. In 1969, Fousek and Janovic [14] used symmetry preservation concept and the coupling between polarization and elastic strain to derive possible domain wall orientations in ferroelectric systems. From elastic compatibility constraints, they also introduced the concept of strange walls and predicted that the orientation of such walls must be temperature dependent; unlike regular permissible domain walls whose orientations are fixed with respect to the crystal coordinates.

Symmetry preservation is rather elementary for modeling ferroelectric systems of simple cubic symmetry using Landau-Devonshire type of models. However, problems exist when dealing with order parameter gradient terms in the free energy expansion. Some earlier models only include one gradient term in the energy expansion [15], which could not reflect the anisotropic nature of the crystal system. In other cases, dependent terms had been added to the free energy expansion [9, 10, 16]. Although such dependent terms do not cause serious damage to the qualitative description of the phase transition because such extra dependent coefficients will eventually merge with independent coefficients and lead to the same differential equation when performing energy minimization, they do create confusion on the concept of independent symmetry invariant terms and also increase the difficulty of experimentally determining these expansion coefficients.

Another complication in constructing the free energy density is when the low temperature phase has different unit cell size than that of the parent phase, i.e., cell doubling or quadrupling occurred at the phase transition. A typical example is the so called antiferroelectric phase transition for which the unit cell size of the antiferroelectric phase is at least 2 times of the unit cell of the paraelectric phase. In this paper, we will use a few examples to systematically outline the procedure of constructing the proper form of the free energy density in phenomenological modeling, and for convenience, provide some energy expansion forms for a few typical ferroelectric crystal symmetries. In addition, we will illustrate how to model phase transitions involving cell doubling or quadrupling resulting from a soft mode at the Brillouin zone boundaries.

## II. Construction of Free Energy Based on Crystal Symmetry

The starting point of a phenomenological model is the construction of a nonlinear "free energy", which is a general term for one of the following thermodynamic functions: the Helmholtz free energy, the Gibbs free energy, the internal energy or the enthalpy. Which thermodynamic function is actually used depends upon the environmental and boundary conditions associated with the underlying problem. For ferroelectric systems, the convenient form is the Helmholtz free energy, which describes an isothermal process so that we can study temperature induced phase transition.

It is interesting to note that the construction of the free energy is based on the crystal symmetry of the *unit cell* in the high temperature phase, i.e., based on the *microscopic* crystal symmetry, while the phenomenological theory is generally used to describe *macroscopic* phenomena and all the expansion coefficients are determined using macroscopically measurable quantities. In other words, the microscopic and macroscopic symmetries are assumed to be the same in the model construction, which is true only for single domain single

crystals. In order to link the expansion coefficients to macroscopic material properties, one must consider the relationship between the microscopic symmetry and the macroscopic symmetry. It is not appropriate to directly use the free energy pertinent to a single domain system for a ceramic system. In reality, single crystals of some systems may be too difficult to obtain, for example, the  $\text{Pb}(\text{Zr}_x\text{Ti}_{1-x})\text{O}_3$  [PZT] system, while PZT ceramic is widely used for electromechanical devices. The experimentally measured material properties for poled PZT ceramics are based on conic (macroscopic) symmetry while the microscopic crystal symmetry of each grain is either rhombohedral or tetragonal at room temperature. Therefore, phenomenological theory for PZT ceramic should involve orientational average of the theoretical model constructed for single crystals and the related expansion coefficients must be obtained through an average scheme.

In general, the construction of the free energy density should start with the soft mode that drives the phase transition. The amplitude of the soft mode is a good choice to be the "order parameter" whose nonzero value will produce the symmetry change from the high temperature phase to the low temperature phase. In practice, other quantities that have the same representation and more convenient to describe the indented physical phenomena may be selected to be the order parameter. For demonstration purpose, let us look at a perovskite ferroelectric system because many well-known ferroelectric materials have perovskite structure, for example,  $\text{BaTiO}_3$ ,  $\text{PbTiO}_3$ , PZT, etc. The point group of the paraelectric phase for a perovskite structure is simple cubic  $O_h$  ( $m\bar{3}m$  in international notation). The softening of a zone center  $\Gamma_4^-$  optical mode leads to the formation of a dipole in each unit cell. The polarization  $\mathbf{P}$  as a 3-dimensional average vector field can form a set of bases for the irreducible representation  $\Gamma_4^-$ , hence, it can be used as the order parameter to describe the ferroelectric phase transition. Although strictly speaking, it would be more appropriate to use the electric displacement as the order parameter because it is the conjugate thermodynamic variable of the electric field  $\mathbf{E}$  [17], the polarization vector  $\mathbf{P}$  is certainly more convenient in describing a ferroelectric phase transition and the difference between  $\mathbf{D}$  and  $\mathbf{P}$  is rather small in ferroelectric systems. There are several possible symmetry compatible low temperature phases resulting from this  $\Gamma_4^-$  mode softening, including tetragonal  $C_{4v}$ , orthorhombic  $C_{2v}$ , rhombohedral  $C_{3v}$ , monoclinic  $C_2$  and triclinic  $C_1$ .

The Landau free energy density up to the sixth power in  $\mathbf{P}$  may be given by [4, 7]

$$\begin{aligned} f_L = & \alpha_1(P_1^2 + P_2^2 + P_3^2) + \alpha_{11}(P_1^2 + P_2^2 + P_3^2)^2 + \alpha_{12}(P_1^2P_2^2 + P_2^2P_3^2 + P_1^2P_3^2) \\ & + \alpha_{111}(P_1^6 + P_2^6 + P_3^6) + \alpha_{112}[P_1^4(P_2^2 + P_3^2) + P_2^4(P_1^2 + P_3^2) + P_3^4(P_1^2 + P_2^2)] \\ & + \alpha_{123}P_1^2P_2^2P_3^2 \end{aligned} \quad (1)$$

A common practice is to keep the expansion terms in Eq. (1) up to the 4th power in  $\mathbf{P}$  when describing a second order phase transition, and up to the 6th power in  $\mathbf{P}$  when describing a first-order phase transition.

To summarize, the construction of the free energy density involves the following three steps:

1. Find the symmetry of the high temperature phase and the irreducible representation of the soft mode for the intended phase transition. For example, the perovskite structure has a symmetry group of  $O_h$  in the high temperature phase and the irreducible representation of the soft mode that leads to the ferroelectric phase is the transverse  $\Gamma_4^-$  mode at the Brillouin zone center.

2. Choose an appropriate order parameter that can describe the symmetry change at the phase transition, which is zero above and nonzero below the phase transition temperature  $T_c$  and is also a convenient quantity for describing the intended phase transition. The components of the order parameter must form a basis set for the irreducible representation of the soft mode. For a proper ferroelectric system, the convenient choice of the order parameter is the polarization, which forms the same bases for the irreducible representation  $\Gamma_4^-$  as that of the amplitude components of the transverse optical soft mode.
3. Derive symmetry invariant polynomials of the order parameter and the secondary order parameter plus all coupling terms between the order parameter and secondary order parameter, based on the image of the symmetry group of the high temperature phase. Keep the expansion terms of the primary order parameter up to the 4th power when describing a second order phase transition and to the 6th power when describing a first order phase transition.

Using the above three steps, the free energy density may be constructed for any ferroelectric system of known symmetry. Table 1 lists the free energy densities for describing a few ferroelectric phase transitions together with the corresponding soft mode in terms of its

**Table 1**  
List of the Landau free energy density for a few typical proper ferroelectrics.

Parent phase	Compatible product phases (Irrep.)	Free energy density
$O_h$	$C_{4v}$ ( $\Gamma_4^-$ ) $C_{2v}$ $C_{3v}$ $C_2$ $C_1$	$f_{O_h} = \alpha_1 P^2 + \alpha_{11} P^4 + \alpha_{12} (P_1^2 P_2^2 + P_2^2 P_3^2 + P_1^2 P_3^2) + \alpha_{111} P^6 + \alpha_{112} [P_1^4 (P_2^2 + P_3^2) + P_2^4 (P_1^2 + P_3^2) + P_3^4 (P_1^2 + P_2^2)] + \alpha_{123} P_1^2 P_2^2 P_3^2$ , where $P^2 = P_1^2 + P_2^2 + P_3^2$
$T_h$	$C_{2v}$ ( $\Gamma_4^-$ ) $C_3$ $C_2$ $C_1$	$f_{T_h} = f_{O_h} + \alpha_{166} (P_1^4 P_2^2 + P_2^4 P_3^2 + P_3^4 P_1^2)$
$T$	$C_2$ ( $\Gamma_4$ ) $C_3$ $C_1$	$f_T = f_{T_h} + \alpha_{3T} P_1 P_2 P_3 + \alpha_{5T} (P_1^3 P_2 P_3 + P_2^3 P_1 P_3 + P_3^3 P_1 P_2)$
$D_{6h}$	$C_{6v}$ ( $\Gamma_2^-$ )	$f_{D_{6h}}^{(1)} = \alpha_3 P_3^2 + \alpha_{33} P_3^4 + \alpha_{333} P_3^6$
	$C_{2v}$ ( $\Gamma_6^-$ ) $C_2$	$f_{D_{6h}}^{(2)} = \alpha_1 (P_1^2 + P_2^2) + \alpha_{11} (P_1^2 + P_2^2)^2 + \alpha_{111} (P_1^2 + P_2^2)^3 + \alpha_{6D} (P_1^6 - 15 P_1^4 P_2^2 + 15 P_1^2 P_2^4 - P_2^6)$
$D_{3h}$	$C_{3v}$ ( $\Gamma_2^-$ )	$f_{D_{3h}}^{(1)} = \alpha_3 P_3^2 + \alpha_{33} P_3^4 + \alpha_{333} P_3^6$
	$C_2$ ( $\Gamma_3^-$ ) $C_m$ $C_1$	$f_{D_{3h}}^{(2)} = \alpha_1 (P_1^2 + P_2^2) + \alpha_{11} (P_1^2 + P_2^2)^2 + \alpha_{111} (P_1^2 + P_2^2)^3 + \alpha_{a12} (P_1^6 - 3 P_1^4 P_2^2 + 3 P_1^2 P_2^4 - P_2^6)$

irreducible representation. One may find expansion forms for additional systems in other published sources [18, 19]. A general trend can be observed from Table I: more and more terms need to be added to the expansion as the symmetry of the high temperature phase is lowered from cubic system  $O_h$  to  $T_h$  then to  $T$ . Here, we have truncated the free energy density at the 6th power in  $P$ . If the transition is of second order, one should set all the 6th power coefficients to zero. It is, of course, possible to describe a second order phase transition using expansion up to the 6th power in  $P$  with the coefficients of the 4th and the 6th powers all set to positive. However, in such treatment, the critical exponent will be different from that of the 4th power expansion theory. There are attempts of using expansion up to the 8th power of  $P$  for better fitting some experimental data [20], but in general, higher power expansion is not recommended because the concept of critical exponent that are used very often by physicists will lose its meaning. It is also very difficult to experimentally measure such higher order nonlinear phenomena to determine the expansion coefficients, making such high power expansion models little use for quantitatively explaining related experimental results.

Because there may be several variants in the low temperature phase which are energetically degenerate, twinning between low temperature states is very common. In fact, domains and domain walls are crucial factors in determining the macroscopic physical quantities of solids in the low temperature phase. In addition to the permissible orientations of domain walls [14], the thickness and energy associated with domain walls are also very important to know. For a ferroelectric crystal, the dipoles inside the domain wall region will be either reduced in amplitude or rotated from the ideal direction [9, 10, 21]. Therefore, domain walls will profoundly affect the macroscopic properties of solids. In order to describe such atomically coherent inhomogeneous structures, i.e., the domain walls and interfaces in general, one must add energy penalty associated with such inhomogeneous structures, i.e., to add the order parameter gradient terms to the free energy expansion. The gradient energy terms also should be invariants under the symmetry group of the parent phase. Although the original paper by Ginzburg and Landau had only one gradient term because superconductivity did not require coupling with crystal structure, models for ferroelectric phase transition must follow the crystal symmetry requirement because it describes crystal structure changes. It is of course an over simplification if one only includes a single gradient term, but it is also not desirable to add unnecessary terms for practical purposes.

We must remember that the expansion is for energy density not for the total energy, so that global symmetries embedded in the volume integration must also be considered when distinguish independent and non-independent terms. For example, for the cubic  $O_h$  symmetry, there are seven 4th rank gradient invariants allowed by the simple cubic symmetry, three of them are combinations of  $P_i P_{j,k,l}$  and the other four invariants are the combinations of  $P_{i,j} P_{k,l}$ , where indices after comma in the subscripts represent partial derivatives with respect to the corresponding space variables. However, in reality, only 3 out of these 7 invariant terms are *truly independent*. Therefore, the proper form of the polarization gradient energy density for a cubic perovskite system is

$$f_g = g_{11} (P_{1,1}^2 + P_{2,2}^2 + P_{3,3}^2) + g_{12} (P_{1,1} P_{2,2} + P_{1,1} P_{3,3} + P_{2,2} P_{3,3}) + g_{44} (P_{1,2}^2 + P_{1,3}^2 + P_{2,1}^2 + P_{2,3}^2 + P_{3,1}^2 + P_{3,2}^2) \quad (2)$$

There have been some confusion in the literature on the form of this gradient energy density. Nambu and Sagala [9] added an additional term to the gradient expansion in Eq. (2) with

the intension of being more accurate, some other researchers then followed the suit [10, 16]. Their gradient energy takes the following form:

$$f_g = G_{11}(P_{1,1}^2 + P_{2,2}^2 + P_{3,3}^2) + G_{12}(P_{1,1}P_{2,2} + P_{1,1}P_{3,3} + P_{2,2}P_{3,3}) \\ + \frac{1}{2}G_{44}[(P_{1,2} + P_{2,1})^2 + (P_{1,3} + P_{3,1})^2 + (P_{2,3} + P_{3,2})^2] \\ + \frac{1}{2}G'_{44}[(P_{1,2} - P_{2,1})^2 + (P_{1,3} - P_{3,1})^2 + (P_{2,3} - P_{3,2})^2] \quad (3)$$

Obviously, if one expand the squares in the  $G_{44}$  and  $G'_{44}$  terms and compare with terms in Eq. (2), it is easy to see that

$$g_{44} = \frac{1}{2}(G_{44} + G'_{44}) \quad (4)$$

The question is about the additional cross term:

$$(G_{44} - G'_{44})(P_{1,2}P_{2,1} + P_{2,3}P_{3,2} + P_{1,3}P_{3,1}) \quad (5)$$

which produces an extra expansion coefficient. It can be verified that this is not an independent invariant combination but the same as the  $g_{12}$  term in Eq. (2) [22]. One can easily see this point by performing a Fourier transform of the volume integration of the energy density. For example, the corresponding terms in the  $k$ -space for both  $P_{1,2}(x)P_{2,1}(x)$  and  $P_{1,1}(x)P_{2,2}(x)$  are  $k_1k_2P_1(k)P_2(k)$ . For the same reason,  $P_{1,3}(x)P_{3,1}(x)$  is the same as  $P_{1,1}(x)P_{1,3}(x)$ , and  $P_{2,3}(x)P_{3,2}(x)$  is the same as  $P_{2,2}(x)P_{3,3}(x)$ . Therefore, the additional term in Eq. (5) is not independent and can be combined with the second term in Eq. (3) to give only 3 independent polarization gradient combinations under the  $O_h$  point group. Naturally, the two set of coefficients have another relationship:

$$g_{12} = G_{12} + (G_{44} - G'_{44}) \quad (6)$$

This point can also be seen from the related differential equations after performing energy minimization. The combination  $G_{12} + (G_{44} - G'_{44})$  always appears together as a group [9, 10, 16].

The anisotropic nature of the polarization gradient can tell us a lot about the crystal system, including surface effects, domain wall thickness, domain wall energy and equilibrium domain size for a given grain size. For convenience and to match up with the formulas given in Table 1, the corresponding proper forms of the gradient energy density are given in Table II together with soft modes that lead to compatible low temperature ferroelectric phases.

### III. Treating Phase Transitions Involving the Change of Unit Cell Size

At this point, it is useful to point out that the *dimension* of the order parameter is not the same as the *dimension* of real space but the *dimension* of a *configurational space*. We may have a 3-D material, but the order parameter dimension could be 1, 2, 3, or even higher than 3 when the soft mode is at the Brillouin zone boundaries. To emphasize this point,

Table 2

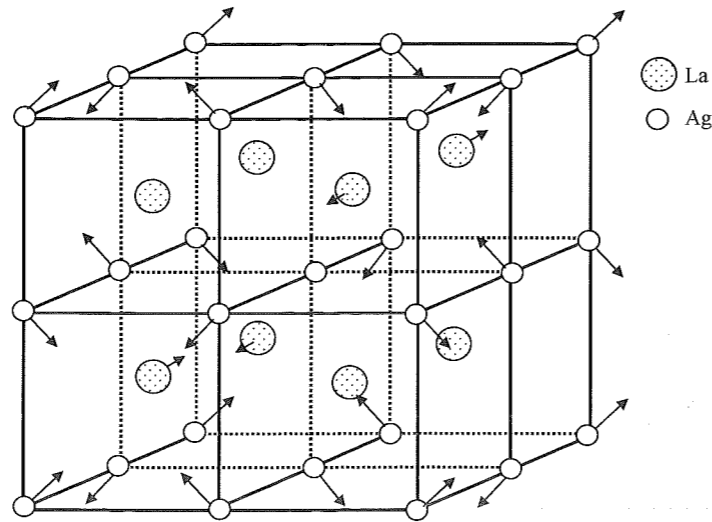
List of the gradient invariant terms needed for proper ferroelectric phase transitions.

Parent phase	Compatible product phases	(Irrep.)	Free energy density of polarization gradients
$O_h$	$C_{4v}$ $C_{2v}$ $C_{3v}$ $C_s$ $C_1$	$(\Gamma_4^-)$	$f_g = g_{11}(P_{1,x}^2 + P_{2,y}^2 + P_{3,z}^2) \\ + g_{12}(P_{1,x}P_{2,y} + P_{1,x}P_{3,z} + P_{2,y}P_{3,z}) \\ + g_{44}(P_{1,y}^2 + P_{1,z}^2 + P_{2,x}^2 + P_{2,z}^2 + P_{3,x}^2 + P_{3,y}^2)$
$T_h$	$C_{2v}$ $C_3$ $C_s$ $C_1$	$(\Gamma_4^-)$	$f_g = g_{11}(P_{1,x}^2 + P_{2,y}^2 + P_{3,z}^2) + g_{12}(P_{1,x}P_{2,y} + \\ P_{1,x}P_{3,z} + P_{2,y}P_{3,z}) + g_{44}(P_{1,y}^2 + P_{2,z}^2 + P_{3,x}^2) \\ + g_{66}(P_{1,z}^2 + P_{2,x}^2 + P_{3,y}^2)$
$T$	$C_2$ $C_3$ $C_1$	$(\Gamma_4)$	
$D_{6h}$	$C_{6v}$ $C_{2v}$ $C_2$	$(\Gamma_2^-)$ $(\Gamma_6^-)$	$f_g = g_{33}P_{3,z}^2 + g_{31}(P_{3,x}^2 + P_{3,y}^2) \\ f_g = g_{11}(P_{1,x}^2 + P_{1,y}^2 + P_{2,x}^2 + P_{2,z}^2) + g_{12}(P_{1,x} + P_{2,y})^2 \\ + g_{13}(P_{1,z}^2 + P_{2,z}^2) + g'_{12}(P_{1,y}^2 + P_{2,x}^2 - 2P_{1,x}P_{2,y})$
$D_{3h}$	$C_{3v}$ $C_2$ $C_m$ $C_1$	$(\Gamma_2^-)$ $(\Gamma_3^-)$	$f_g = g_{33}P_{3,z}^2 + g_{31}(P_{3,x}^2 + P_{3,y}^2) \\ f_g = g_{11}(P_{1,x}^2 + P_{1,y}^2 + P_{2,x}^2 + P_{2,y}^2) + g_{12}(P_{1,x} + P_{2,y})^2 \\ + g_{13}(P_{1,z}^2 + P_{2,z}^2) + g'_{12}(P_{1,y}^2 + P_{2,x}^2 - 2P_{1,x}P_{2,y}) \\ + g_{3d}(P_{1,x}P_{2,z} + P_{1,y}P_{1,z} + P_{1,z}P_{2,x} - P_{2,y}P_{2,z})$

we have used the  $\{x, y, z\}$  notation in Table 2 for the partial derivatives instead of the  $\{1, 2, 3\}$  notation used in Eq. (2). This dimension difference is not obvious when the order parameter is 3-dimensions or less but become very obvious if we look at an order parameter with dimensions more than 3.

Based on the soft mode concept, the order parameter can be chosen as the amplitude of normal modes related to the phase transition. A normal mode represents a pattern of lattice motion, which is intrinsic to the lattice structure. The lattice configuration of the low temperature phase as well as its unit cell size can be determined using the "soft" normal mode solution. In general, we need to know the space groups of the low and high temperature phases rather than just point groups associated with the phase transition. More importantly, the lattices involved may extend several base unit cells if the phase transition produces a change of the unit cell size.

To demonstrate the procedure of constructing the free energy density for the case of an order parameter having more than 3-dimensions, we use  $\text{LaAg}_{1-x}\text{In}_x$  as an example. Its high temperature phase has a  $\text{CsCl}$  simple cubic structure with the space group  $O_h$  and there is a zone boundary soft mode  $M_5^-$ , which can produced a low temperature tetragonal phase with the space group  $D_{4h}^{18}$ . To account for this structural phase transition and the cell quadrupling phenomenon, the order parameter must be 6 dimensional [23]. For the analysis, it is also



**Figure 1.** Extended CsCl structure with illustration of lattice motion in the  $M_5^-$  mode. The domain pattern corresponding to the state described by order parameter value  $(0, 0, Q_0, Q_0, 0, 0)$ .

necessary to use an extended CsCl cell that will contain 8 base unit cell of  $\text{LaAg}_{1-x}\text{In}_x$  as illustrated in Fig. 1. The set of normal mode coordinates  $\mathbf{Q} = (Q_1, Q_2, Q_3, Q_4, Q_5, Q_6)$  belongs to the star of the wave vector  $k$  at the M-point of the Brillouin zone. Each  $Q_i$  component is linked to the displacement  $\mathbf{u}$  and  $\mathbf{v}$  of the two sublattices of the CsCl structure:

$$\begin{aligned}
 Q_1 &= \sum_{L=1}^8 [u_x(L) + v_y(L)](-1)^{l_x+l_y}, \\
 Q_2 &= \sum_{L=1}^8 [u_y(L) + v_x(L)](-1)^{l_x+l_y}, \\
 Q_3 &= \sum_{L=1}^8 [u_z(L) + v_x(L)](-1)^{l_x+l_z}, \\
 Q_4 &= \sum_{L=1}^8 [u_x(L) + v_z(L)](-1)^{l_x+l_z}, \\
 Q_5 &= \sum_{L=1}^8 [u_y(L) + v_z(L)](-1)^{l_y+l_z}, \\
 Q_6 &= \sum_{L=1}^8 [u_z(L) + v_y(L)](-1)^{l_y+l_z}
 \end{aligned} \quad (7a-f)$$

Here  $L$  labels the 8 unit cell, while  $l_i$  ( $i = x, y, z$ ) is an integer labels the origin of the  $l$ th cell from the coordinate origin measured in lattice constant  $a$ .

Based on simple cubic symmetry, one can derive invariants involving different powers of the order parameter  $\mathbf{Q}$ . Because the phase transition is of first order, the free energy

density  $F_L$  expanded up to the 6th power of the order parameter is:

$$\begin{aligned}
 F_L &= A (Q_1^2 + Q_2^2 + Q_3^2 + Q_4^2 + Q_5^2 + Q_6^2) + B_1(Q_1^2 + Q_2^2 + Q_3^2 + Q_4^2 + Q_5^2 + Q_6^2)^2 \\
 &\quad + B_2(Q_1^2 Q_3^2 + Q_1^2 Q_5^2 + Q_3^2 Q_5^2 + Q_2^2 Q_4^2 + Q_2^2 Q_6^2 + Q_4^2 Q_6^2) + B_3(Q_1^2 Q_4^2 \\
 &\quad + Q_2^2 Q_5^2 + Q_3^2 Q_6^2) + B_4(Q_1^2 Q_6^2 + Q_2^2 Q_3^2 + Q_4^2 Q_5^2) + B_5(Q_1^2 Q_2^2 + Q_3^2 Q_4^2 + Q_5^2 Q_6^2) \\
 &\quad + C_1(Q_1^2 + Q_2^2 + Q_3^2 + Q_4^2 + Q_5^2 + Q_6^2)^3 + C_2(Q_1^2 + Q_2^2 + Q_3^2 + Q_4^2 + Q_5^2 + Q_6^2) \\
 &\quad \times (Q_1^2 Q_3^2 + Q_1^2 Q_5^2 + Q_3^2 Q_5^2 + Q_2^2 Q_4^2 + Q_2^2 Q_6^2 + Q_4^2 Q_6^2) \\
 &\quad + C_3(Q_1^2 + Q_2^2 + Q_3^2 + Q_4^2 + Q_5^2 + Q_6^2)(Q_1^2 Q_4^2 + Q_2^2 Q_5^2 + Q_3^2 Q_6^2) \\
 &\quad + C_4(Q_1^2 + Q_2^2 + Q_3^2 + Q_4^2 + Q_5^2 + Q_6^2)(Q_1^2 Q_6^2 + Q_2^2 Q_3^2 + Q_4^2 Q_5^2) \\
 &\quad + C_5(Q_1^2 + Q_2^2 + Q_3^2 + Q_4^2 + Q_5^2 + Q_6^2)(Q_1^2 Q_2^2 + Q_3^2 Q_4^2 + Q_5^2 Q_6^2) \\
 &\quad + C_6[(Q_1^2 + Q_2^2 - Q_3^2 - Q_4^2)(Q_1^2 Q_5^2 + Q_2^2 Q_6^2 - Q_3^2 Q_5^2 - Q_4^2 Q_6^2) \\
 &\quad + (Q_3^2 + Q_6^2 - Q_1^2 - Q_2^2)(Q_3^2 Q_5^2 + Q_4^2 Q_6^2 - Q_1^2 Q_3^2 - Q_2^2 Q_4^2) \\
 &\quad + (Q_3^2 + Q_4^2 - Q_5^2 - Q_6^2)(Q_1^2 Q_3^2 + Q_2^2 Q_4^2 - Q_1^2 Q_5^2 - Q_2^2 Q_6^2)] + C_7[(Q_1^4 - Q_4^4) \\
 &\quad \times (Q_2^2 + Q_5^2 - Q_3^2 - Q_6^2) + (Q_2^4 - Q_5^4)(Q_1^2 + Q_4^2 - Q_3^2 - Q_6^2) + (Q_3^4 - Q_6^4) \\
 &\quad \times (Q_1^2 + Q_4^2 - Q_2^2 - Q_5^2)] + C_8[(Q_1^4 - Q_4^4)(Q_2^2 + Q_3^2 - Q_4^2 - Q_5^2) + (Q_2^4 - Q_3^4) \\
 &\quad \times (Q_1^2 + Q_6^2 - Q_4^2 - Q_5^2) + (Q_4^4 - Q_5^4)(Q_2^2 + Q_3^2 - Q_1^2 - Q_6^2)] + C_9[(Q_1^4 - Q_2^4) \\
 &\quad \times (Q_3^2 + Q_4^2 - Q_5^2 - Q_6^2) + (Q_3^4 - Q_4^4)(Q_5^2 + Q_6^2 - Q_1^2 - Q_2^2) + (Q_5^4 - Q_6^4) \\
 &\quad \times (Q_1^2 + Q_2^2 - Q_3^2 - Q_4^2)] + C_{10}(Q_1 Q_2 Q_3 Q_4 Q_5 Q_6) \\
 &\quad + C_{11}[(Q_3 + Q_4)^2 \{(Q_1 + Q_2)^2 (Q_5 + Q_6)^2 + (Q_2 - Q_1)^2 (Q_6 - Q_5)^2\} \\
 &\quad + (Q_4 - Q_3)^2 \{(Q_1 + Q_2)^2 (Q_6 - Q_5)^2 + (Q_2 - Q_1)^2 (Q_6 + Q_5)^2\}]
 \end{aligned} \quad (8)$$

Similarly, we can derive the order parameter gradient energy expansion, which enables the model to describe domain walls, antiphase boundaries and other inhomogeneous structures. For simple cubic symmetry, there are 5 independent gradient invariant combinations if we only keep the order parameter gradient expansion up to the quadratic term:

$$\begin{aligned}
 F_G &= g_1(Q_{1,x}^2 + Q_{2,y}^2 + Q_{3,z}^2 + Q_{4,x}^2 + Q_{5,y}^2 + Q_{6,z}^2) \\
 &\quad + g_2(Q_{1,y}^2 + Q_{2,x}^2 + Q_{3,x}^2 + Q_{4,z}^2 + Q_{5,z}^2 + Q_{6,y}^2) \\
 &\quad + g_3(Q_{1,z}^2 + Q_{2,z}^2 + Q_{3,y}^2 + Q_{4,y}^2 + Q_{5,x}^2 + Q_{6,x}^2) \\
 &\quad + g_4(Q_{1,y} Q_{2,x} + Q_{3,x} Q_{4,z} + Q_{5,z} Q_{6,y}) \\
 &\quad + g_5(Q_{1,x} Q_{2,y} + Q_{3,z} Q_{4,x} + Q_{5,y} Q_{6,z})
 \end{aligned} \quad (9)$$

Equation (9) gives us a good example to see the difference between the *configurational space* (6-dimensional) and the *real space* (3-dimensional).

Using this model, one could easily derive 12 domain states in the low temperature phase through energy minimization process and find out the displacement space profile in the domain wall region. There are 3 possible tetragonal axes resulting from the cubic

to tetragonal phase transition, and there are 4 domain states with phase difference of the lattice pattern for each given tetragonal axis. All 12 domain states can be unambiguously represented by the following "frozen in" soft mode solutions [23]:

$$(\pm Q_0, 0, 0, 0, \pm Q_0); (0, \pm Q_0, \pm Q_0, 0, 0, 0); (0, 0, 0, \pm Q_0, \pm Q_0, 0). \quad (10a-c)$$

Detailed lattice patterns corresponding to these domain configurations and related twinning solutions can be found in Ref [23]. Our purpose here is only to demonstrate the power of such phenomenological treatment that can go much beyond the original description of a one-dimensional second order phase transition, and to show the difference between *configurational space* and *really space*, which could be confusing because most publications in the literature on such topics using the same {1, 2, 3} subscript format for both order parameter components and space variables.

#### IV. Summary and Conclusions

Thermodynamic phenomenological theory is very convenient and more accurate to describe structural phase transitions compared to other theories, such as first principle's calculations. At the moment, because computational limitation and also because we still do not have a very clear picture on the fundamental interactions in the microscopic level to make the first principle's calculation more realistic, phenomenological theory is an excellent alternative, which can link different physical quantities and predict the variation trend of these physical quantities. The expansion coefficients of the phenomenological models can be directly fitted to experimental results so that the model could be tuned quite accurate for each given system. For a ferroelectric system, many spatial and temperature variations of dielectric and elastic quantities can be predicted once the free energy expansion coefficients are determined from experiments. If the free energy can be constructed properly, the phenomenological theory can even be used to describe complicated phase transitions that involve the change of unit cell size.

In the phenomenological treatment, the foremost important task is to construct the correct form of the free energy expansion based on crystal symmetry and the irreducible representation of the related soft mode. We have outlined the basic procedure for getting the free energy expansion and explained why some symmetry invariant combinations may not be independent in the order gradient expansion terms. In addition, symmetry invariant combinations of the order parameter up to the 6th power and the gradient terms up to the second power are given in Tables I & II for describing a few commonly encountered ferroelectric phase transitions.

Using  $\text{LaAg}_{1-x}\text{In}_x$  as an example, we have also illustrated the procedure to construct the free energy expansion of a 6-dimensional order parameter to describe a phase transition involving cell quadrupling, for which the soft mode is at the Brillouin zone boundary. This particular example also clearly demonstrated the distinction between the *configurational space* and the *real space*, which cannot be easily visualized from models only involve 3 or less than 3 dimensional order parameters. The reason to emphasize this difference between *configurational space* and *real space* is that the symmetry operations of a given crystal are defined in reference to "real space" coordinates attached to the crystal. The change of indices of the order parameter may not follow the same pattern as space variables under the same symmetry operation. This is another crucial point in deriving the correct free energy forms based on crystal symmetry.

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