

Polarization Gradient Coefficients and the Dispersion Surface of the Soft Mode in Perovskite Ferroelectrics

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The gradient coefficients in the Landau-Ginzburg theory are crucial for quantitative description of domain walls in ferroelectrics. The magnitude of these gradient coefficients are a measure of nonlocal coupling strength of the polarization. In this paper, we intend to explain the physical meaning of these gradient coefficients in terms of lattice dynamics and give some relationships between these gradient coefficients and the dispersion surface of the soft mode. The implications for the study of over damped soft modes are also discussed.

§1. Introduction

Many ferroelectric materials have perovskite structure with a cubic symmetry in the paraelectric phase. The symmetry of the low temperature ferroelectric phase can be tetragonal, rhombohedral or orthorhombic. Ferroelectric phases usually have more than one variants and these variants may coherently coexist within the symmetry frame of the parent phase, forming the so called twin structures. It is shown that these twin structures can be well described by Landau-Ginzburg (LG) type models.^{1,2)} All the expansion coefficients in the Landau theory correspond to certain macroscopic physical quantities and can be obtained experimentally. However, the physical meaning of the gradient coefficients, which regulate the domain wall formation and control the domain wall width in the twin structures, still needs to be specified.

A paraelectric-ferroelectric phase transition is characterized by a softening of a transverse optic mode at the Brillouin zone center due to the cancelation of the long range Coulomb forces and the short range repulsive forces.³⁾ The soft mode is stabilized above the phase transition temperature by the anharmonic interactions whose strength weakens as the temperature decreases. Using mean field theory, one can still formally retain the terminology of normal modes if the "soft mode" frequency is assigned to be temperature dependent.

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Close to the phase transition temperature, the dominant contribution in the lattice Hamiltonian is from the soft mode. Therefore, one may simply study the soft mode behavior to characterize the phase transition near T_c . For an inhomogeneous system, the spatial variation of the order parameter must be considered. This is done by adding an energy term induced by the order parameter gradients. Because the inclusion of both nonlinear and nonlocal terms in the energy expansion, one may expect to obtain large amplitude soliton-like solutions which can describe the domain walls (the transition region between coherent twin structures).⁴⁻⁶⁾ The physical meaning of these gradient coefficients can be seen from the study of small amplitude oscillations for which the nonlocal coupling can be treated as perturbations.^{6,7)} We will show in this paper how these polarization gradients can be derived from a simplified lattice dynamical model.

Since polarization is the density of dipoles per unit volume, it is proportional to the magnitude of the associated optical mode. As will be shown in the third section of this paper that the lattice potential for a given optical mode can be written in terms of the polarization vector. Therefore, the Landau-Ginzburg potential can be directly used in the lattice dynamical calculations in the small representation of the soft mode.

§2. Gradient Coefficients and Dispersion Surface of the Soft Mode

From soft mode theory, the potential energy for a cubic system may be expanded in terms of the eigenvector of the soft mode³⁾

$$G = \frac{\kappa}{2} (u_1^2 + u_2^2 + u_3^2) \quad (1)$$

where κ is related to the temperature dependent soft mode frequency, $\kappa \propto (T - T_c)$, and u_i ($i = 1, 2, 3$) are the components of the eigenvector of the soft mode. For the ferroelectric phase transition u is a relative displacement field.

If u is inhomogeneous, we must include the gradient energy in the energy expansion. For cubic symmetry the gradient energy may be written as follows,

$$G_g = \frac{\delta_{11}}{2} (u_{1,1}^2 + u_{2,2}^2 + u_{3,3}^2) + \delta_{12} (u_{1,1} u_{2,2} + u_{1,1} u_{3,3} + u_{2,2} u_{3,3}) + \frac{\delta_{44}}{2} ((u_{1,2} + u_{2,1})^2 + (u_{1,3} + u_{3,1})^2 + (u_{2,3} + u_{3,2})^2) \quad (2)$$

Assuming the effective mass for the mode is M then the equations of motion become

$$M\ddot{u}_1 + \kappa u_1 - \delta_{11} u_{1,1} - \delta_{12} (u_{2,2} + u_{3,3}) - \delta_{44} (u_{1,2} + u_{2,1} + u_{1,3} + u_{3,1}) = 0, \quad (3a)$$

$$M\ddot{u}_2 + \kappa u_2 - \delta_{11} u_{2,2} - \delta_{12} (u_{1,2} + u_{3,3}) - \delta_{44} (u_{1,2} + u_{2,1} + u_{2,3} + u_{3,2}) = 0, \quad (3b)$$

$$M\ddot{u}_3 + \kappa u_3 - \delta_{11} u_{3,3} - \delta_{12} (u_{1,3} + u_{2,2}) - \delta_{44} (u_{1,3} + u_{3,1} + u_{2,3} + u_{3,2}) = 0, \quad (3c)$$

eq. (3a-c) have plane wave solution of the form

$$u = U \exp [j(\omega t - k \cdot x)]. \quad (4)$$

Substituting eq. (4) into eqs. (3a-c) gives the eigenvalue problem

$$M\omega^2 U = \tilde{D}(k)U \quad (5)$$

where $\tilde{D}(k)$ is the dynamical matrix

$$\tilde{D}(k) = \begin{pmatrix} k + \delta_{11} k_1^2 + \delta_{44} (k_2^2 + k_3^2) & \delta_{12} k_1 k_2 & \delta_{12} k_1 k_3 \\ \delta_{12} k_1 k_2 & \kappa + \delta_{11} k_2^2 + \delta_{44} (k_1^2 + k_3^2) & \delta_{12} k_2 k_3 \\ \delta_{12} k_1 k_3 & \delta_{12} k_2 k_3 & \kappa + \delta_{11} k_3^2 + \delta_{44} (k_1^2 + k_2^2) \end{pmatrix} \quad (6)$$

If the depolarization field is included, the equations of motion (3a-c) will contain one more term representing this contribution, which will split the longitudinal and transverse optical modes.^{8,9)} The depolarization field is given by

$$E(k) = -\frac{(P \cdot k) k}{\epsilon_0 k^2} \quad (7)$$

The additional contribution is a linear function of the polarization vector P which is proportional to the relative displacement field u . Adding eq. (7) to the r.h.s. of eq. (3a-c) leads to the dynamical matrix for a given k . In what follows, we will treat three k -values in the three principle directions of the k -space.

A. $k = [k, 0, 0]$.

Define $P_i = Zeu_i$, where Z is a constant which has a unit of inverse volume and e is the electron charge unit. The meaning of Z will be clear from later derivations. For this k value, the dynamical matrix can be simplified to the following form

$$\tilde{D}(k) = \begin{pmatrix} \kappa + A + \delta_{11} k^2 & 0 & 0 \\ 0 & \kappa + \delta_{44} k^2 & 0 \\ 0 & 0 & \kappa + \delta_{44} k^2 \end{pmatrix} \quad (8)$$

where A is a constant defined by

$$A = (1/\epsilon_0)(Ze)^2. \quad (9)$$

From eq. (8) one can easily derive the dispersion relations for the longitudinal (ω_L) and transverse (ω_T) modes respectively:

$$\omega_L^2 = \frac{1}{M} (\kappa + A + \delta_{11} k^2) \quad (10a)$$

$$\omega_T^2 = \frac{1}{M} (\kappa + \delta_{44} k^2) \quad (10b)$$

B. $k = (k/\sqrt{2})[1, 1, 0]$

The electrostatic force from the depolarization field is now given by

$$\frac{Ze(P_1 + P_2)}{2\epsilon_0} [1, 1, 0] = \frac{A(u_1 + u_2)}{2} [1, 1, 0] \quad (11)$$

Therefore the dynamical matrix is

$$\bar{D}(k) = \begin{pmatrix} \kappa + A/2 + (\delta_{11} + \delta_{44})k^2/2 & A/2 + (\delta_{12}/2)k^2 & 0 \\ A/2 + (\delta_{12}/2)k^2 & \kappa + A/2 + (\delta_{11} + \delta_{44})k^2/2 & 0 \\ 0 & 0 & \kappa + \delta_{44}k^2 \end{pmatrix} \quad (12)$$

and the dispersion relations are

$$\omega_L^2 = \frac{1}{M} \left[\kappa + A + \frac{1}{2} (\delta_{11} + \delta_{12} + \delta_{44}) k^2 \right] \quad (13a)$$

$$\omega_{T_1}^2 = \frac{1}{M} \left[\kappa + \frac{1}{2} (\delta_{11} - \delta_{12} + \delta_{44}) k^2 \right] \quad (13b)$$

$$\omega_{T_2}^2 = \frac{1}{M} [\kappa + \delta_{44} k^2] \quad (13c)$$

Here the two transverse modes are not degenerate.

C. $k = (k/\sqrt{3})[1, 1, 1]$.

For this case the Coulomb force from the depolarization field is

$$\frac{Ze(P_1 + P_2 + P_3)}{3\epsilon_0} [1, 1, 1] = \frac{A(u_1 + u_2 + u_3)}{3} [1, 1, 1] \quad (14)$$

and the dynamical matrix becomes

$$\bar{D}(k) = \begin{pmatrix} \kappa + A/3 + (\delta_{11}/3 + 2\delta_{44}/3)k^2 & A/3 + (\delta_{12}/3)k^2 & A/3 + (\delta_{12}/3)k^2 \\ A/3 + (\delta_{12}/3)k^2 & \kappa + A/3 + (\delta_{11}/3 + 2\delta_{44}/3)k^2 & A/3 + (\delta_{12}/3)k^2 \\ A/3 + (\delta_{12}/3)k^2 & A/3 + (\delta_{12}/3)k^2 & \kappa + A/3 + (\delta_{11}/3 + 2\delta_{44}/3)k^2 \end{pmatrix} \quad (15)$$

The dispersion relations are therefore given by

$$\omega_L^2 = \frac{1}{M} \left[\kappa + A + \frac{1}{3} (\delta_{11} + 2\delta_{12} + 2\delta_{44}) k^2 \right] \quad (16a)$$

$$\omega_T^2 = \frac{1}{M} \left[\kappa + \frac{1}{3} (\delta_{11} - \delta_{12} + 2\delta_{44}) k^2 \right] \quad (16b)$$

Note that the dispersion relations derived above are for the cubic phase near $k=0$ but not for the low temperature ferroelectric

phase.

§3. The Expansion Coefficients and Lattice Dynamics

Taking the limit $k \rightarrow 0$ in the dispersion relations derived above, one finds that the coefficient κ/M becomes the soft transverse mode frequency square,

$$\lim_{k \rightarrow 0} \omega_T^2 = \kappa/M \quad (17)$$

The longitudinal mode will not become soft at $T = T_c$ because of the depolarization field contribution A ,

$$\lim_{k \rightarrow 0} \omega_L^2 = \frac{1}{M} (\kappa + A) \quad (18)$$

The simplest model to calculate these coefficients in terms of microscopic quantities is to study the $k=0$ mode for a biatomic system using rigid ion model, in which the soft mode represents the relative displacement field, the mass is the relative mass, and the polarization is equal to the ionic charge multiplied by the relative displacement then divided by the unit cell volume. However, in the perovskite structure there are three different types of ions, hence, a more realistic model would be a three body system model. In what follows we will use a one dimensional rigid ion model for BaTiO_3 as an example to illustrate the relationship between the coefficients in eq. (1) and the microscopic quantities.

According to the structural work of Shirane *et al.*,¹⁰⁾ the soft optical mode in BaTiO_3 consists of the relative motion of Titanium, Barium and Oxygen (Fig. 1(a)). Because the center of mass and the center of charge for each type of ions coincide, we can effectively treat this system as a three-body system in the lattice dynamical calculations. For convenience the ion groups are labeled as follows (see Fig. 1(b)): Ba—1; Ti—2; and 3O—3.

The potential energy represents the $k=0$ mode for this three-body system is

$$\Phi = \frac{\kappa_1}{2} (x_1 - x_2)^2 + \frac{\kappa_2}{2} (x_2 - x_3)^2 \quad (19)$$

In order to derive the equations of motion one should also consider the Lorentz field, which leads to the following differential equations:

$$m_1 \ddot{x}_1 = -\kappa_1 (x_1 - x_2) + \frac{1}{3\epsilon_0} q_1 P \quad (20a)$$

$$m_2 \ddot{x}_2 = -\kappa_1 (x_2 - x_1) - \kappa_2 (x_2 - x_3) + \frac{1}{3\epsilon_0} q_2 P \quad (20b)$$

$$m_3 \ddot{x}_3 = -\kappa_2 (x_3 - x_2) + \frac{1}{3\epsilon_0} q_3 P \quad (20c)$$

$$q_1 + q_2 + q_3 = 0 \quad (21)$$

$$P = (q_1 x_1 + q_2 x_2 + q_3 x_3) / a_0^3 \quad (22)$$

where a_0 is the lattice constant, q_1, q_2, q_3 are the charges of the three ion groups, P is the

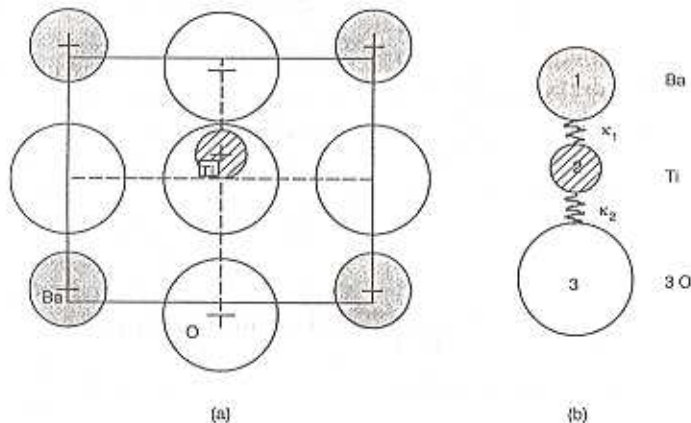


Fig. 1. (a) Illustration of the ionic displacements in BaTiO_3 from ref. 10. (b) One dimensional model for the soft mode.

polarization.

For convenience let us introduce two new variables

$$u = x_1 - x_3; \quad v = x_2 - x_3.$$

Using eqs. (21) and (22), and the new variables u and v the equations of motion (20a-c) can be simplified to become

$$\ddot{u} = au + bv \quad (23a)$$

$$\ddot{v} = cu + dv \quad (23b)$$

where

$$a = -\frac{k_1}{m_1} + \frac{q_1}{3\epsilon_0 a_0^3} \left(\frac{q_1}{m_1} + \frac{q_1 + q_2}{m_3} \right)$$

$$b = -\left(\frac{k_2}{m_3} - \frac{k_1}{m_1} \right) + \frac{q_2}{3\epsilon_0 a_0^3} \left(\frac{q_1}{m_1} + \frac{q_1 + q_2}{m_3} \right)$$

$$c = \frac{k_1}{m_2} + \frac{q_1}{3\epsilon_0 a_0^3} \left(\frac{q_2}{m_2} + \frac{q_1 + q_2}{m_3} \right)$$

$$d = -\left(\frac{k_1 + k_2}{m_2} + \frac{k_2}{m_3} \right) + \frac{q_2}{3\epsilon_0 a_0^3} \left(\frac{q_2}{m_2} + \frac{q_1 + q_2}{m_3} \right)$$

eqs. (23a, b) have the harmonic oscillator solution

$$u = u_0 \exp(j\omega t) \quad (24)$$

$$v = v_0 \exp(j\omega t) \quad (25)$$

and the eigenfrequency ω is given by

$$\omega_{\pm}^2 = \frac{1}{2} [-a-d \pm \sqrt{(a+d)^2 - 4(ad-bc)}]. \quad (26)$$

In any given mode the relative displacement u and v are proportional to each other. For the coordinate system in Fig. 1, u and v always have the same sign. Assuming one of the modes, for example ω_- , becomes soft at lower temperatures due to the decrease of the coupling strength between different ions, then, the magnitude of u and v have the following relationship:

$$v_0 = \frac{1}{2b} (d-a + \sqrt{(a+d)^2 - 4(ad-bc)}) u_0 \quad (27)$$

From eqs. (21) and (22) the polarization P is given by

$$P = (q_1 u + q_2 v) / a_0^3$$

$$= \left[q_1 + \frac{q_2}{2b} (d-a + \sqrt{(a+d)^2 - 4(ad-bc)}) \right] \times u / a_0^3 \quad (28)$$

Therefore, in this mode

$$Ze = \left[q_1 + \frac{q_2}{2b} (d-a + \sqrt{(a+d)^2 - 4(ad-bc)}) \right] / a_0^3 \quad (29)$$

The value of P can be obtained from pyroelectric measurements and u may be calculated from X-ray diffractions of the low and high temperature phases, hence, Ze can also be obtained experimentally.

Since v and P are linearly proportional to u , we could simplify the problem by constructing a new single variable potential $G = (\kappa/2)u^2$ which gives rise to the following equation of motion.

$$\ddot{u} = au + bv$$

$$= \frac{1}{2} [-a-d - \sqrt{(a+d)^2 - 4(ad-bc)}) u$$

$$= -\frac{\kappa}{M} u \quad (30)$$

where κ has the dimension of force constant and M has the dimension of mass according to the definition of a , b , c and d . For a three dimensional system, the constructed potential which leads to eq. (30) will have the same form as eq. (1) according to symmetry. Because u is also proportional to the polarization P [eq. (28)], we may also write down the constructed potential in terms of the polarization vector P , which becomes the Landau potential for a ferroelectric system $G = (\alpha/2)P^2$, $\alpha = \kappa / (Ze)^2$.

For longitudinal vibrations, we have to add the depolarization field ($-P/\epsilon_0$) to the equation of motion eq. (20a-c), which will add a positive contribution to the eigenfrequency preventing it to become soft like the transverse mode. Formally, the relationship between ω_L and ω_T may be written as

$$\omega_L^2 = \omega_T^2 + \frac{A}{M} \quad (30)$$

where A is a positive constant reflecting the contribution of the depolarization field.

§4. Summary and Conclusions

It is shown that the polarization gradient coefficients in the Landau-Ginzburg theory can be directly related to the dispersion surface of the soft mode. Therefore, their physical meaning becomes apparent. The correspondence between the Landau theory and the lattice dynamic potential was illustrated through a simple one dimensional rigid ion model for BaTiO_3 at $k=0$. Since the polarization and the relative displacement field have a linear relationship, the polarization coefficients in the Landau-Ginzburg theory may be calculated from the measured dispersion curves near the soft mode. For cubic symmetry there are only three independent gradient coefficients, the dispersion anisotropy of the soft mode can be determined through measurements along the three principal directions. These gradient coefficients in principle can be obtained through inelastic neutron scattering experiments. However, in many cases these dispersion curves are very difficult to measure because of the high transition temperature. To my knowledge, a complete set of the dispersion relations do not exist in the literatures for the known ferroelectric materials. One of the intentions of this paper is to re-emphasize the importance to measure these dispersion curves which can be used for the study of domain walls in ferroelectrics.

An interesting point should be also men-

tioned is the possibility of obtaining the dispersion surface of the soft mode through direct measurements on the domain wall profiles,¹³⁾ because the gradient coefficients can be extracted from fitting the measured polarization profiles to the soliton-like solutions of nonlinear nonlocal continuous medium theory.^{2,6)} This could be very useful to study the dispersion surface of the over damped soft mode, such as in BaTiO_3 , which can not be obtained through inelastic neutron scattering.

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