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Auteur : Chao, Chih-Hsuan Promoteur(s) : Ghosez, Philippe Faculté : Faculté des Sciences Diplôme : Master en sciences physiques, à finalité approfondie Année académique : 2021-2022 URI/URL : http://hdl.handle.net/2268.2/16133

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Advanced Materials for Innovation and Sustainability

Why is calcium titanate antiferrodistortive, while lead zirconate is antiferroelectric?

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Master en Sciences Physiques, à finalité approfondie (AMIS) Université de Liège 2021-2022

Abstract

Antiferroelectric (AFE) materials have been of interest in the application of high-energy-density capacitors and strain-induced actuators. However, there are only a few identified AFE materials, most belong to oxide perovskites, such as PbZrO₃, PbHfO₃, and NaNbO₃. We rationalize the limited number by providing their restricted criteria. The ground state of an AFE is nonpolar and experiences a phase transition to a symmetry-related polar phase under a sufficiently large electric field. To exhibit the phase transition, the energy of the polar phase should be close to the nonpolar ground state and their energy barrier should be flat enough. For the nonpolar perovskites, it is commonplace that the high energy barrier hinders the AFE characteristic. The purpose of the thesis is to understand the microscopic origin of the flat energy barrier in the prototypical AFE material, $PbZrO_3$. We make this by comparing $PbZrO_3$ to $CaTiO_3$ in the second-principles models since these two materials share similar structures at high temperatures. We identify that the difference in atomic interactions, Pb-O in $PbZrO_3$ and Ca-O in CaTiO₃, is crucial for the energy barrier between the nonpolar ground states and the polar phases. Additionally, by tuning the coefficients, we reproduce the nonpolar-polar phase transition path of $PbZrO_3$ on the $CaTiO_3$ second-principles model. The Pb-O interactions cannot be reproduced by the hydrostatic pressure in $CaTiO_3$.

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Abbreviations

- **AFD** Antiferrodistortive
- **AFE** Antiferroelectric
- **AFM** Antiferromagnetic
- **ASR** Acoustic sum rule
- CTO CaTiO₃
- **DFPT** Density functional perturbation theory
- **DFT** Desity functional theory
- **FE** Ferroelectric
- **FM** Ferromagnetic
- **IFC** Interatomic force constant
- LGD Landau-Ginzburg-Devonshire
- PE Paraelectric
- **PES** Born-Oppenheimer potential energy surface
- PZO PbZrO₃
- **RS** Reference structure
- **SAT** Symmetry-adapted terms
- **SP** Second-principles

Chapter 1

Introduction

Perovskite, originally defined as minerals of $CaTiO_3$ (CTO), was named after a Russian mineralogist, Lev Perovski. Since the description of CTO crystal structure in the early 20th century, the definition of perovskite gradually extended to a group of compounds, which share the same high-symmetry crystal structure with CTO at high temperature. Thus, the chemical formula of perovskites is written in the same form, ABX_3 , where A and B are cations, such as barium, calcium, and lead ions, and X is an anion, such as oxygen and sulfur. Here, we will focus on the oxide perovskites with X = O. It is customary to demonstrate the unit cell of the high-symmetry phase in cubic, as illustrated in Figure 1.1. In the cell, cation A and B are respectively located at the corner and in the middle of the cell, while anions are situated at the center of six faces, forming an octahedral oxygen cage around a B cation.



Figure 1.1: Ionic configuration of perovskite materials in cubic phase. The pink, blue, and gray dots are representative of A, B, and X ions. X ions around B ions form a regular octahedron, whose faces are colored in gray.

During the decrease in temperature, the ionic configuration of perovskites can deviate slightly from the cubic phase, resulting in low-symmetry condensed phases. *Goldschmidt tolerance factor* is a well-known index to predict the distortion pattern of condensed phases from the cubic one [1]. It is a static argument that measures the stability of ions, in comparison with the compact cubic structure by the equation,

$$t = \frac{(r_A + r_X)}{\sqrt{2}(r_B + r_X)},$$
(1.1)

where r denotes the radius of the free ion in the subscripts. The factor $\sqrt{2}$ is the ideal ratio of A-X to B-X bond length in the cubic phase. A compact ideal perovskite possesses a tolerance

factor 1. When t < 1, A-ion is smaller than that in the ideal perovskite; the distortion is mostly dominated by oxygen cage rotation (Figure 1.2 (a)) with minute A-ion distortion (Figure 1.2 (b)), such as CTO ($t \approx 0.97$) and SrZrO₃ ($t \approx 0.95$) [2]. When t > 1, it turns that B-ion is smaller than the ideal case. Thus, the distortion is mostly dominated by B-ion displacement (Figure 1.2 (c)), for example, BaTiO₃ ($t \approx 1.07$) and PbTiO₃ ($t \approx 1.02$) [2]. However, the tolerance factor does not provide the information about the inter-cell correlation of distortion. The magnitude and direction of cation distortion might be different in the adjacent cells, while along the rotation axis of the oxygen cage, there is freedom for adjacent layers to rotate different degree. Therefore, the rich distortion freedom in the perovskites leads to a wide range of condensed phases.



Figure 1.2: Schematic representations of distortion pattern (a) A-ion distortion (b) B-ion distortion (c) oxygen cage rotation in a single lattice layer (001), according to the prediction of Goldschmidt tolerance factor. The multiple arrows indicate the uncertainty of direction.

The diverse distortion pattern of perovskites results in their versatile electric properties and ensuing applications. Hence, they have attracted intensive research in the experimental and theoretical aspects in recent decades [3]. According to the behavior of the material property, polarization **P**, with respect to an external electric field **E**, we can classify perovskites into four kinds: paraelectric (PE), ferroelectric (FE), antiferroelectric (AFE), and antiferrodistortive (AFD). Figure 1.3 (a) illustrates the distinct S-shape P-E curve of PE perovskites. At 0-field, the PE materials possess a net-zero value of polarization. When providing a small electric field, the polarization climb along the steep slope until a critical electric field. At a higher electric field, the increase in the electric field only induces a minute change change in polarization. Most cubic perovskites at high temperatures belong to this category. FE perovskites exhibit spontaneous polarization at 0-field. There are two or more possible directions for spontaneous polarization and can be switched from one to another by an external electric field. They feature a polarization hysteresis loop with respect to the electric field, as illustrated in Figure 1.3 (b). FE perovskite was firstly discovered in $BaTiO_3$. Subsequently, $PbTiO_3$ and $KNbO_3$ are also identified as FE materials. Despite the great number of non-perovskite FE materials, the industry mainly relies on the FE oxides in the application of data storage, sensors, etc [4]. Consequently, we display the typical double hysteresis loop of AFE perovskites in Figure 1.3 (c). They manifest zero polarization at 0-field. With the application of an external electric field, the polarization increases linearly with a gradual slope. Around the forward cohesive field E_F , the polarization surges due to the onset of spontaneous polarization in materials. After that, AFE materials present the linear response at larger field. When we start to decrease the electric field, the polarization drops dramatically around the backward cohesive field E_B ($E_B < E_F$), since the spontaneous polarization vanishes. Therefore, AFE materials manifest a double hysteresis loop. The first AFE material, $PbZrO_3$ (PZO) was reported by Shirane et al. [5]. Following the discovery of PZO, several AFE perovskites are identified in the consequent years, including PbHfO₃ and NaNbO₃. The last category, AFD, only shows a linear response of polarization with respect to an external electric field, as shown in Figure 1.3 (d). In practice, A large number of perovskites belongs to this category, including CTO, $SrZrO_3$, and $SrTiO_3$ [6].



Figure 1.3: Schematic representation of (a) S curve in PE materials, (b) (single) hysteresis loop in FE materials, (c) double hysteresis loop in AFE materials, and (d) linear relation in AFD materials. The shaded area, $U = \int \mathbf{E} \cdot d\mathbf{P}$, is the recoverable energy density stored in these four materials under an electric field.

The scientific intent for AFE materials is due to their application in high-energy-density capacitors [7]. We demonstrate the energy storage U of these four materials by the shaded area in the Figure 1.3. As shown in these figures, AFE materials show higher energy density storage under an electric field and are more competent for high-energy capacitors. Unfortunately, compared to other categories, only a limited number of AFE materials are identified, among them mostly are perovskites. Therefore, studying the underlying principles for AFE perovskites becomes essential to search for new AFE perovskites.

Since the discovery of FE materials, several theories have developed to describe its mechanism and to predict the material properties [4]. In the early stages, the most successful Landau-Ginzburg-Devonshire (LGD) model expands the energy on a polynomial function in respect of macroscopic thermodynamic properties. Here, we give the simplest example of LGD model for FE materials, which expands free energy to 4th order regarding the polarization along the z-axis,

$$G(P_z, T) = G_0 + \alpha(T)P_z^2 + \beta P_z^4 - E_z \cdot P_z.$$
 (1.2)

The coefficients of the expansion model were determined by contemporary experimental results. With the obtained coefficients, the model was able to predict the spontaneous polarization at arbitrary temperature. Consequently, Cochran introduced microscopic expansion parameters, normal modes, in LGD model. Normal modes are a set of mutually-orthogonal atomic displacements, which are well-compatible with the atomic distortion in perovskites. Starting from 1990s, firstprinciples calculation, referring to the computation of material properties from the knowledge of basic physics quantities and theories, became widespread due to the revolution of computational power. Hence, some static properties are predictable by computational simulation. Nonetheless, the size of simulation systems is still limited in a few hundred atoms and the timescale in a few picoseconds (10^{-12} s) . It brings difficulties to describe the lattice dynamics at a finite temperature, such as the polarization in FE and AFE materials. One developing solution is to build the connection between LGD model and first-principles calculation. The LGD model is expanded with respect to lattice degrees of freedom, and the coefficients are determined by fitting the results of first-principles calculations. It releases a part of the computational burden and keeps the computational prediction power without the involvement of empirical results, hence, receives its name, second-principles method (SP method). So far, the second-principles model for FE materials, PTO and STO [8], and for an AFD material, CTO [9], has been established and describe well the behavior at finite temperature. These models are validated to predict the phase transition temperature and equilibrium structure of metastable phases in respect of temperature.

Among a large number of perovskites, CTO has a similar tolerance factor as the prototypical AFE material PZO does. They possess nonpolar ground states with different space group symmetry; PZO is *Pbam*, while CTO is *Pnma*. Besides, as the temperature increases from their ground state, their phase transition behavior displays a large difference in the temperature range and in intermediate phases. Finally, under an application of electric field, PZO manifests a double hysteresis loop of polarization, classifying it as AFE materials; CTO shows a linear response of polarization. Hence, CTO is classified as an AFD material.

It is questionable why PZO is AFE while CTO is not, in consideration of their structural similarity in the cubic phase. It is also attractive to investigate if CTO can be made AFE under appropriate external constraints. These are the questions we want to address in the present work relying on SP modeling.

This work is organized as follows. In chapter 2, we stepwise introduce the building block of SP model in theoretical and computational aspects. All of them are based on the modern strategy to solve the Schrödinger equation. Chapter 3 explicitly elucidates the distortion patterns of perovskites from the microscopic perspective. We relate them to the polarization behavior in materials and deduce the clear criteria of AFE materials. Consequently, we address these criteria on concerned materials, PZO and CTO, in chapter 4, and rationalize their ground state difference. In chapter 5, we attempt to identify the essential terms in CTO SP model to make it an AFE energy landscape by imposing some external constraints. Finally, we summarize this thesis in chapter 6.

Chapter 2

From First- to Second-principles Modelling

Generally, first-principles calculations refer to the computation at a quantum level; namely, obtaining the energy and material properties by solving Schrödinger equation. The modern strategies to conduct first-principles calculations is too time-consuming to describe the full energy landscape. SP model tackles this problem by expressing the energy landscape in a polynomial function. The coefficients are derived by first-principles techniques, including density functional theory (DFT) and density functional perturbation theory (DFPT). Hence, it preserves the predicting capability of first-principles calculations, and can easily deal with lattice dynamics. In this chapter, we demonstrate the theoretical scheme to establish an SP model based on first-principles calculations [8], the algorithm in the software package ABINIT and MULTIBINIT, and computational parameters.

2.1 Generalities

In quantum mechanics, we describe substance with particle wave functions $\Psi(\mathbf{r}, \mathbf{R}, t)$, which can be obtained by solving Schrödinger equation,

$$\hat{H}\Psi(\mathbf{r},\mathbf{R},t) = i\hbar\frac{\partial}{\partial t}\Psi(\mathbf{r},\mathbf{R},t), \qquad (2.1)$$

where the variables \mathbf{r} , \mathbf{R} , and t respectively represent the coordinates of electrons, the coordinates of nuclei, and the time. The square of a wave function is the physical quantity, possibility density function. Therefore, the wave function shall obey the constrain,

$$\langle \Psi | \Psi \rangle = 1. \tag{2.2}$$

In the stationary condition, the Hamiltonian operator \hat{H} is independent on the time variable. Hence, it allows the separation of spatial and temporal variables to decompose the Schrödinger equation. With the solution of the temporal Schrödinger equation, the full wave function is written as

$$\Psi(\mathbf{r}, \mathbf{R}, t) = \psi(\mathbf{r}, \mathbf{R}) exp(-\frac{iEt}{\hbar}).$$
(2.3)

The spatial wave function $\psi(\mathbf{r}, \mathbf{R})$ is then solved by the stationary Schrödinger equation,

$$\hat{H}(\mathbf{r}, \mathbf{R})\psi(\mathbf{r}, \mathbf{R}) = E\psi(\mathbf{r}, \mathbf{R}), \qquad (2.4)$$

in which the Hamiltonian operator in the simplest case is written as,

$$\hat{H}(\mathbf{r}, \mathbf{R}) = -\frac{1}{2} \sum_{i} \nabla_{i}^{2} - \sum_{I} \frac{1}{2M_{I}} \nabla_{I}^{2} + \frac{1}{2} \sum_{i \neq j} \frac{1}{|\mathbf{r}_{i} - \mathbf{r}_{j}|} + \frac{1}{2} \sum_{I \neq J} \frac{Z_{I} Z_{J}}{|\mathbf{R}_{I} - \mathbf{R}_{J}|} - \sum_{i, I} \frac{Z_{I}}{|\mathbf{r}_{i} - \mathbf{R}_{I}|}, \quad (2.5)$$

The terms individually denote the kinetic energy of electrons, the kinetic energy of nuclei, Coulomb repulsion energy between electrons, Coulomb repulsion energy between nuclei, and Coulomb attraction between electrons and nuclei. Accordingly, we write out the individual terms of the Hamiltonian operator in the following form,

$$\hat{H}(\mathbf{r}, \mathbf{R}) = \hat{T}_e(\mathbf{r}) + \hat{T}_N(\mathbf{R}) + \hat{V}_{ee}(\mathbf{r}) + \hat{V}_{NN}(\mathbf{R}) + \hat{V}_{eN}(\mathbf{r}, \mathbf{R}).$$
(2.6)

The stationary Schrödinger equation is not analytically solvable for many-body systems. With the adoption of the Born-Oppenheimer approximation, we decompose the Schrödinger equation into electric and nuclei ones [10]. It supposes the instantaneous optimization of electron coordinates with respect to ionic configurations due to their large mass difference. Therefore, the spatial wave function is reformulated as the product of the nuclei and electron wave function

$$\psi(\mathbf{r}, \mathbf{R}) = \psi_e(\mathbf{r}; \mathbf{R})\psi_N(\mathbf{R}). \tag{2.7}$$

After substituting the reformulated wave function into Schrödinger equation, and approximating that the electronic wave function changes slowly with respect to the nuclei coordinates, the Schrödinger equation decomposes into

$$\begin{cases} \hat{H}_e \psi_e(\mathbf{r}; \mathbf{R}) = E_e(\mathbf{R}) \psi_e(\mathbf{r}; \mathbf{R}) \\ \hat{H}_N \psi_N(\mathbf{R}) = E \psi_N(\mathbf{R}) \end{cases},$$
(2.8)

where electron and nuclei Hamiltonian operators are

$$\begin{cases} \hat{H}_e(\mathbf{r}, \mathbf{R}) = \hat{T}_e(\mathbf{r}) + \hat{V}_{ee}(\mathbf{r}) + \hat{V}_{NN}(\mathbf{R}) + \hat{V}_{eN}(\mathbf{r}, \mathbf{R}) = \hat{T}_e(\mathbf{r}) + \hat{V}_{ee}(\mathbf{r}) + \hat{V}_{ext}(\mathbf{r}; \mathbf{R}) \\ \hat{H}_N(\mathbf{R}) = \hat{T}_N(\mathbf{R}) + E_e(\mathbf{R}) \end{cases}$$
(2.9)

Compared to the energy in the electronic Schrödinger equation, only the kinetic energy of nuclei is added to the total energy. Hence, supposing the freezing nuclei motion in a given configuration, the electron energy with respect to ionic configuration, $E_e(\mathbf{R})$, constructs the Born-Oppenheimer potential energy surface (PES). At 0K, the ground state of the system is located at the minimum of PES (neglecting quantum fluctuation), while the energy of the system fluctuated on the PES at finite temperature due to nuclei vibration. Therefore, we focus on solving the electronic Schrödinger equation in the first-principles calculations. Nowadays, many softwares conducting first-principles calculations follow Kohn-Sham's formalism of density functional theory (DFT) [11]. It uses an ionic configuration and the hypothetical electron density to construct a non-interacting fictitious system and derive the electronic energy and wave function. Nonetheless, it requires first-principles calculations on numerous ionic configurations to set up a good description of PES, which is timeconsuming.

To circumvent the cumbersome calculations, SP model expands the PES by a Taylor-like polynomial function at a reference structure (RS) with respect to lattice degrees of freedom λ (systematical ways to describe ionic configuration **R** in periodic system),

$$E(\lambda) = E_{RS} + \left. \frac{\partial E}{\partial \lambda} \right|_{RS} \lambda + \frac{1}{2} \left. \frac{\partial^2 E}{\partial \lambda^2} \right|_{RS} \lambda^2 + \frac{1}{6} \left. \frac{\partial^3 E}{\partial \lambda^3} \right|_{RS} \lambda^3 + \cdots, \qquad (2.10)$$

and determine the coefficients from a limited set of first-principles data.

Throughout this work, we use the CTO SP model in the reference paper [9], whose construction follows the algorithm presented in the reference paper [8]. The 0th-ordered coefficient, the energy of the reference structure, is directly determined by first-principles calculations. To reduce the terms in the PES model, a typical choice of a RS is an energy local minimum or a saddle point, where the first derivative of energy vanishes. When the material property of a (meta) stable phase is of interest, the phase is chosen as the RS. On the other hand, when the space group symmetry of the (meta) stable phases belongs to the subgroup of a higher one, it is convenient to set the highsymmetry structure as the RS. The high symmetry structure would be located at a saddle point on the PES, and we can use the RS as the benchmark to compare the stability of phases. Based on the electronic wave function and energy of RS, the coefficients of harmonic terms are obtained by density functional perturbation theory (DFPT) [12]. Finally, the anharmonic coefficients are fitted by the results of first-principles calculations on several ionic configurations. According to the approach to obtain the coefficients, we can divide the SP model into three parts,

$$E(\lambda) = \underbrace{\widetilde{E}_{RS}}_{PS} + \underbrace{\widetilde{E}_{har}(\lambda)}_{PT} + \underbrace{\widetilde{E}_{Anh}(\lambda)}_{FAnh}.$$
(2.11)

Our second-principles model uses the software package ABINIT to perform the first-principles calculations, and construct harmonic coefficients through the algorithm of DFPT. Besides, they also use ABINIT to produce the first-principles data for the *training set*, a collection of ionic configurations to fit the anharmonic coefficients. The computed results are lateral fitted by the software package MULTIBINIT.

2.2 Perturbation parameters

The common perturbation parameters λ include homogeneous strains, which describe the shape change in the unit cell, and atomic displacements in the relative coordinate of the unit cell, and electric field. We define the structural parameters (strains and atomic displacements) in a periodic system through the deviation of the atomic position from the reference structure. At the reference structure, the atomic position vector is given by

$$\mathbf{r}_{ai} = \mathbf{R}_a + \boldsymbol{\tau}_i, \tag{2.12}$$

where \mathbf{R}_a denotes the vector of the lattice point *a* with respect to the origin, while $\boldsymbol{\tau}_i$ denotes the position of atom *i* inside a unit cell with respect to the lattice point. At a perturbed ionic configuration, the atomic position vector relative to the reference structure is given by a matrix \mathbf{M} and an atomic displacement vector \mathbf{u}_{ai} ,

$$\mathbf{r}'_{ai} = \mathbf{M}\mathbf{r}_{ai} + \mathbf{u}_{ai} = (\boldsymbol{\eta}_{inh} + \boldsymbol{\eta}_h)(\mathbf{R}_a + \boldsymbol{\tau}_i) + \mathbf{u}_i$$
(2.13)

The matrix **M** is composed of inhomogeneous strain η_{inh} and homogeneous strain η_h . They are respectively responsible for the rigid rotation and shape deformation of lattice grid. Figure 2.1 illustrates the individual contributions from the reference structure to the perturbed one. The rigid rotation of the lattice grid does not lead to an energy difference, the shape deformation causes the change in the bond length and therefore the energy. In the following content, we take the homogeneous strain as the perturbation, and the subscript h would be dropped.



Figure 2.1: Atomic position vector evolution from (a) reference structure. The stepwise involvement of (b) inhomogeneous strain η_{inh} , (c) homogeneous strain η_h , and (d) atomic displacement **u** result in the final atomic position vector in the distorted structure. The block with solid line is the unit cell, while the block with dashed line is the one in the previous step.

Conjugating coefficients. The lower-order derivatives of the energy with respect to these parameters correspond to a range of physical quantities. The first-order energy derivative with respect to \mathbf{u} , $\boldsymbol{\eta}$, and $\boldsymbol{\xi}$ corresponds to force \mathbf{F}_i , stress $\boldsymbol{\sigma}$, and polarization \mathbf{P} , while the second-order energy derivative with respect to those parameters results in interatomic force constant matrix \mathbf{K} , elastic modulus matrix \mathbf{c} , and low-frequency dielectric permittivity tensor $\boldsymbol{\varepsilon}^{\infty}$. The mixed first-order energy derivative with respect to \mathbf{u} and $\boldsymbol{\eta}$ is defined as the strain-phonon coupling coefficient matrix $\boldsymbol{\Lambda}$, while that with respect to \mathbf{u} and $\boldsymbol{\xi}$ is Born effective charge \mathbf{Z}^* , and that with respect to $\boldsymbol{\eta}$ and $\boldsymbol{\xi}$ is the piezoelectric tensor \mathbf{d} . Table 2.1 summarizes these physical quantities and their related perturbation parameters.

 Table 2.1: Physical meanings of the energy derivatives in the lower order

	1st		2nd	
		u	η	ξ
u	F	Κ	Λ	Z^*
η	σ	Λ	с	d
ξ	Р	Z^*	d	ε^{∞}

Base transformation of atomic perturbations. In most condensed phases of perovskites, the atomic perturbations manifest a periodicity, and the position of atom *i* in each cell forms the points on a periodic function. Hence, we can use the wave-vector-characterized perturbations, $\lambda = \delta e^{i\mathbf{q}\cdot\mathbf{r}}$, to describe the atomic perturbations. We express the conjugating harmonic coefficient with a tilde, $\tilde{\mathbf{K}}(\mathbf{q})$, in order to distinguish it from that of atomic displacements. Here, \mathbf{q} denotes the wave vector of the perturbations. Its inverse implies the number of cubic cells to construct the supercell to describe the full perturbation pattern. Among the q-points, we call those corresponding to the small supercell "high-symmetry q-points", and give them symbolic Greek letters. We list the high-symmetry q-points of cubic perovskites, which are used in this work, in Table 2.2. We can take a step further to combine several atomic distortion waves at a given q-point to a set of *phonon modes*, whose conjugated coefficients are the eigenvalues of $\tilde{\mathbf{K}}(\mathbf{q})$, so that the interaction between two phonon modes vanishes. Figure 2.2 depicts these three kinds of bases in a two-atomic lattice model in a $2 \times 1 \times 1$ supercell. The atomic can only distort along the z-axis. These bases are individually sufficient to construct any atomic distortion in the z direction

letter	q_x	q_y	q_z	supercell (respect to cubic cell)
Γ	0	0	0	$1 \times 1 \times 1$
X	0	0	1/2	$1 \times 1 \times 2$
M	0	1/2	1/2	$1 \times 2 \times 2$
R	1/2	1/2	1/2	$2 \times 2 \times 2$
Σ	0	1/4	1/4	$1 \times 4 \times 4$
S	1/2	1/4	1/4	$2 \times 4 \times 4$

Table 2.2: Greek notation, reciprocal coordinates, and distortion periodicity of high-symmetry q-points in cubic perovskite

in the supercell. To be general, all the phonon modes in the reciprocal space can construct any atomic perturbations in the real space. Our second-principles model uses the first basis for atomic perturbation parameters. The wave-vector-characterized perturbation is used for computational calculation, while phonon modes basis is for the curvature analysis of PES.



Figure 2.2: Three atomic distortion bases, including (a) Single atomic displacement, (b) wave-vectorcharacterized displacement, and (c) phonon modes, for the two-atomic model in a $2 \times 1 \times 1$ supercell. The atoms are located at (0.5,0.3) and (0.5,0.7), whose positions at coordinate y are labelled by the dashed lines.

2.3 Density functional theory

Among the method to approach the solution of the electronic Schrödinger equation, DFT has achieved the most successful results so far. The term, density functional, denotes that the variable of the Schrödinger equation adopts the electron density $\rho(\mathbf{r})$ instead of the electronic coordinates \mathbf{r} . It reduces the dimension of the Schrödinger equation from $3N_{el}$ to 3. The modern formalism of density functional theory has been established for over half of a century[13]. In 1964, Hohenberg and Kohn showed the one-to-one correspondence between external potential V_{ext} and ground state electron density $\rho_{GS}(\mathbf{r})$ [14]. It indicates the ground state can be derived by minimizing the energy functional,

$$E[\rho(\mathbf{r}), V_{ext}(\mathbf{r})] = \langle \psi | \hat{H} | \psi \rangle = \int V_{ext}(\mathbf{r}) \rho(\mathbf{r}) d\mathbf{r} + \langle \psi | \hat{T} + \hat{V}_{ee} | \psi \rangle$$
(2.14)

In 1965, Kohn and Sham formulated a good approximation of the second term in energy functional. They set up a fictitious system, where the non-interaction fermions move in an effective potential V_{eff} . Due to its non-interaction feature, the Schrödinger equation can be formulated as a single-particle partial differential equation, which is called the *Kohn-Sham equation*,

$$\hat{f}_{KS}\phi = \epsilon\phi, \qquad (2.15)$$

where

$$\hat{f}_{KS} = -\frac{1}{2}\nabla_i^2 + V_{eff}[\rho(\mathbf{r})] = -\frac{1}{2}\nabla_i^2 + \int \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' + V_{XC}[\rho(\mathbf{r})].$$
(2.16)

The obtained eigenfunctions are named *Kohn-Sham orbitals*. The non-interaction fermions fill in these orbitals from the bottom of the energy level. With the adoption of the fictitious system, the energy functional becomes,

$$E[\rho(\mathbf{r}), V_{ext}(\mathbf{r})] = \int V_{ext}(\mathbf{r})\rho(\mathbf{r})d\mathbf{r} + \sum_{i} \langle \phi_i | \hat{T} | \phi_i \rangle + \frac{1}{2} \int \int \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' d\mathbf{r} + E_{XC}[\rho(\mathbf{r})]. \quad (2.17)$$

The physical meanings of the first three terms in energy functional are the interaction between electrons and external fields, the fictitious kinetic energy, and the classical Coulombic repulsion between electrons. The final term, exchange-correlation energy functional includes the correction of the kinetic energy and captures all quantum effects, which lack analogy in classical physics. The DFT accuracy relies on the analytical form of exchange-correlation energy functional, which is divided into two main categories: *local density approximation* (LDA) and *generalized gradient approximation* (GGA). LDA expands the energy functional only on electron density $\rho(\mathbf{r})$, while GGA expands it on both electron density and gradient of electron density $|\nabla \rho(\mathbf{r})|$. The equation energy functional varies with systems so that we need to specify the name of functional, usually its inventor. Our model uses the GGA exchange-correlation energy functional with the Wu-Cohen parameterization, which is implemented in the package ABINIT [9].

Computational parameters. In the real computation, the Kohn-Sham orbitals are expanded on a set of orthogonal basis. The common orthogonal bases are atomic orbitals and plane waves. The former is frequently used in more localized systems, such as molecules, while the latter is more useful in periodic systems. Our second-principle model was based on the first principle calculation by the package ABINIT, which takes the plane waves as the basis set. The Kohn-Sham orbitals are written as

$$\phi(\mathbf{r}) = \int c_{\mathbf{q}} e^{i\mathbf{q}\cdot\mathbf{r}} d\mathbf{q} = \sum_{m} \int_{B.Z.} c_{\mathbf{k},\mathbf{m}} e^{i(\mathbf{k}+\mathbf{G}_{m})\cdot\mathbf{r}} d\mathbf{k}, \qquad (2.18)$$

where \mathbf{G}_m is the reciprocal lattice point, and \mathbf{k} is the vector in the first Brillouin zone. To limit the number of plane waves, we set an upper bound, energy cutoff E_{cut} . For $\hbar \mathbf{q} > E_{cut}$, we set the coefficients as zero. Inside the energy cutoff, we simplify the integral by the summation over a k-point grid.

$$\phi(\mathbf{r}) = \sum_{m} \int_{B.Z} c_{\mathbf{k},\mathbf{m}} e^{i(\mathbf{k}+\mathbf{G}_m)\cdot\mathbf{r}} d\mathbf{k} \to \sum_{\mathbf{k},\mathbf{m}} c_{\mathbf{k},\mathbf{m}} e^{i(\mathbf{k}+\mathbf{G}_m)\cdot\mathbf{r}}$$
(2.19)



Figure 2.3: The blue markers label the wave vectors of plane wave basis set (a) in the complete set and (b) in the real computation, with 4×4 k-point grid and a $E_{cut} = 1.5$ [Bohr⁻¹].

Hence, the optimization of energy functional turns to tune a limit number of coefficients $c_{\mathbf{k},\mathbf{m}}$. Before initiating a first-principles calculation, a convergence test on the density of the k-point grid and the value of energy cutoff is necessary to check the sufficiency of coefficients in this material. Our CTO model used a $8 \times 8 \times 8$ k-point grid and an energy cut, $E_{cut} = 40$ [Hartree] (≈ 1090 [eV]), in first-principles calculations.

2.4 Harmonic coefficients

2.4.1 Density functional perturbation theory

Theoretically, *perturbation theory* can determine all the coefficients in the polynomial function of PES from the solution of the Schrödinger equation at a RS [12]. It expands the Hamiltonian operator, eigenvalues, and eigenfunctions on Taylor's series with respect to a time-independent perturbation parameter λ at RS,

$$\begin{cases} \hat{H}(\lambda) = \hat{H}^{(0)} + \hat{H}^{(1)}\lambda + \hat{H}^{(2)}\lambda^2 + \dots \\ |\Psi_n(\lambda)\rangle = |\Psi_n^{(0)}\rangle + |\Psi_n^{(1)}\rangle\lambda + |\Psi_n^{(2)}\rangle\lambda^2 + \dots \\ E_n(\lambda) = E_n^{(0)} + E_n^{(1)}\lambda + E_n^{(2)}\lambda^2 + \dots \end{cases}$$
(2.20)

The superscript d denotes a dth-order correction, while the energy corrections are the coefficients in the second-principles model. We insert equation 2.20 into the electronic Schrödinger equation (equation 2.8) and the constraints of the wave function (equation 2.2), they are decomposed into sets of equations due to the arbitrariness of λ .

$$\begin{cases} \lambda^{0} : \{\hat{H}^{(0)} - E_{n}^{(0)}\} |\Psi_{n}^{(0)}\rangle = 0 \\ \lambda^{1} : \{\hat{H}^{(0)} - E_{n}^{(0)}\} |\Psi_{n}^{(1)}\rangle + \{\hat{H}^{(1)} - E_{n}^{(1)}\} |\Psi_{n}^{(0)}\rangle = 0 \\ \lambda^{2} : \{\hat{H}^{(2)} - E_{n}^{(2)}\} |\Psi_{n}^{(0)}\rangle + \{\hat{H}^{(1)} - E_{n}^{(1)}\} |\Psi_{n}^{(1)}\rangle + \{\hat{H}^{(0)} - E_{n}^{(0)}\} |\Psi_{n}^{(2)}\rangle = 0 \\ \dots \end{cases}$$
(2.21)

$$\begin{cases} \lambda^{0} : \langle \Psi_{n}^{(0)} | \Psi_{n}^{(0)} \rangle = 1 \\ \lambda^{1} : \langle \Psi_{n}^{(0)} | \Psi_{n}^{(1)} \rangle + \langle \Psi_{n}^{(1)} | \Psi_{n}^{(0)} \rangle = 0 \\ \lambda^{2} : \langle \Psi_{n}^{(0)} | \Psi_{n}^{(2)} \rangle + \langle \Psi_{n}^{(1)} | \Psi_{n}^{(1)} \rangle + \langle \Psi_{n}^{(2)} | \Psi_{n}^{(0)} \rangle = 0 \\ \dots \end{cases}$$
(2.22)

We can derive the energy correction of concerned-order i by inserting the correction of the wave function $\langle \Psi^{(i-d)} |$ in the set of equations 2.21 and summing over these equations. We take the 2nd-order energy correction for example,

$$0 = \langle \Psi_n^{(2)} | \{ \hat{H}^{(0)} - E_n^{(0)} \} | \Psi_n^{(0)} \rangle + \langle \Psi_n^{(1)} | \{ \hat{H}^{(1)} - E_n^{(1)} \} | \Psi_n^{(0)} \rangle + \langle \Psi_n^{(1)} | \{ \hat{H}^{(0)} - E_n^{(0)} \} | \Psi_n^{(1)} \rangle + \langle \Psi_n^{(0)} | \{ \hat{H}^{(2)} - E_n^{(2)} \} | \Psi_n^{(0)} \rangle + \langle \Psi_n^{(0)} | \{ \hat{H}^{(1)} - E_n^{(1)} \} | \Psi_n^{(1)} \rangle + \langle \Psi_n^{(0)} | \{ \hat{H}^{(0)} - E_n^{(0)} \} | \Psi_n^{(2)} \rangle$$
(2.23)

In the above equation, the summation of terms in each row and each column is zero. We eliminate the first row and the last column from the equation. In the remaining terms, we can further simplify the equation by introducing equation 2.22. Finally, we derive the 2nd-order energy correction,

$$E_n^{(2)} = \langle \Psi_n^{(1)} | \{ \hat{H}^{(0)} - E_n^{(0)} \} | \Psi_n^{(1)} \rangle + \langle \Psi_n^{(1)} | \hat{H}^{(1)} | \Psi_n^{(0)} \rangle + \langle \Psi_n^{(0)} | \hat{H}^{(1)} | \Psi_n^{(1)} \rangle + \langle \Psi_n^{(0)} | \hat{H}^{(2)} | \Psi_n^{(0)} \rangle .$$
(2.24)

Following the scheme, the corrections of energy and wave function are known to n-th order, we can compute the (2n+1)th-order correction of energy. It's the "2n+1" theorem in perturbation theory. Since the derivation of energy correction terms follows the DFT strategy, we name the full method *density functional perturbation theory*. With the coefficients obtained by DFPT, the accuracy of PES is not assured to be higher as we truncated the energy correction at a higher order. Additionally, it is time-consuming to compute high-order energy corrections. Therefore, we only keep the result of DFPT to the harmonic level, which has corresponding physical quantities. For the high-order terms, we derive the coefficient by fitting the first-principles results, which assure a higher accuracy compared to DFPT.

In ABINIT, it is optional to derive harmonic coefficients by DFPT during the first-principles calculations. ABINIT uses the wave-vector-characterized perturbations, $\lambda_1 = \delta_{i\alpha} e^{i\mathbf{q}\cdot \mathbf{r}}$ and $\lambda_2 = \delta_{j\beta} e^{i\mathbf{q}\cdot \mathbf{r}}$, to compute the energy correction terms, instead of atomic displacements [15, 16]. To distinguish them from the atomic displacements, we use the tilde to specify the energy correction of wave-vector characterized perturbations, $\tilde{E}_{ij\alpha\beta}^{(2)}(\mathbf{q})$. We drop the band subscript n, since we only concern the lowest energy band. The term is linked with the harmonic coefficient with a factor of 2,

$$\widetilde{K}_{ij\alpha\beta}(\mathbf{q}) = 2\widetilde{E}^{(2)}_{ij\alpha\beta}(\mathbf{q}).$$
(2.25)

Consequently, we demonstrate the strategy to transform the harmonic coefficients of wave-vectorcharacterized perturbations into those of atomic displacements and phonon modes.

2.4.2 Coefficients in the basis of atomic displacements

We derive the IFC matrix by inverse Fourier transformation of wave-vector-characteristic harmonic coefficients [16]. Practically, the integral is by a summation on a $l \times m \times n$ q-point grid,

$$K_{ij\alpha\beta}(0,b) = \frac{(2\pi)^3}{\Omega_0} \int_{BZ} \widetilde{K}_{ij\alpha\beta}(\mathbf{q}) e^{i\mathbf{q}\cdot\mathbf{R}_a} d\mathbf{q} \to K_{ij\alpha\beta}(0,b) = \frac{(2\pi)^3}{\Omega_0} \sum_{q \in grid} \widetilde{K}_{ij\alpha\beta}(\mathbf{q}) e^{i\mathbf{q}\cdot\mathbf{R}_a}.$$
 (2.26)

2.4. HARMONIC COEFFICIENTS

The discreteness of inverse Fourier transform approximates the IFCs in the $l \times m \times n$ supercell, and considers the IFC vanishes outside the supercell. Nonetheless, the dipole-dipole interaction between local dipole moments results in the slow decay of IFC regarding the distance. The long-range IFCs are underestimated. We deal with the issue by taking dipole-dipole interaction separately. We write out the dipole-dipole interaction in analytic form both real and reciprocal space. For the IFC in the supercell, we subtract the effect of dipole-dipole interaction to get the *short-range interactions* in the reciprocal space,

$$\widetilde{K}_{ij\alpha\beta}^{SR}(\mathbf{q}) = \widetilde{K}_{ij\alpha\beta}(\mathbf{q}) - \widetilde{K}_{ij\alpha\beta}^{DD}(\mathbf{q}).$$
(2.27)

Subsequently, we make a Fourier summation of short-range interactions,

$$K_{ij\alpha\beta}^{SR}(\mathbf{0},\mathbf{b}) = \sum_{q \in grid} \widetilde{K}_{ij\alpha\beta}^{SR}(\mathbf{q}) e^{i\mathbf{q}\cdot\mathbf{R}_a}.$$
(2.28)

Finally, we add the dipole-dipole interaction in the real space,

$$K_{ij\alpha\beta}(\mathbf{0},\mathbf{b}) = K_{ij\alpha\beta}^{SR}(\mathbf{0},\mathbf{b}) + K_{ij\alpha\beta}^{DD}(\mathbf{0},\mathbf{b}).$$
(2.29)

Note that we directly take the dipole-dipole interaction for IFCs outside the supercell. Our SP model adopts the atomic displacement for the perturbation parameters so that they are the harmonic coefficients appear in the model.

2.4.3 Coefficients in the basis of phonon modes

We obtain the harmonic coefficients for phonon modes by solving the eigenvalue equation,

$$\sum_{j\beta} \widetilde{K}_{ij\alpha\beta}(\mathbf{q})\eta_n(\mathbf{q}) = \Lambda_n(\mathbf{q})\eta_n(\mathbf{q}), \qquad (2.30)$$

where the indices of eigenvectors $i\alpha$ are replaced with the notation of phonon modes, n, which arranges in the order of eigenvalues from the small value. With the adoption of the phonon modes basis, the mixed first-derivative of energy with respect to phonon modes vanishes,

$$E = E_{RS} + \frac{1}{2} \sum_{abij\alpha\beta} K_{abij\alpha\beta} u_{ai\alpha} u_{bj\beta} \to E = E_{RS} + \frac{1}{2} \sum_{\mathbf{q}} \sum_{n} \Lambda_n(\mathbf{q}) \eta_n^2(\mathbf{q}).$$
(2.31)

In fact, the eigenvalues $\Lambda_{n,i\alpha}$ are correlated with physical values due to the relationship between IFCs and atomic force,

$$F_{ai\alpha} = -\sum_{bj\beta} K_{abij\alpha\beta} u_{bj\beta} = M_i \frac{\partial^2 u_{ai}}{\partial t^2}.$$
(2.32)

We make a Fourier transformation on both sides of the equation,

$$M_i(i\omega_n(\mathbf{q}))^2\eta_n(\mathbf{q}) = -\sum_n \widetilde{K}_{ij\alpha\beta}\eta_n(\mathbf{q}), \qquad (2.33)$$

where $\omega(\mathbf{q})$ is the frequency of wave transportation. By eliminating the negative sign on both sides of the equation, we obtain the eigenvalue

$$\Lambda_n(\mathbf{q}) = M_i \omega_n(\mathbf{q})^2. \tag{2.34}$$

We can take one step further to let the reciprocal IFC to absorb the effect of atomic mass. This matrix is called a *dynamical matrix* with the notation $\tilde{D}_{ij\alpha\beta}$. Consequently, we derive the eigenvalues and eigenvectors of the dynamical matrix.

$$\omega_n(\mathbf{q})^2 \underbrace{\gamma_n(\mathbf{q})}_{\sqrt{M_i}\eta_n} = \sum_n \underbrace{\widetilde{D}_{ij\alpha\beta}}_{\widetilde{K}_{ij\alpha\beta}/\sqrt{M_i}M_j} \underbrace{\gamma_n(\mathbf{q})}_{\sqrt{M_j}\eta_n} \cdot (2.35)$$

We write the energy function with respect to the eigenvectors of the dynamical matrix,

$$E = E_{RS} + \frac{1}{2} \sum_{\mathbf{q}} \sum_{n} \omega_n^2(\mathbf{q}) \gamma_n(\mathbf{q}).$$
(2.36)

The square of eigenfrequency, $\omega_n^2(\mathbf{q})$, indicates the curvature of energy landscape with respect to an eigenvector of a phonon mode. Phonon modes with negative curvature ($\omega^2 < 0$) are unstable or soft since the reference structure is located at an unstable equilibrium point along the phonon mode distortion (dashed red curve in Figure 2.4). Conversely, phonon modes with positive curvature ($\omega^2 > 0$) are stable (dashed blue curve in Figure 2.4).



Figure 2.4: The solid curves are the energy landscape along the eigenvector of two phonon modes at the harmonic level. The blue solid curve corresponds to the stable phonon modes with positive curvature, so that the distortion is unfavorable, while the red solid curve corresponds to the unstable phonon modes with negative curvature so that the distortion is favorable. The dashed curves are the full energy landscapes, which consider anharmonic effects.

In the end, we clarify the terminology relating to phonon modes for the following context. Generally, we refer to a certain phonon mode by its symbolic Greek letter (when at high-symmetry q-point) and the subscript n (the one in the equation 2.30), such as Γ_1 . Due to the symmetry, there might be some *degenerate* phonon modes, whose eigenfrequencies are the same. We refer to a collection of degenerate phonon modes by putting multiple subscripts, for example, $\Gamma_{1,2,3}$. As for eigenvalues and eigenvectors of IFC in reciprocal lattice and dynamical matrix, we denote $\eta_n(\mathbf{q})$ as (phonon) eigendisplacement, $\gamma_n(\mathbf{q})$ as phonon modes, and $\omega_n(\mathbf{q})$ as eigenfrequencies or phonon frequencies.

Phonon dispersion curve. To visualize all unstable phonon modes, we plot phonon frequencies regarding q-points on a *phonon dispersion curve*. We label the imaginary phonon frequencies (its

square corresponds to the negative coefficient) in the negative direction on the phonon dispersion curve. Practically, we compute the phonon frequencies on the discrete q-points and interpolate the discrete phonon frequencies in the same notation of phonon modes to form the phonon band structure. In this work, we plot the phonon dispersion curve on $2 \times 2 \times 2$ q-points grid.

2.5 Anharmonic coefficients fitting

In the previous section, we have shown that the truncation order of DFPT causes a problem in the accuracy of PES. Hence, instead of using the anharmonic coefficients from DFPT, our SP model fits these coefficients from the first-principles energy data of a set of ionic configuration, which we refer to a *training set*. According to the associated parameters, the anharmonic part can be further divided into three parts: anharmonic phonon, anharmonic strain, and their mixture, as written in the following,

$$E_{Anh}(\mathbf{u},\boldsymbol{\eta}) = E_{Anh}^{p}(\mathbf{u}) + E_{Anh}^{s}(\boldsymbol{\eta}) + E_{Anh}^{sp}(\mathbf{u},\boldsymbol{\eta}).$$
(2.37)

We list the terms in these parts to the third order,

$$E_{Anh}^{p}(\mathbf{u}) = \frac{1}{6} \sum_{ijk\alpha\beta\gamma} \frac{\partial^{3}E}{\partial u_{i\alpha}\partial u_{j\beta}\partial u_{k\gamma}} \bigg|_{RS} u_{i\alpha}u_{j\beta}u_{k\gamma} + \dots = \frac{1}{6} \sum_{ijk\alpha\beta\gamma} K_{ijk\alpha\beta\gamma}^{(3)}u_{i\alpha}u_{j\beta}u_{k\gamma} + \dots$$
(2.38)

$$E_{Anh}^{s}(\boldsymbol{\eta}) = \frac{1}{6} \sum_{abc} \left. \frac{\partial^{3} E}{\partial \eta_{a} \partial \eta_{b} \partial \eta_{c}} \right|_{RS} \eta_{a} \eta_{b} \eta_{c} + \dots = \frac{1}{6} \sum_{abc} C_{abc}^{(3)} \eta_{a} \eta_{b} \eta_{c} + \dots$$
(2.39)

$$E_{Anh}^{sp}(\mathbf{u},\boldsymbol{\eta}) = \frac{1}{6} \sum_{aij\alpha\beta} \frac{\partial^{3}E}{\partial \eta_{a}\partial u_{i\alpha}\partial u_{j\beta}} \Big|_{RS} \eta_{a} u_{i\alpha} u_{j\beta} + \frac{1}{6} \sum_{abi\alpha} \frac{\partial^{3}E}{\partial \eta_{a}\partial \eta_{b}\partial u_{i\alpha}} \Big|_{RS} \eta_{a} \eta_{b} u_{i\alpha} + \dots = \frac{1}{6} \sum_{aij\alpha\beta} \Lambda_{ai\alphaj\beta}^{(1,2)} \eta_{a} u_{i\alpha} u_{j\beta} + \frac{1}{6} \sum_{ab} \sum_{i\alpha} \Lambda_{abi\alpha}^{(2,1)} \eta_{a} \eta_{b} u_{i\alpha} + \dots$$
(2.40)

We label the indices of the unit cell as the letters starting from a, while the letters starting from i denotes the indices of an atom and the lower case Greek letters are directional indices.

The coefficients, the energy derivative with respect to atomic displacement, are not mutually independent. They abide by translational invariance. That is, the material properties, such as energy and forces on atoms, are invariant with the rigid translation. This constraint leads to the dependence between energy derivatives, the so-called *acoustic sum rules* (ASRs),

$$\sum_{i} K^{(n)}_{ijk\dots\alpha\beta\gamma\dots} = 0.$$
(2.41)

The construction of anharmonic terms shall include this constraint by adjusting *on-site force* constant. For example, in the harmonic level, we set the self-force constant

$$K_{ii\alpha\beta}^{(2)} = -\sum_{j\neq i} K_{ij\alpha\beta}^{(2)}.$$
(2.42)

The fitting process on the higher order coefficients becomes complicated when imposing the ASRs [8]. Alternatively, our model uses the atomic displacement difference as the perturbation, which

automatically satisfies ASRs. Accordingly, the anharmonic phonon and the anharmonic mixture parts become,

$$E^{p}(\mathbf{u}) = \frac{1}{6} \sum_{ijklmn\alpha\beta\gamma} \widetilde{K}^{(3)}_{ijklmn\alpha\beta\gamma} (u_{i\alpha} - u_{j\alpha}) (u_{k\beta} - u_{l\beta}) (u_{m\gamma} - u_{n\gamma}) + \dots$$
(2.43)

$$E_{Anh}^{sp}(\mathbf{u},\boldsymbol{\eta}) = \frac{1}{6} \sum_{a} \sum_{ij\alpha\beta} \widetilde{\Lambda}_{aijkl\alpha\beta}^{(1,2)} \eta_a(u_{i\alpha} - u_{j\alpha})(u_{k\beta} - u_{l\alpha}) + \frac{1}{6} \sum_{ab} \sum_{ij\alpha} \widetilde{\Lambda}_{abi\alpha}^{(1,2)} \eta_a \eta_b(u_{i\alpha} - u_{j\alpha}) + \dots$$
(2.44)

The tilde notation distinguishes the coefficients of atomic displacement differences from those of atomic displacements.

Symmetry considerations. In consideration of RS, some perturbations are symmetry equiva-



Figure 2.5: A cross-section of PES, whose energy curve is fitted by the results of first-principles calculations (black dot). The blue fitting curve is bounded, and the red curve is unbounded on the right end.

lent through point-symmetry operations. We can group these terms into symmetry-adapted terms (SATs), and reduce the independent terms in the model. We present the brief strategy that the software MULTIBINIT finds SATs. First, we define the set of point-symmetry operations of RS. We apply a general symmetry operation $\{\mathbf{S}|\mathbf{t}\}$, which includes a rotation matrix \mathbf{S} and translational vector \mathbf{t} , on each atom in RS. The symmetry operation is classified as point-symmetry operations of RS, when it satisfies

$$\{\mathbf{S}|\mathbf{t}\}(\mathbf{R}_a + \boldsymbol{\tau}_i) = \mathbf{R}'_a + \boldsymbol{\tau}'_i = \mathbf{R}_b + \boldsymbol{\tau}_j.$$
(2.45)

It implies that for each atom i in cell a, the symmetry operation brings it to a new position, where there was an atom in the same species before the symmetry operation. MULTIBINIT iteratively applies the point-symmetry operations of RS to each term, build the group of SATs, and choose the representative anharmonic coefficients for each SAT. Then, it adopts the revised Escorihuela-Sayalero's algorithm to filter the most important SATs and fit their values [17].

At the end, some high-order terms with positive coefficients are added to the model, since the negative coefficients at the truncated order lead to the physically-incorrect unbounded PES, as illustrated in the red lines of Figure 2.5. In our CTO model, the first-principles model data are fitted on the 4th-order polynomial function, and 60 SATs are chosen. The other 300 terms in the 6th- or 8th-order are used to bound the PES.

2.6 Conclusions

We summarize the progress of the SP model establishment and involving techniques in Figure 2.6. The Born-Oppenheimer approximation separates the electron and nuclei coordinates freedom, and split the system into electric and nuclei ones. SP model is the polynomial expansion of electric energy at a stationary ionic configuration. We use Kohn-Sham's formalism of DFT to compute the energy of RS, and apply it in the scope of DFPT to get harmonic coefficients, such as elastic constant and Born-effective charge. As for IFCs, the software package use wave-vector perturbation to derive the IFCs in reciprocal space. We can obtain IFCs through the Fourier summation on a q-point grid. On the other hand, the eigenvalues and eigenvectors of the IFC in reciprocal space build the phonon modes in the phonon dispersion curve, which is useful to identify local minima on the PES. The establishment of a training set is based on the knowledge of these local minima. Finally, we utilize DFT to compute the energy of the training set, and fit the anharmonic coefficients.



Figure 2.6: Flow chart of SP model establishment

Chapter 3

Structures and Properties of Perovskites

In this chapter, we aim to associate the polarization behavior of perovskites with (i) their distortion patterns and (ii) the energy landscape, especially for the concerned property, AFE. We start by summarizing distortion patterns of typical soft phonon modes and providing the definition of AFE the in early stage. Subsequently, we bring the concept of soft phonon modes into AFE and give it an explicit definition.

3.1 Usual phonon instabilities

Through the relative size of ions, the Goldschmidt tolerance factor predicts the local atomic distortions in perovskites; however, it does not provide global information about the periodicity of distortion patterns. Nowadays, the prediction of atomic distortions relies on phonon analysis around a RS. The sign of conjugated eigenvalues (ω^2) determines the stability of phonon modes, while the q-point describes the periodicity of distortion patterns. We summarize the distortion patterns of some typical soft phonon modes at high-symmetry q-points around the cubic phase and list their resulting phases by space group symmetry in Table 3.1. To explain the patterns generically, we define the *unstable cation* (A or B) through the Goldschmidt tolerance factor. For t < 1, unstable cation is A cation; for t > 1, it is B cation.

At Γ -point, the typical unstable phonon modes, $\Gamma_{1,2,3}$, are three-fold degenerated due to the symmetry of the cubic phase. These phonon modes are dominated by the displacement of unstable cation against oxygen anions and are periodic in $1 \times 1 \times 1$ supercell. We plot the eigendisplacement of Γ_1 for unstable A and B cations in Figure 3.1 (a) and (b). We simplify the distortion pattern of unstable cations (while oxygen moves in the opposite direction) by an arrow representation. Following this simplification, both Figure 3.1 (a) and (b) are represented in figure 3.1 (c). The combination of these degenerate modes at Γ results in distortion directions along [001] (Figure 3.1 (c)), [011] (Figure 3.1 (d)), and [111]. They separately condense the cubic phase to low-symmetry phases with the space group symmetry *P4mm*, *Amm2*, and *R3m*.

At X-point, the typical softest phonon modes, $X_{1,2}$ are two-fold degenerate, whose characterized wave propagates along [100]. They correspond to the transverse anti-parallel distortion of unstable cation along [010] and [001], as shown in Figure 3.2 (a) and (b). The single mode and their linear combination lead to two distorted directions along [001] and [011], respectively resulting in *Pmma* and *Cmmm* phases.

At M-point, the typical unstable phonon mode, M_1 corresponds to the *in-phase* oxygen cage rotations, which in the adjacent layer rotate in the same magnitude and the same direction (Figure

Phases	Soft phonon modes	polar	antipolar	Oxygen
P4mm	Γ_1	[100]		
Amm2	$\Gamma_1 + \Gamma_2$	[110]		
R3m	$\Gamma_1 + \Gamma_2 + \Gamma_3$	[111]		
Pmma	X_1		[100]	
Cmcm	$X_1 + X_2$		[110]	
P4mbm	M_1			$a^0 a^0 c^+$
Cmmm	M_2		[100]	
Pmma	$M_2 + M_3$		[110]	
P4nmm	M_4		[001]	
I4mcm	R_1			$a^{0}c^{-}c^{-}$
Imma	$R_1 + R_2$			$a^{0}c^{-}c^{-}$
$R\bar{3}c$	$R_1 + R_2 + R_3$			$a^-a^-a^-$
I4/mmm	R_4		[100]	
Imma	$R_4 + R_5$		[110]	
R3m	$R_4 + R_5 + R_6$		[111]	
Pnma	$M_1 + R_1 + R_2$			$a^{+}c^{-}c^{-}$
R3c	$\Gamma_1 + \Gamma_2 + \Gamma_3 + R_1 + R_2 + R_3$	[111]		$a^-a^-a^-$

Table 3.1: Space group symmetry of condensed phases, involved unstable phonon modes, and distortion pattern.



Figure 3.1: The eigendisplacement of single phonon mode at Γ -point for (a) unstable cation A (t < 1) and (b) cation B (t > 1) in the cubic cell. Schematic representation of distortion pattern in combination of phonon modes (c) Γ_1 and (d) $\Gamma_1 + \Gamma_2$.



Figure 3.2: Displacement pattern of unstable ion against oxygen in the single layer of (001) plane for the phonon mode (a) X_1 , (b) X_2 , (c) M_2 , (d) M_3 , and (e) M_4 . Dots are symbolic of the arrows pointing out of the plane, and the crosses are of arrows into the plane.

3.3). Therefore, the distortion pattern can be described in a $2 \times 2 \times 1$ supercell, which constructs P4mbm phase from the cubic phase. The degenerate second unstable phonon modes, $M_{2,3}$ are made of anti-parallel distortion of unstable cation along two propagated directions [100] and [010], leading to the distortion in a $2 \times 2 \times 1$ supercell. Hence, the distortion along [100] and [010] are symmetry-equivalent. The single mode and the combination of these two modes bring the distortion along [100] and [110] directions, as shown in figure 3.2 (c) and (d). These two distortion pattern brings the cubic phase to *Cmmm* and *Pmma* phase. The M_4 mode also corresponds to the wave-characterized perturbation of unstable cation propagating along [100] and [110]. Their common transverse distortion along [001] results in the phase P4mmm. The distortion pattern is illustrated in figure 3.2 (e).

At *R*-point, the typical unstable phonon mode, $R_{1,2,3}$ is three-fold degenerate. They correspond to the *anti-phase* oxygen cage rotations, which in the adjacent layer rotate in the same magnitude but in the opposite direction. Figure 3.3 depicts the one with the rotation axis along the z direction. By combining these three modes, the oxygen cage rotation with the rotation axis along [100], [110], and [111] brings the cubic phase to lower symmetry structure, *I4mcm*, *Imma*, and $R\bar{3}c$. The second lowest phonon modes at *R*-point, $R_{4,5,6}$, are also three-fold degenerate. They are in charge of the anti-parallel arrangement of unstable cations along [100], [010], and [001]. The combination of these three modes results in the anti-parallel distortion along [001], [011], and [111] directions, which respectively result in the phase *I4/mmm*, *Imma*, and *R3m*.



Figure 3.3: Schematic representation of (a) in-phase $(a^0a^0c^+)$ (b) anti-phase $(a^0a^0c^-)$ oxygen cage rotation from the top view.

It is necessary to classify the terminology to describe these common distortion patterns in both the literature and our work. In the perovskites, the distortion of charged components creates local dipole moments. For the phonon modes at Γ -point, the local dipole moments are aligned in the same direction. Hence, the phonon modes and the correlated phases are *polar*. As for the phonon modes at other q-points, the local dipole moments are compensated in the supercell; hence, the phonon modes and corresponding phases are *antipolar* or *nonpolar*. Intriguingly, most literature regards the anti-parallel distortions of unstable cations as antipolar, while the oxygen cage rotation as nonpolar. In fact, it is not formally correct since oxygen also carries a charge so that oxygen rotation produces an antipolar lattice of dipoles as well. Still, we will stick here with the usual conventions. We describe the distortion pattern of unstable cations by marking it as (anti-) polar with its direction, while we use Glazer's notation to express the oxygen cage rotation pattern in the form of $a^{+,-,0}b^{+,-,0}c^{+,-,0}$. The letters indicate the magnitude of rotation with respect to the rotation axis x, y, and z. The superscript +, -, and 0 are respectively symbolic of in-phase, anti-phase, and no rotation. For example, we label the phonon mode M_1 , in-phase oxygen cage rotation, in $a^0 a^0 c^+$, and the phonon mode R_1 , anti-phase oxygen cage rotation, in $a^0 a^0 c^-$.

Besides, it is likely that (meta) stable phases are made of two or more phonon modes at different q-points. For example, Pnma phase is made of in-phase oxygen cage rotation distortion around one direction and out-phase oxygen cage rotation distortion around the other two directions. R3c phase is formed by involving polar distortion along [111] direction and anti-phase rotation $a^-a^-a^-$.

3.2 Antiferroelectricity

Before the discovery of AFE materials, AFE was already a concept inspired by antiferromagnetic (AFM) materials, whose magnetization **M** shows a double hysteresis loop with respect to a magnetic field **H**. AFM materials also manifest an abnormal magnetic susceptibility at the phase transition between paramagnetic and AFM phases. The magnetic susceptibility χ of AFM materials was formulated in the Curie-Weiss law,

$$\chi(T) = C/(T+\theta), \tag{3.1}$$

where C and θ are material-dependent constants. Around 1950, it was shown that the dielectric susceptibility of SrTiO₃ follows the form of equation 3.1. For that reason, scientists guessed the existence of AFE materials, which manifests a double hysteresis loop of polarization with respect to an electric field (Figure 1.3 (c)).

Accordingly, Kittel proposed the first theoretical model for AFE materials in 1951 [18], which is widely acknowledged to pinpoint the beginning of AFE history. The model follows the scheme of FE, ferromagnetic (FM), and AFM materials.

From the microscopic perspective, the onset of magnetization is attributed to local magnetic moments, which originate from the intrinsic spin and orbital motion of electrons. The local magnetic moments are randomly oriented in a paramagnetic phase at high temperatures. As the temperature decreases until the Curie temperature T_c , the paramagnetic phase experiences a "disorderorder" transition to a magnetically-ordered phase, since some alignment of local dipole moments becomes energetic favorable. For FM materials, the alignment pattern is parallel (first row in Table 3.4); for AFM materials it is anti-parallel (second row in Table 3.4). In FM materials, the aligned direction of local magnetic moments is switchable between two or more energy-equivalent states at 0-field through an external magnetic field. In AFM materials, the external field favors the parallel alignment of local magnetic moments; hence, at a critical field, the anti-parallel alignment is switched to the parallel alignment.

On the other hand, polarization is the summation of local dipole moments, which result from the displacement of positive and negative charge mass center. It is subtle to define local dipole moments in the periodic system. In conventions, we define them from a displacive picture in the cubic cell, as shown in section 3.1. At high temperatures, the cubic perovskite might result from randomly-oscillated atoms around the cubic configuration or an average structure of some distorted phases. In the former case, there is no local dipole moment and experiences a displacive phase transition during cooling. In the latter case, there are some randomly oriented local dipole moments in the cubic phase. As the temperature decreases until the critical temperature, it experiences a disorder-order transition. In both cases, the decrease in temperature leads to the onset of local dipole moments. In the first discovered FE perovskite, $BaTiO_3$, the local dipoles behave as the local magnetic dipole moments in FM materials (third row in Figure 3.4). Thus, Kittel set a two-sublattice model, whose local dipole moments orientation follows the local magnetic moment pattern in AFM materials (fourth row in Figure 3.4).



Figure 3.4: Schematic representation of local magnetic/dipole moments pattern in two sublattice model for (a) FM, (b) AFM, (c) FE, and (d) AFE materials at 0-field and a sufficiently large field.

Kittel established the LGD-like energy function with respect to the local dipole moment in the sublattice a and b,

$$G(P_a, P_b, T) = G_0 + \alpha (P_a^2 + P_b^2) + \alpha' P_a P_b + \beta (P_a^4 + P_b^4) + \gamma (P_a^6 + P_b^6) - (P_a + P_b) E$$

where the harmonic coefficient is temperature-dependent, $\alpha = \frac{\alpha'}{2} + \lambda(T - T_c)$ so that local dipole moments (P_a and P_b) vanish above Curie temperature T_c . From the energy model, predict the dielectric behavior of AFE materials through the definition of dielectric susceptibility,

$$\chi = \left. \frac{dP}{dE} \right|_{E=0}.\tag{3.2}$$

The model was against the hypothesis of the dielectric susceptibility of AFE materials and deduced another equation form of their dielectric susceptibility from his model. Here, we only provide the descriptive results. At the Curie temperature, the dielectric susceptibility of AFE material in Kittel's model is not anomalously large as FE materials. In the second-order transition case, where $\beta > 0$ and $\gamma > 0$, the dielectric constant is continuous; as for the first-order case, where $\beta < 0$ and $\gamma > 0$, it is discontinuous.

Soon after the publication of Kittel's paper, Shirane reported PZO as the first discovered AFE material [5]. They observed the abnormal dielectric constant from 227°C to Curie temperature (233°C) under a large external electric field (23-30 [kV/cm]). The observation was rationalized by the double hysteresis curve with respect to an electric field, suggesting the AFE characteristic of PZO. Immediately after that, Sawaguchi, Maniwa, and Hoshino reported the crystal structure of PZO by x-ray analysis, revealing the antipolar arrangement of lead ions [19].

Macroscopically, the double hysteresis relationship between polarization and the electric field is insufficient to assess the AFE character. FE materials can indeed exhibit the same characteristic under specific conditions [7]. First, there are many defects pinning the local dipole in FE materials, which hinder their alignment; hence, no polarization is observed at 0-field. A large electric field can overcome the pinning force, and the material becomes polarized. Second, a double hysteresis loop can also be observed in the short temperature range above PE-FE phase transition temperature. In this case, the ground state is the high-symmetry paraelectric phase. It is switchable to the polar phase under an electric field. The related research lays down a two-fold definition of AFE materials in the phenomenological perspective in Lines and Glass's book [20]: AFE materials manifest dielectric anomaly around the PE-AFE phase transition temperature, and transform from a nonpolar into a polar phase under a sufficiently large electric field.

Nonetheless, the connection block between the macroscopic phenomena and microscopic model is ambiguous due to the subtle behavior of local dipole moments in AFE oxides. Do the local dipole moments really "switch" under an electric field? We can visualize the dipole moment by phonon analysis [21]. We decompose the structural difference between a condensed phase and the cubic phase into strains and several phonon modes. The condensed phases involved with polar modes (Γ -point) are polar, while the others are nonpolar phases. For the polar modes, the ions displace in the same direction in the adjacent cell, forming the parallel alignment of local dipole moments, hence, producing a spontaneous polarization. For nonpolar modes, the distortion pattern has a period larger than the primitive cubic phase. The wave-like local dipole moments cancel mutually, resulting in a net-zero polarization. Note that it is possible that a polar phase is composed of both polar and nonpolar modes. In this perspective, Kittel's model for AFE materials is a specific case at the nonpolar mode, X.

The classification of condensed phase, polar and nonpolar ground states, is necessary but not sufficient to classify FE and AFE materials.

For FE materials, there should be one or more symmetry-related variants of the polar ground state. It is possible to switch from one to another by an electric field. We display the relation of hysteresis loop (macroscopic phenomenon) and energy landscape along a polar mode (microscopic view) in Figure 3.5 (a) and (b). Suppose there are two local minima corresponding symmetryrelated variants and the initial orientation is set as the negative direction (blue dot). At 0-field (blue curve), the two variants possess the same energy since they can transform into each other by a symmetry operation. The application of an electric field changes the curve by a linear term, $\Delta G = -\mathbf{P} \cdot \mathbf{E}$. A minute field along the positive direction favors the other symmetry-related variant. However, it does not switch to the other one until the cohesive field E_{cr} due to the energy barrier. Around the cohesive field, the barrier becomes flat enough to allow the switch from negative to positive orientation (red curve). Hence, the polarization changes notably (red point). Conversely, the application of electric field in the negative direction induces the switch from positive to negative orientation around the cohesive field $-E_{cr}$ due to the energy barrier as well (green dot).



Figure 3.5: (a) Single hysteresis loop of polarization with respect to the electric field in FE materials. (b) Energy landscape along the eigenvector of polar phonon modes at electric field labeled with color in (a). The blue dot and curve indicate the 0-field, red ones are for the positive cohesive field and green ones are for the negative cohesive field.



Figure 3.6: (a) Double hysteresis loop of polarization with respect to the electric field in AFE materials. (b) Energy landscape at electric field labeled with color in (a). The positive x-axis is along the distortion toward a polar phase, the negative x-axis is along the distortion of the nonpolar ground state. The solid lines are along the ground state-reference structure-polar path (path 1), while the dashed lines are along the lowest energy path (path 2).

For AFE materials, there should be one or more metastable polar phases deviated from the same paraelectric phase (in perovskite it is the cubic phase), and a sufficiently large electric field can induce the nonpolar-polar phase transition. We display how this criterion leads to the characterized double hysteresis loop in Figure 3.6. Figure 3.6 (a) illustrates the energy landscape with respect to the electric field. The x-axis in the negative direction denotes the distortion along nonpolar modes, along which it arrives at the ground state at the energy minimum. The x-axis in positive

direction points toward the configuration of a symmetry-related polar phase, which involves polar modes and probability nonpolar modes. At 0-field, the nonpolar ground state possesses lower energy than the polar phase (blue curve). The applied electric field lowers the energy of the polar phase by $G = -\mathbf{P} \cdot \mathbf{E}$, but does not change the energy of nonpolar phase. Above $E = E_0$, the polar phase becomes more stable, but it requires a larger electric field to induce the nonpolar-polar phase transition due to the energy barrier. We define the electric field at the nonpolar-polar phase transition as the forward cohesive field E_F (red curve). Conversely, the reversed polar-nonpolar phase transition is observed around the backward cohesive field E_B (green curve). Similarly, E_B is smaller E_0 due to the energy barrier. Hence, the energy barrier between nonpolar and polar phases brings the double hysteresis characteristics.

Most perovskites do satisfy the first and second criteria, but not the third one since the critical cohesive fields usually exceed the breakdown electric field of the materials. To make critical fields in the workable range, the energy of a polar phase should be comparable with the ground state, and the energy barrier between the ground state and the polar phase should be low enough to allow the phase transition. The restricted energetic criteria of the energy landscape result in a small number of AFE materials. For the other nonpolar materials, their **P-E** curves behave as AFE materials at a small field; it's a linear response, hence, they are AFD materials.

3.3 Conclusions

Through the phonon analysis, we can classify condensed phases of perovskites into polar or nonpolar ones. Accordingly, we lay down explicit criteria for AFE perovskites. (i) The ground state is nonpolar. (ii) There are polar metastable phases, which are composed of more than one phonon modes at Γ -point and probably other phonon modes around cubic structure. The energy of polar phase is comparable to the ground state. (iii) The energy barrier between nonpolar and polar phases is flat enough to allow the phase transition. We will examine these criteria on PZO and CTO in the following chapter.

Chapter 4

Comparison of PbZrO₃ and CaTiO₃

The structures of PZO and CTO are similar at high temperatures. They are in the cubic phase and possess close Goldschmidt tolerance factors, which measure the compactness of a cubic perovskite. As the cooling of the temperature, they experience phase transition to the different ground states and exhibit other metastable phases. We make a careful analysis of their respective phonon dispersion curves and energy landscape. We also compare their IFC in real space to track the possible origin of their distinct behavior at the harmonic level.

4.1 Lead zirconate

The most widely accepted ground state of PZO at 0K is described by a 40-atom unit cell, whose group symmetry is *Pbam*. It deviates from the cubic phase by the unit cell distortion to the orthorhombic one and involves the phonon modes at R, Σ , and S-points. Respectively, they account for 59.7%, 36%, and 4.1% of atomic distortion. Σ -mode is in charge of the antipolar motion of *Pb* ions along [110], while R mode is indicative of the oxygen cage rotation $a^-a^-c^0$. Smode oxygen rotation around the x-axis, with the 90° phase shift between adjacent layers [22]. We use a ($\mathbf{b}_1 = \mathbf{a}_1 - \mathbf{a}_2$, $\mathbf{b}_2 = 2\mathbf{a}_1 + 2\mathbf{a}_2$, $\mathbf{b}_3 = 2\mathbf{a}_3$) supercell to describe the periodicity of *Pbam* phase, where ($\mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_3$) are unit vectors of pseudo-cubic phase. Interestingly, the combination of R and Σ modes is sufficient to reach the *Pbam* ground state, while the S-mode appears as trilinear coupling term $\gamma_{\Sigma}\gamma_R\gamma_S$.

Recently, the 40-atoms ground state of PZO became controversial in some papers. J. S. Baker et al. [23] plotted the phonon dispersion curve of PZO around Pbam structure and found an unstable mode at Z-point $(0, 0, \frac{1}{2})$. The Z-point is unfolded into five phonon modes at $T(\frac{1}{2}, \frac{1}{2}, \frac{1}{4})$, $\Lambda(\frac{1}{2}, \frac{1}{2}, \frac{1}{4})$, and $\Delta(\frac{1}{2}, \frac{1}{2}, \frac{1}{4})$ -point in cubic perovskite. By introducing these phonon modes in the structure relaxation, they arrived at an 80-atoms ground state with space group symmetry *Pnam*, whose energy is 1 [meV/f.u.] lower than the *Pbam* one. Hugo Armberri et al. [24] built a 30atom phase with group symmetry *Ima2*, which is the simplest ferrielectric phase compatible with large instability at *R*-point in cubic PZO. By involving zero-point energies (the quantum vibration energy of ions at 0K), they reported this phase as the ground state of PZO from 0 to around 200 K. So far, these two proposed ground states are not experimentally observed. In the *Pnam* case, the authors ascribed it to the small distinction between *Pbam* and *Pnam* phases, which might be experimentally indistinguishable. Nonetheless, they did not rule out the possibility that *Pnam* is the artificial theoretical ground state due to the inadequate approximation in computations. In the *Ima2* case, the authors argued that the phase transformation from AFE to the ferrielectric phase is hindered by the low kinetic energy around transition temperature. Hence, we still take 40-atom AFE phase as the ground state in this work.

We make the phonon analysis around the cubic PZO structure. The first-principles calculations give us the length of the PZO unit cell in the cubic phase, 7.82 [Bohr]. We illustrate the phonon dispersion curve around the cubic phase in Figure 4.1. The cubic PZO displays the instabilities at all high-symmetry q-points, Γ , X, M, and R. Along the path passing through high-symmetry points, the most unstable phonon modes form a relatively flat band. The phonon modes at M and R show the strongest instabilities ($\omega \approx 177.9i$ and $183.6i \ cm^{-1}$)⁻¹, which corresponds to in-phase rotation and anti-phase rotation distortions. Apart from the lowest band, PZO also exhibits other unstable modes at M and at R points. We combine the wide variety of unstable phonon modes to form the potential phases in local minima on PES, which are listed in Table 3.1.



Figure 4.1: Phonon dispersion curve $\omega(\mathbf{q})$ of PZO. The imaginary eigenfrequencies are plotted in the negative direction.

We perform the first-principles calculations to find the energy minimum by involving unstable phonon modes in the cubic phase. The structural relaxation does not only find the optimized ionic configuration but also optimizes the shape of the unit cell. We record the energy gains of each phase with respect to the cubic phase in Figure 4.2, in the order of their magnitude. The phase R3c, involving polar and oxygen cage rotation distortion, shows close energy gains as the ground state does. The energy difference between Pbam and R3c phase is less than 1 [meV/f.u.] $(\Delta E_{Pbam} \approx -286.47 \text{ and } \Delta E_{R3c} \approx -285.72 \text{ [meV/f.u.]})$. It satisfies the first energy criterion for the AFE characteristic to manifest nonpolar-polar phase transition. Overall, PZO manifests quite close energy gains in the phases associated with the most unstable modes at Γ , M, and R-points. Although configuration path on PES remains veiled during nonpolar-polar phase transition, it gives the hint that the phase transition involves a series hopping between these local minima,

¹Phonon frequencies are reported in cm^{-1} which is not a priori appropriate but conventional in the field. It corresponds to the wavelength of the photon of the same energy. Using $hf = hc/\lambda$ we get 1 $[cm^{-1}] = 0.299$ [THz].



instead of overcoming the big obstacle at the cubic phase.

Figure 4.2: Energy gains of (meta) stable phases in PZO with respect to the cubic phase. The phases are in the order of magnitude of energy gain.

We turn to investigate the behavior of PZO in finite temperatures. PZO displays the cubic phase at high temperature and experiences phase transformation to the *Pbam* ground state at $T_c = 505K$. Rather than a displacive transition, the PE-AFE phase transition is in line with disorder-order one; namely, the cubic phase is an average structure of low-symmetry phases in some temperature regions above T_c [25]. There are some disputes over intermediate phases between PE and AFE phases. Bin Xu *et al.* suggested *R3c* and some average structures between *R3c* and *Pbam* phase as the candidates of intermediate phases through a theoretical study [25]. It is in agreement with some previous papers, which reported polar rhombohedral phase around T_c in the experiments.

Intensive studies have been done to search for the physical mechanism at the PE-AFE phase transition. Unlike the proper phase transition in FE materials, such as BaTiO₃, whose PE-FE phase transition is driven by the soft phonon mode at Γ -point, PZO does not show soft nonpolar phonon modes in the vicinity below T_c in the experiment [26] and computational study [25]. Although the existing effective Hamiltonian models address the critical role of unstable phonon modes at R and Σ -points, and their coupling effect [27, 28], these models fail to predict the phase transition temperature and do not suffice to explain the driven force of the PE-AFE phase transition. Therefore, some works proposed the missing terms in the effective Hamiltonian model that trigger the improper PE-AFE phase transition in PZO. Tagantsev *et al.* reported the polar soft mode as the driven force of the PE-AFE phase transition. The flexoelectric coupling ($\nabla \eta \cdot P - \nabla P \cdot \eta$) transforms the polar soft mode into the instability of nonpolar modes [26]. This mechanism has been questioned due to its small coefficient obtained in the later paper [25]. Jorge Íñiguez *et al.* concluded that the trilinear coupling ($\gamma_R \gamma_\Sigma \gamma_S$) makes *Pbam* phase win over other competing phases and bring the onset of multi-modes at phase transition temperature [29]. In the recent work, Shapovalov and M. Stengel firstly endow the simple description of the unstable phonon mode at the S-point [22]. Following the strategy of flexoelectric coupling construction in the ref [26], they built the rotopolar coupling term $(\phi_y(\phi_x \nabla_x P_y - P_y \nabla_x \phi_x))$, where ϕ_x, ϕ_y , and P respectively denote the amplitude of deviation regarding to 90°-phase oxygen cage rotation, anti-phase oxygen cage rotation, and local polarization. By transforming these order parameters into the unstable phonon modes, the rotopolar coupling term recovers the trilinear term in the ref [29].

4.2 Calcium titanate

The ground state of CTO is described by a 20-atom unit cell, which possesses the space group symmetry *Pnma*. With the pseudo-cubic axis (\mathbf{a}_1 , \mathbf{a}_2 , \mathbf{a}_3), we describe its periodicity in a ($\mathbf{c}_1 = 2\mathbf{a}_1$, $\mathbf{c}_2 = 2\mathbf{a}_2$, $\mathbf{c}_3 = 2\mathbf{a}_3$) supercell. Its distortion from the cubic phase is dominated by phonon mode at R, M, and X-points, which are responsible for 60.4%, 28.3%, and 11% of distortion. The R-mode is in charge of the anti-phase oxygen cage rotation $a^-a^-c^0$, the M-mode accounts for the in-phase oxygen cage rotation $a^0a^0a^+$, and the X-mode captures the antipolar motion of Ca ion along [110] direction. Amazingly, the combination of R and M modes is sufficient to reach the Pnma ground state while the X mode is a secondary mode resulting from a trilinear coupling $\gamma_R \gamma_M \gamma_X$.

We make the phonon analysis on cubic CTO. From the first-principles calculations, we deduce the relaxed unit cell length of CTO in the cubic phase, 7.25 [Bohr]. We plot the phonon dispersion curve around the cubic structure in Figure 4.3. In contrast to PZO, CTO possesses less unstable modes, which are distributed at Γ , M, and R points. The most unstable mode appears at M and R points ($\omega \approx 198.2i$ and $209.2i \ cm^{-1}$). Except for the degenerate unstable modes in the lowest band, CTO does not show other instabilities.



Figure 4.3: Phonon dispersion curve $\omega(\mathbf{q})$ of CTO. The imaginary eigenfrequencies are plotted in the negative direction.

4.2. CALCIUM TITANATE

Starting from the cubic phase distorted by unstable phonon modes, we do structural relaxations on the CTO SP model to find local minima on PES. We plot the energy gains of (meta) stable phases with respect to the cubic phase in Figure 4.4, in the same order as in Figure 4.2. CTO is short of instability in $X_{1,2}$, $M_{2,3}$, M_4 , and $R_{4,5,6}$ modes. Therefore, the corresponding local minima disappear on the PES of CTO. The relaxation of these phases brings the structure back to the stationary configuration, usually the cubic phase, $Pm\bar{3}m$. Consequently, they manifest zero energy gain in the bar chart. Besides, the energy gains of pure polar phases are notably small compared to other phases. In contrast, the polar phase R3c, coupled with oxygen cage rotation, shows comparable energy to the ground state of CTO ($\Delta E_{Pnma} \approx -376.73$ and $\Delta E_{R3c} \approx -351.02$ [meV/f.u.]). Therefore, CTO satisfies the second AFE criterion. For that reason, we ascribe the lack of AFE characteristic in CTO to the third criterion, the energy barrier between nonpolar and polar phases. It can be rationalized by the abrupt local minima distribution on the CTO energy landscape.



Figure 4.4: Energy gains of (meta) stable phases in CTO with respect to the cubic phase. The phases are in the order of magnitude of energy gain of PZO.

The phase transition behavior of the CTO at higher temperatures is more complicated than that of PZO, and its intermediate states are contentious. Experimentally, the recent papers reported that CTO undergoes a phase transition from Pnma $(a^-a^-c^+)$ to I4mcm $(a^0a^0c^-)$ around 1512K, and to cubic phase around 1636K [30, 31]. Although some previous works reported an orthogonal intermediate state, Cmcm (antipolar [110]), between Pnma and I4mcm phases in the region approximately between 1400-1500K, the theoretical phonon analysis at 0K disagrees this observation [32]. Cmcm can be obtained from the phonon displacement in combination of the degenerate X_1 and X_2 modes. To the best of our knowledge, no temperature evolution of CTO phonon dispersion curve have been reported to analyze their stability. Nonetheless, from the CTO phonon dispersion curve at 0K (figure 4.3), these modes possess positive eigenfrequencies, hence are stable at 0K. These modes probably become unstable during the increase in temperature, but the Cmcm phase is unlikely to be more energetically favorable than other phases, which is correlated with unstable modes at 0K.

The application of pressure on the CTO also leads to the phase transformation from the equilibrium ground state *Pnma*. Under the homogeneous pressure, it is observed experimentally that *Pnma* phase remains in the ground state up to 55-60 [GPa] [33]. Theoretically, the result of first-principles calculation agrees with the experimental observation, and further predicts a phase transition to *Cmcm* phase at 65 [GPa] [34]. The phase transition of CTO regarding to epitaxial strain has also been investigated through first-principles calculation [35, 36]. These works predicted the phase transformation to FE states both in textile (≈ 1.5 [GPa]) and compressed epitaxial strain (≈ -3 [GPa]), both of which are verified experimentally [37, 38].

4.3 Comparisons

In section 4.1 and 4.2, we examine separately the properties of PZO and CTO. First, both PZO and CTO exhibit a nonpolar ground state, but with different space group symmetries, *Pbam* and *Pnma*. Second, a high-symmetry-related polar phase, R3c, has an energy slightly larger than the ground states of two materials. It is difficult to examine the third criterion since it requires a full investigation of all possible paths for the phase transition. Nonetheless, from the result, PZO is AFE, and CTO is AFD. Thus, we can rationalize that the energy barrier is flat between *Pbam* and *R3c* phases in PZO, while in CTO it is large between *Pnma* and *R3c* phases. The energy barrier prevents the manifestation of the nonpolar-polar phase transition in the CTO.

But what is the microscopic origin of the flat energy barrier between *Pbam* and *R3c* phases? We can find some clues from the phonon analysis at RS and from the distribution of local minima on PES (energy gains of the metastable phases). In the phonon analysis, we should note that it is inadequate to compare directly the eigenfrequencies directly since the basis of phonon modes includes atomic mass. We generalize the unit by adopting the CTO mass in PZO phonon modes. It changes the magnitude of eigenfrequencies by $M_{PZO}\omega_n^2(\mathbf{q}) = M_{CTO}\omega_{n,new}^2(\mathbf{q})$, but does not change their signs. We plot the new phonon dispersion curve $\omega_{n,new}(\mathbf{q})$ for PZO, which we refer to PZO (CTO) phonon dispersion curve in the following context. We compare the phonon dispersion curves of CTO (black dashed lines) and PZO (CTO) (red solid lines) in Figure 4.5.

PZO (CTO) and CTO show great similarities in the flat branch between the strong unstable modes, M_1 and R_1 . The difference in unstable curves mainly appears at the antipolar modes $(X_{1,2}, M_{2,3}, M_4, R_{4,5,6})$. They are all stable in CTO, while are unstable in PZO. Besides, the polar modes ($\Gamma_{1,2,3}$) are more stable on PZO (CTO) phonon dispersion curve ($\omega_{PZO,\Gamma} \approx 187.3i$ and $\omega_{CTO,\Gamma} \approx 139.1i \ cm^{-1}$). Consequently, we compare the energy gains of *Pbam* phases and metastable phases in a $2 \times 2 \times 2$ supercell in PZO and CTO (Figure 4.2 and 4.4). During the phase transition from cubic to *P4mm* phase, CTO only gains around 90 [meV/f.u.], which is smaller than half of the energy gains in PZO. The other two polar phases, *Amm2* and *R3m*, show even much larger differences in energy gains between these two materials. On the other hand, PZO manifests (meta) stable phases related to the unstable antipolar modes, which are stable in CTO. By comparing their eigenfrequencies at RS in the generalized basis and the local minima on PES, we point out the importance of unstable antipolar modes and sufficiently stable polar modes for AFE energy landscape.

Compared to the phonon frequencies, IFCs in real space, have a more intuitive physical meaning. IFC is often analogized to the opposite of the stiffness of a fictitious linear spring between atoms since its relation to force on an atom, $F_i = -F_j = -K_{ij}u_j$, follows the format of Hooke's law,



Figure 4.5: Solid: phonon dispersion curve of PZO with the mass of CTO. Dashed: phonon dispersion curve of CTO.

 $F_i = kx_i$. The sign of IFCs provides a direct perspective of the stability of interatomic distance. The negative IFCs correspond to the normal spring. The spring tends to recover under stretch or compression; namely, the atomic pairs are against atomic displacements (Figure 4.6 (a)). The positive IFCs correspond to fictitious springs, which are inclined to stretch or compress themselves to relax the stored energy. Hence, the atomic displacement of the atomic pairs is energy favorable. We introduce two common distortions of atomic pairs. When $\alpha = \beta$ is parallel to the interatomic bond, the chain of atomic pairs forms a longitudinal distortion wave. (Figure 4.6 (b)). When $\alpha = \beta$ is perpendicular to the interatomic bond, the chain of atomic pairs forms a transverse distortion wave (Figure 4.6 (c)). Besides, we can classify the distortions of atomic pairs into polar or nonpolar. If the two atoms are the same species, the distortion is antipolar. Otherwise, it is polar.

So far, we have a comprehensive description of the CTO energy landscape in the SP model, i.e. we know all the essential IFCs, but which IFCs lead to the unstable antipolar mode and the relatively stable polar modes in PZO? We attempt to identify them by making a direct comparison in IFCs.



Figure 4.6: Distortion pattern predicted by the single value of IFC, such as (a) stable chain (b) unstable chain along the longitudinal direction, and (c) unstable chain along the transverse direction.

We firstly compare our IFCs to the previous works [39, 40] in Table 4.1 and 4.2. The relative positions of labeled atoms are illustrated in Figure 4.7. In the PZO literature (first column of two tables), the researchers used an LDA exchange-correlation energy functional with Perdew-Punger parametrization. The plane wave is expanded on a $4 \times 4 \times 4$ k-point grid within an energy cutoff of 850 [eV] [39]. In the CTO literature (third column of two tables), the researchers used the same exchange-correlation energy functional as our model (GGA PBEsol) in first-principles calculations, and expanded the plane wave of cubic structure on $6 \times 6 \times 6$ with energy converging to 0.5 [meV] (the energy cutoff is not explicitly specified) [40]. Table 4.1 records the IFCs in the basis of local coordinates for symmetric IFCs. Here, the *local coordinates* denote the mutually orthogonal eigenvectors of symmetric IFC. The first unit vector is along the longitudinal direction of the interatomic bond, while the other two unit vector points toward the transverse directions. We label the longitudinal IFC in the parallel notation, $\|$, and the other two IFCs the perpendicular notation, \perp , with subscripts 1 and 2. For $\parallel_1 = \parallel_2$, we drop the subscripts. Table 4.2 records the IFCs in the basis of Cartesian coordinates for non-symmetric IFCs. As shown in the first and the second column in the two tables, our PZO IFCs differ from the previous work surprisingly only by 1 to 2% despite of the large difference in exchange-correlation energy functional. On the other hand, the CTO IFCs of the model manifest close values to the literature, since there is only a minute difference in the k-point grid density and energy cutoff. This confirms that IFCs are quantities that can be robustly obtained so that comparison from one material to another is meaningful.



Figure 4.7: Schematic representation of relative atomic positions for Table 4.1 and 4.2.

Table 4.2: Non-symmetric IFC matrices in Cartesian coordinates. The source in the four columns are ref [39], our PZO model, ref [40], and our CTO model [9]. The IFC with negative corresponds to normal spring.

	PZO[39]		PZO		CTO[40]			СТО				
$O_1 - O_2$	+0.0038	0	0	+0.00373	0	0	+0.0057	0	0	+0.00571	0	0
	0	-0.0065	-0.0110	0	-0.00628	-0.01068	0	-0.0120	-0.0322	0	-0.01170	-0.03221
	0	-0.0229	-0.0065	0	-0.02258	-0.00628	0	-0.0177	-0.0120	0	-0.01752	-0.01170

Now, we compare the IFCs for atomic pairs, whose interatomic distance is not larger than the length of the unit cell.

First, we discuss polar atomic pairs. In both PZO and CTO, the IFC of $A_1 - O_1$ is positive at longitudinal distortion, while negative at transverse directions. Hence, the ionic chain A-O-A (for example, along [110]) tends to form a short-long bond arrangement (Figure 4.6 (b)). On the other hand, the IFCs of $B_1 - O_1$ in both cases are negative in all directions. Thus, the ionic chain B-O-B (for example, along [100]) is inclined to remain at the original position (Figure 4.6 (b)). The tendency of adjustment in the interatomic distance is in agreement with the prediction of the

Table 4.1: Diagonalized terms in symmetric IFCs [Hartree/bohr² between labeled atomic pairs in local coordinates. The relative position between atoms is plotted in figure 4.7. \parallel and \perp individually indicate the longitudinal and transverse direction with respect to the interatomic bond. The first and second columns are PZO IFCs, respectively from the ref [39] and our model. The third and fourth columns are CTO ones from ref [40] and our model. The IFCs with negative correspond to normal springs.

		PZO[39]	PZO	CTO[40]	CTO
$A_1 - O_1$		+0.0139	+0.01222	+0.0108	+0.01083
	\perp_1	N/D	-0.00512	-0.0055	-0.00568
	$\perp_2(zz)$	-0.0103	-0.01026	-0.0116	-0.01151
$B_1 - O_1$		-0.0687	-0.05550	-0.0382	-0.03821
	\perp	-0.0100	-0.01064	-0.0184	-0.01879
$A_1 - B_1$		-0.0271	-0.02674	-0.0266	-0.02697
	\perp	+0.0145	+0.01430	+0.0150	+0.01493
$A_1 - A_2$		-0.0094	-0.00922	-0.0085	-0.00829
	\perp	+0.0056	+0.00543	+0.0040	+0.00379
$B_1 - B_2$		-0.0499	-0.04972	-0.0788	-0.07910
	\perp	+0.0054	+0.00535	+0.0084	+0.00988

Goldschmidt tolerance factor that A-atom is the unstable cation. Furthermore, it can be proved by directly investigating the eigendisplacements of the unstable phonon mode Γ_1 in both materials. As shown in Table 4.3, the unstable eigendisplacements at Γ in both materials are dominated by A-ion motion. In PZO, the longitudinal and transverse spring between $A_1 - O_1$ is softer than CTO by approximately 10%, but only the longitudinal one exhibits instability. It is congruent with more unstable polar phonon modes in PZO. As for $B_1 - O_1$ IFCs, they are stable in all directions for PZO and CTO, but their magnitudes show a large difference in the two materials. For the longitudinal direction, $B_1 - O_1$ spring of PZO is 45% stiffer, while for the transverse direction, it is 43% softer.

Table 4.3: Eigendisplacement (in relative coordinates) of Γ_1 in PZO and CTO

		PZO			CTO	
	х	У	\mathbf{Z}	x	У	\mathbf{Z}
A	0	0	+0.5054	0	0	+0.5948
B	0	0	-0.1741	0	0	+0.2182
O_1	0	0	-0.5719	0	0	-0.5055
O_2	0	0	-0.5719	0	0	-0.5055
O_3	0	0	-0.2596	0	0	-0.3077

Then, we discuss the antipolar atomic pairs. In PZO and CTO, IFCs of $A_1 - A_2$ are negative in the longitudinal direction and positive in the transverse directions. The ionic chain A-A-A (for example, along [100]) tends to form a transverse wave, as shown in Figure 4.6 (c). IFCs of $B_1 - B_2$ display the same trend as those of $A_1 - A_2$. The transverse springs between $A_1 - A_2$ are softer in PZO by 43%, while between $B_1 - B_2$ they are more compliable in CTO by 45%. Nonetheless, the $B_1 - B_2$ distortion might be suppressed by the strong stability of another nearest B - B atomic pair (for example, bond along [010]) in the longitudinal direction. In contrast, the longitudinal interaction between nearest A - A is much smaller. From the beforehand study in phonon stability, we speculate that it suppresses the antipolar distortion of $A_1 - A_2$ in CTO, while it is not the case in PZO. Nonetheless, it is difficult to deduce in which range of values the stable IFCs in the longitudinal direction eliminates the instability in transverse directions.

Consequently, we investigate the oxygen cage rotation in IFCs. In Cartesian coordinates, the non-symmetric $O_1 - O_2$ IFC matrix is divided into a 2×2 matrix, which is responsible for oxygen displacement in the plane (1,0,0), and a 1×1 matrix, which is in charge of the transverse distortion along the z-axis. The terms in the 2×2 matrix are negative, implying that oxygen atoms show a tendency to maintain their distance. This observation is in line with the common distortion pattern, oxygen cage rotation since $O_1 - O_2$ distance does not change during the cage rotation. On the other hand, the $O_1 - O_2$ IFC is positive along the transverse direction [100], implying its possibility to form polar or antipolar distortion, as shown in figure 4.6 (c).

Finally, we look into the on-site force constants at the harmonic level, whose definition is given in equation 2.42. On-site force constant measures the stability of isolated atomic motion against other atoms. Their values are given in table 4.4. We should note that the sign of on-site force constant gives the opposite indication of IFCs. Here, the positive IFCS are stable, while the negative are unstable. As shown in table 4.4, the on-site force constants are all positive. Hence, isolated atomic distortions are energy unfavorable, and atomic displacement coupling in the adjacent cells (such as A-O-A polar chain) is required for structure instabilities. It is worth noting that the on-site force constant of the A atom in both materials, is much smaller than that of the B atom. It is in line with the tolerance factor, that A atom is less stable due to its relatively small size in the cubic phase.

 Table 4.4: On-site force constant, positive = stable

		PZO[39]	PZO	CTO[40]	СТО
А	(xx=yy=zz)	+0.0129	+0.01653	+0.0269	+0.02689
В	(xx=yy=zz)	+0.2302	+0.20730	+0.2236	+0.22432
Ο	(xx=yy)	+0.0166	+0.02034	+0.0432	+0.04340
Ο	(zz)	+0.2758	+0.24597	+0.2624	+0.26331

Overall, the sign of all IFCs are the same in PZO and CTO, indicating that they show similar stability from the local perspective. There are notable differences in magnitudes of some IFCs, but it is complicated to conclude from the comparison, which one is critical. The underlying reason is that, unlike phonon modes, IFCs correspond to pairs of atomic distortion. The atomic distortion of a single atom is correlated to a large amount of IFCs. They might mutually compensate so that it is inappropriate to ascribe certain polar/nonpolar distortions to a few anomalous IFCs. In opposite, we should project the effect of each IFCs on the basis of phonon modes.

4.4 Conclusions

In this chapter, we have compared structural and energetic information about PZO and CTO, including the ground state, metastable phases, and the phase transition during variations in temperature. Correspondingly, we show that these two materials satisfy the first two AFE criteria. The ground state of PZO and CTO are nonpolar, with the different space group symmetries, *Pbam* and *Pnma*. Besides, the energy of the polar phase R3c is close to the energies of the ground states in both materials. Nonetheless, we have known empirically that PZO is an AFE material, while

CTO is not. Hence, we speculate the energy barrier between Pbam and R3c in PZO is low, and between Pnma and R3c is high in CTO. We compare the phonon instabilities and the energies of local minima in two materials.

It is questionable which factors are related to the height of the energy barrier. From the comparison of phonon instabilities and energy of metastable phases, we deduce that the unstable antipolar and sufficiently unstable polar modes are essential for the low energy barrier between Pbam and R3c phases. Nonetheless, we cannot find some decisive parameters in the SP model by a direct comparison in coefficients.

Chapter 5

Can we make Calcium Titanate Antiferroelectric?

We have revealed the underlying reasons that hinder CTO an AFE material. The large energy barrier hinders the phase transition between Pnma and R3c phases. From the phonon analysis and investigation of the energy of metastable phases, we identify that polar/antipolar phonon modes and phases are crucial for the flat energy barrier between Pbam and R3c phases in PZO. Accordingly, we want to take a step further, identifying which terms in the CTO SP model are essential for the onset of the low energy path between Pbam and R3c phases. In other words, can we realize this phase transition path in CTO? We cannot reach a content conclusion from a direct comparison of the IFCs in the previous chapter. In this chapter, alternatively, we modify the coefficients in CTO SP model to imitate the PZO energy landscape. We examine the similarity of the modified CTO SP model and PZO energy landscape by three indices, (i) the ground state Pbam, (ii) the comparable phonon instabilities at high-symmetry q-points, and (iii) the similar energy gains of local minima.

5.1 Modification of interatomic force constants

In this section, we investigate the effect of individual IFCs on phonon instability. Our intention here is to identify the critical IFCs to produce a similar energy curve at RS on the CTO energy landscape. Hence, we modify a single IFC and compare the phonon dispersion curve of the modified CTO SP model with the PZO (CTO) phonon dispersion curve (red lines in Figure 4.5).

Initially, we eliminate the possibility that long-range IFCs, which is directly obtained by dipoledipole interactions $(K_{ij\alpha\beta} = K^{DD}_{ij\alpha\beta})$, play crucial roles in phonon instabilities. We replace the Born effective charge and optical dielectric constant of CTO with those of PZO, and plot the resulting phonon dispersion curve in the solid curves of Figure 5.1. In comparison to the CTO (dashed curves), they only make an observable effect on the highest band and do not affect the stability of the unstable modes. Therefore, we can ascribe the phonon dispersion curve difference between CTO and PZO to IFCs in a short distance.

Now, we turn to observe the influence of individual IFCs on phonon instabilities, especially for those whose interatomic distance of atomic pairs is shorter than the length of the cubic unit cell. We tune IFCs in Cartesian coordinates by multiplying a positive factor f, in order to avoid changing the type of interatomic springs. During the modification of coefficients, we "strengthen" the interaction by multiplying a factor f > 1 and "weaken" the interaction by multiplying a factor



Figure 5.1: Phonon dispersion curve of the modified CTO model, with all harmonic coefficients replaced by those of PZO except for IFCs.

f < 1.

Firstly, we investigate the change in the phonon dispersion curve by tuning the interaction between the nearest B-O atomic pairs. Since their bond is parallel to one unit vector of Cartesian coordinates, the IFC in Cartesian coordinates is the same as in local coordinates. Figure 5.2 (a) and (b) respectively illustrate the modified phonon dispersion curve whose longitudinal term is multiplied by a factor of 0.7 and the transverse term by a factor of 0.85. Compared with the original IFCs (dashed lines), the weakening of B-O longitudinal interaction enhances the instability of the following modes: $\Gamma_{1,2,3}$, $X_{3,4}$, $M_{2,3}$, and M_4 modes. On the other hand, the weakening in the transverse interaction increases the overall instabilities in the lowest band and in the phonon modes $M_{2,3}$. However, it does not relatively enhance the polar instability with respect to oxygen cage rotation modes. Besides, the modification on the two IFCs in the nearest B-O does not change the eigenfrequencies in the antipolar modes at $R_{4,5,6}$. Hence, it is impossible to approach the phonon instabilities in PZO (CTO) by exclusively tuning the B-O interaction.

Table 5.1: Symmetric IFC matrices in Cartesian coordinates. The IFC with negative corresponds to normal spring.

		PZO			СТО	
$A_1 - O_1$	+0.00355	+0.00867	0	+0.00258	+0.00826	0
	+0.00867	+0.00355	0	+0.00826	+0.00258	0
	0	0	-0.01026	0	0	-0.01151
$A_1 - B_1$	+0.00062	-0.01368	-0.01368	+0.00097	-0.01397	-0.01397
	-0.01368	+0.00062	-0.01368	-0.01397	+0.00097	-0.01397
	-0.01368	-0.01368	+0.00062	-0.01397	-0.01397	+0.00097



Figure 5.2: Solid lines: phonon dispersion curve of the modified CTO model with adjustment on nearest B-O interaction, (a) (left) $f(\parallel)=0.7$ (b) (right) $f(\perp)=0.85$. Dashed lines: CTO phonon dispersion curve.



Figure 5.3: Solid lines: Phonon dispersion curve of the modified CTO model with adjustment on nearest A-O interaction, (a) (left top) $f(\parallel_d)=1.4$, (b) (right top) $f(\parallel_{od})=1.3$, (c) (left bottom) $f(\perp)=0.8$, (d) (right bottom) $f(\parallel_{od})=1.6$ and $f(\perp)=0.65$. Dashed lines: (a) to (c) CTO phonon dispersion curve, (d) PZO phonon dispersion curve in CTO mass basis (the same as figure 4.5).

Consequently, we study the change in the phonon dispersion curve by modifying the nearest A-O interactions. The local coordinates of A-O IFCs is not the same as Cartesian coordinates; hence, we write the symmetric matrix in the first row of Table 5.1. There are three independent terms in IFC matrix in Cartesian coordinates, the parallel diagonal term $(||_d)$, the parallel off-diagonal term $(||_{od})$, and the perpendicular term $(\perp = \perp_2)$. They are related to the IFCS in local coordinates by

$$\begin{cases} \|_{d} = \frac{1}{2}(\| + \bot_{1}) \\ \|_{od} = \frac{1}{2}(\| - \bot_{1}) \end{cases}$$
(5.1)

Figure 5.3 (a), (b), and (c) displays the individual effect of these three terms on the phonon dispersion curve. The strengthening of parallel diagonal interactions enhances the overall instability in the lowest band. Besides, it notably increases the instability of the antipolar modes $X_{1,2}$, $M_{2,3}$, M_4 and $R_{4,5,6}$. The strengthening of parallel off-diagonal interactions increases the instability mainly at $M_{2,3}$ and $R_{4,5,6}$, while the eigenfrequencies of phonon modes at the lowest band are fixed. The weakening of perpendicular interactions strengthens the instabilities of all antipolar modes, $X_{1,2}$, $M_{2,3}$, M_4 , and $R_{4,5,6}$. In addition, it pins the phonon modes corresponding to oxygen cage rotation, and increases the polar instability at the lowest band. Amazingly, the weakening of perpendicular interactions in the nearest A-O bond distorts the energy landscape in our targeted direction. To adjust the magnitude to the right order, we modify the perpendicular term with an adjustment on the off-diagonal parallel term. The combination reproduces the similar phonon instability of PZO in the modified CTO SP model. (Figure 5.3 (d)). Hence, we believe that the A-O harmonic interaction is critical for the difference between CTO and PZO energy landscape at the harmonic level.

For the IFCs, whose interatomic distance is not smaller than $\sqrt{3}/2$ (relative coordinates, distance between the nearest A-B atomic pairs), tuning of phonon dispersion curve manifests small effects in contrast to A-O and B-O interaction.

We look into the effect of the nearest A-B interaction on the phonon dispersion curve. The nearest A-B bond does not aligne with Cartesian coordinates, hence, we make a basis transformation on the IFCs to Cartesian coordinates. In the Cartesian coordinates, the nearest A-B IFC matrix contains two independent terms, diagonal ($\|_d$) and off-diagonal ($\|_{od}$), as shown in the second row of Table 5.1. The strengthening of diagonal interaction increases the instabilities in the antipolar phonon modes, $X_{1,2}$, $M_{2,3}$, M_4 , and $R_{4,5,6}$ (Figure 5.4 (a)). The trend is similar to the weakening of the A-O perpendicular interaction. However, to tune the eigenfrequencies by the same magnitude, it requires a quite large factor (larger than 3), which is unlikely achievable by replacing atoms. Figure 5.4 (b) illustrates phonon instabilities with strengthening in off-diagonal interaction by a factor of 1.2. It enhances the instability of $M_{2,3}$, and remarkably the second lowest phonon mode at q = (0.25, 0.25, 0.25).

Finally, we investigate the influence of the nearest A-A interactions on the phonon dispersion curve. Their local coordinates are the same as the Cartesian ones. In Figure 5.4 (c), we demonstrate the phonon dispersion curve, whose A-A longitudinal interaction is strengthened by a factor of 1.1. It enhances the instabilities at $M_{2,3}$ and $R_{4,5,6}$. On the other hand, the weakening of transverse interaction displays a similar trend to the strengthening of longitudinal interaction.

Overall, tuning nearest A-B and A-A interactions only favors the antipolar phonon modes, but not polar modes. Hence, these interactions might be the seasoning for the realization of PZO energy landscape. They are not crucial, but may improve the similarity between the modified CTO model and the PZO energy landscape.

So far, we have shown that tuning IFCs of CTO in the short distance, and especially the near-



Figure 5.4: Solid lines: phonon dispersion curve of the modified CTO model with adjustment on nearest A-B interaction, (a) (left top) $f(||_d)=1.4$, (b) (right top) $f(||_{od})=1.2$, and on nearest A-A interaction (c) (left bottom) $f(||_d)=1.1$, (d) (right bottom) $f(\perp)=0.8$. Dashed lines: CTO phonon dispersion curve.



Figure 5.5: Energy gains of metastable phases on different PES. Bar chart: the combination of the anharmonic parts of CTO and the harmonic parts of PZO. Blue dots: CTO SP model. Green crosses: PZO by DFT relaxation.

est A-O interactions, is likely to imitate the PZO energy landscape at the harmonic level. Now, it is necessary to examine if harmonic correction is sufficient to reproduce the energy gains of metastable phases. Here, we use an extreme case by replacing all IFCs in CTO with PZO ones, so that the energy landscape is the same as PZO one at the harmonic level. We refer to this energy landscape as CTO(Anh)+PZO(Ha) model in the following context. On the CTO(Anh)+PZO(Ha) model, we do the structure relaxation on the potential metastable phases, which are predicted by soft modes. The bar chart in Figure 5.5 demonstrates the energy gains of these phases. We also mark the energy gains on the original CTO model with blue dots, and those by first-principles calculations of PZO with green crosses. In comparison to the energy gains of CTO, there are several notable points on this modified model. First, we are able to relax *Pbam* phase, implying that it becomes a local minimum on this PES. Furthermore, *Pbam* becomes the ground state. Second, the harmonic correction dramatically increases the stability of pure polar phases, especially Amm2. Besides, it decreases the stability of pure oxygen rotation phases by 100 [meV]. Third, due to the onset of several unstable modes in the modified model, some metastable phases, corresponding to the pure antipolar modes, appear on the PES. Nonetheless, compared to PZO, the modified PES is still rugged, since some phases show anomalously low energy, including the ground state Pbam, polar phases R3c, Amm2, P4mm, and CTO ground state Pnma. We deduce that the harmonic correction is insufficient to describe the difference between PZO and CTO energy landscape. Nonetheless, we can conclude that A-O interaction is critical to imitate the PZO energy landscape at the harmonic level.

5.2 Anharmonic modification

In the harmonic correction, we have concluded that (i) A-O harmonic interaction dominates the difference in phonon instabilities of CTO and PZO, and that (ii) tuning harmonic parameters is insufficient for CTO to imitate the PZO energy landscape. The artificial CTO(Anh) + PZO(Ha)model results in some anomalous stable phases. Therefore, we turn to search for crucial interactions from a large number of anharmonic coefficients to eliminate the excess energy from these phases. The crucial interaction can be one of two kinds: the interaction contributes excess negative energy or insufficient positive energy. We illustrate the first case in the green curves of Figure 5.6 (a). The green solid line is the cross-section of the model, while the green dashed line is the negative contribution of a single term. We can improve the energy landscape by reducing its magnitude (from the green to the blue dashed one), and the energy gains of local minima will be reduced (blue solid line). We display the second case in the green curves of Figure 5.6 (b). The green solid curve is the total energy curve before modification, while the green dashed line is the positive contribution from a single term. We can reduce the stability of local minima by increasing the magnitude of this coefficient (from green to blue dashed line).



Figure 5.6: Schematic representation for decreasing the energy gains of local minima. (a) Decrease the magnitude of negative coefficients. (b) Increase the magnitude of positive coefficients.

Since the anharmonic interactions lack intuitive physical meanings, we use a direct strategy to predict potential crucial interactions. We list the energy contribution of each anharmonic term in every metastable phase, and arrange them in the order of magnitude in Table 5.2, with the separation of negative and positive contributions. For the sake of simplicity, we label the coefficients with their indices; the full description of SATs and their values in the original model can be referred in Table A.1. Consequently, we find the intersection between those phases showing abnormal instability. In the first case, the most potential candidates are the 10th and 15th anharmonic terms. They dominate negative energy contributions of polar phases, including R3c, R3m, Amm2, and P4mm, in large proportion. Nonetheless, these terms do not account for a large proportion of negative energy contribution in the ground state phases, Pbam and Pnma. Hence, we speculate that the reduction in this terms does not improve much the energy gains of Pbam and Pnma phases. We examine our hypothesis by reducing the 10th anharmonic terms by multiplying a factor 1/2in Figure ??. Compared to the CTO(Anh)+PZO(Ha) model (mark with downward triangles), the term decreases the energy gains of polar phases, especially P4mm and R3c. Nonetheless,

	CTO+PZO		pure PZO	
phases	positive	negative	positive	negative
Pbam	29, 3, 38	39, 30, 28	1, 31, 21	9, 5, 47
R3c	21, 3, 11	18,10,15	1, 21, 31	28, 16, 53
R3m	9, 3, 11	10, 15, 7	3, 1, 25	16, 11, 8
Pnma	21, 3, 9	22, 14, 18	1, 21, 31	14, 9, 26
Imma	9, 11, 3	10,15,18	31, 21, 27	26, 9, 5
Amm2	11, 3, 8	10, 15, 6	1, 3, 25	11, 16, 8
R-3c	2, 9, 38	12, 1, 45	27, 3, 31	9, 5, 2
P4mm	3, 11, 8	10, 15, 6	1, 25, 46	11, 44, 2
I4mcm	2, 38, 25	12, 1, 23	31, 21, 1	9, 5, 8
P4/mbm	2, 38, 25	12, 1, 23	31, 21, 1	9, 5, 8
Cmmm	11, 9, 26	10, 15, 6	26, 19, 3	7, 20, 9
Pmma	11, 9, 26	15, 10, 7	26, 3, 1	7, 20, 11
R-3m	11, 9, 26	10, 15, 7	26, 3, 30	16, 7, 20
Cmcm	11, 9, 3	10, 15, 7	3, 1, 25	16, 28, 10
I4mmm	11, 8, 3	10, 15, 6	26, 19, 43	16, 7, 20
P4nmm	11, 8, 3	10, 15, 6	1, 38, 25	16, 4, 8

Table 5.2: The anharmonic terms with the most significant energy contribution in each phase.

it also reduces the stability of R3m phase, which is already at an adequate energy level in the CTO(Anh)+PZO(Ha) model. Furthermore, the energy gain of *Pbam* is still significantly large. Hence, a decrease in these terms is not a good choice for imitating the PZO energy landscape.

In the second case, the first column of Table 5.2 shows that the third term plays an important role in anharmonic positive energy contribution of our targeted phases. We examine the effect of this term on the energy gains of metastable phases by multiplying a factor of 1.5. The result is presented in Figure 5.8. In comparison to the CTO(Anh)+PZO(Ha) model, the trend of energy gains is much smoother except for the phase Amm2. Besides, the increase in the 3rd term also reduce the energy gains of R3m. It is ambiguous to conclude if this term is crucial. It might play the crucial role, when the combination of multiple interactions is critical for imitating PZO energy landscape.

It is also likely that the term concerning positive energy does not exist in our CTO model. As a reminder, we dropped the unimportant anharmonic terms (there are millions of them) during the establishment of the model, and remained only 60 important terms in the CTO model. Among the dropped terms, there might be some crucial terms for realizing the AFE energy landscape in PZO. Nevertheless, to identify the important terms from them is undoubted looking for a needle in a haystack. Hence, we draw support from an establishing PZO second-principles model.

The PZO SP model is well-established at the harmonic level, but not at the anharmonic level. We obtain the energy gains of the metastable phases through the structural relaxation on the PZO SP model. As shown in Figure A.1, this model cannot predict the correct ground state of PZO, *Pbam*, but the local minima on PES are close to the values from first-principles calculations. We list their anharmonic coefficients in Table A.2.

According to PZO phonon dispersion curve, we identify metastable phases and calculate the corresponding energy on the establishing PZO SP model. We list the most important anharmonic terms of these metastable phases in the third and fourth column of Table 5.2. According to the



Figure 5.7: Energy gains of metastable phases on different PES. Bar chart: CTO(Anh) + PZO(Ha) model with the 10th anharmonic coefficient multiplied by a factor 1/2. Green crosses: PZO by DFT relaxation. Gray inverted triangle: CTO+PZO SP model.



Figure 5.8: Energy gains of metastable phases on different PES. Bar chart: CTO(Anh) + PZO(Ha) model with the 3rd anharmonic coefficient multiplied by a factor 2. Green crosses: PZO by DFT relaxation. Gray inverted triangle: CTO+PZO SP model.



Figure 5.9: Energy gains of metastable phases on different PES. Bar chart: CTO(Anh) + PZO(Ha) model in addition of 1st term in PZO SP model. Blue dots: CTO SP model. Green crosses: PZO by DFT relaxation.



Figure 5.10: Cross section of different PES along the path between RS and relaxed *P4mm* phase. Blue: CTO SP model. Light gray: CTO+PZO SP model. Dark gray: mCTO+PZO SP model.

table, we might identify the potential missing term in our CTO model to imitate the energy landscape of PZO. We find that the first term $(Pb_y - O1_y)^4$, which corresponds to an anharmonic interaction between A-O, contributes a large proportion in most phases, and this term does not appear in our CTO model. Hence, we investigate the effect of this term by adding it to the CTO(Anh) + PZO(Ha) model. We plot the energy gains of each phase with respect to that of the cubic phase in Figure 5.9. Intriguingly, this additional term results in a similar trend of energy gains with the PZO. It reduces the stability of all metastable phases, particularly in those anomalously unstable phases in CTO(Anh)+PZO(Ha) model. Although there are still some peaks in the figure, we can infer that the 1st anharmonic term in the PZO model, $(Pb_y - O1_y)^4$, is crucial for imitating the PZO energy landscape. This is interesting that as at the harmonic level, the key difference between PZO and CTO appears located in the A-O interactions.

In Figure 5.10, we visualize the energy landscape between reference structure and relaxed P4mm phase in the three models, the original CTO mode, CTO(Anh)+PZO(Ha) model, and the CTO(Anh)+PZO(Ha) model with the addition of 1st term in PZO model (referred as mCTO+PZO in the legend). Following the stepwise modification, the polar phase becomes anomalously stable at harmonic correction and is regulated by the additional positive term, $(Pb_y - O1_y)^4$.

5.3 Role of hydrostatic pressure

In the section 5.1 and 5.2, we have concluded that the atomic interactions between nearest lead and oxygen atom plays an important rule in the low energy path between *Pbam* and *R3c* phases. Instead of atomic replacement, can we tune the Ca-O interactions into Pb-O interactions in a practical way? Here, we make an examination of the effect of the negative pressure (homogeneous tensile stress).

First, we do a symmetry-constrained relaxation to derive the equilibrium cubic structure at a specific pressure P. Then, we compare the CTO SP model at P [atm] with PZO again through phonon dispersion curve and energy gains of local minima. Here, we report the effect of pressure by taking P = -10 [atm] (tensile stress) for example. Figure 5.11 illustrates the phonon dispersion curves in the red solid lines. In compare to the phonon dispersion curve at P = 0 [atm] (black dashed lines), the polar phonon modes $\Gamma_{1,2,3}$, the antipolar phonon modes $X_{1,2}$ and $M_{2,3}$ become more unstable. Besides. The instability of phonon modes, which accounts for the oxygen cage rotation, M_1 and $R_{1,2,3}$, becomes less unstable, while the antipolar modes $R_{4,5,6}$ remain the same stability.

Under a constant pressure, the equilibrium structure is located at the minimum of Gibbs free energy. Hence, the energy gains of metastable phases should take the change in cell volume ΔV from the cubic phase into account.

$$\Delta G(\mathbf{u}, \boldsymbol{\eta}, P) = \Delta E(\mathbf{u}, \boldsymbol{\eta}) + P \cdot \Delta V(\boldsymbol{\eta}), \qquad (5.2)$$

Figure 5.12 demonstrates the energy gains of metastable phases at P = -10 [atm]. We fail to relax the *Pbam* structure, which implies there is no local minima in *Pbam* symmetry. Besides, all polar phases become more stable, including the pure polar phases, and the one combined with oxygen cage rotation *R3c*. Indeed, as the tensile pressure exceeds approximately P = -4 [atm], the ground state of CTO becomes polar phase *R3c*. At P = 0 - 4 [atm], the local minima are still too rugged for phase transition between *Pbam* and *R3c*. *Pbam* is even not a ground state or local minimum! At P > 4 [atm], the ground state becomes polar. Thus, we conclude it is impossible to make CTO an AFE material only through the negative pressure.



Figure 5.11: Phonon dispersion curve around CTO relaxed cubic phase at P = 0 (dashed) and at P = -10 [atm] (solid).



Figure 5.12: Energy gains of metastable phases with respect to relaxed cubic phase of CTO at P = -10 [atm]. The blue dots are at P = 0 [atm].

5.4 Conclusions

In the harmonic and anharmonic parts of the CTO model, we individually identify the crucial interactions that distinguish the energy landscape of CTO and PZO. At the harmonic level, we produce similar phonon instabilities in CTO model by tuning the nearest A-O interactions. At the anharmonic level, the addition of 1st term in PZO model to the CTO(Anh)+PZO(Ha) leads to the comparable energy gains of metastable phases with the PZO ones. It is exhilarating that the 1st term in the establishing PZO model, $(A_y - O1_y)^4$, also corresponds to A-O interactions. Hence, we conclude that the Pb-O bond is a crucial ingredient for the emergence of AFE in PZO. We have examined if a homogeneous negative pressure is able to imitate the Pb-O bond in CTO, but we prove that it is not a feasible approach.

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Chapter 6

Conclusions

There are two correlated purposes of this thesis. First is to reveal critical interactions, which make PZO an AFE material, while CTO is an AFD material. Second is to realize the nonpolarpolar phase transition path in PZO on a modified CTO SP model. We choose these two materials to understand AFE characteristics since they manifest similar structures at high temperatures. Nonetheless, PZO condenses to an AFE material, while CTO is an AFD material at low temperatures. Hence, it is noteworthy to reveal the microscopic origin of their difference in the electric property.

We make the analysis by tuning the coefficients of the CTO SP model. A SP model expands PES by a polynomial function at an RS with respect to lattice degree of freedom. For that reason, the calculation of energy on SP models is much faster than that through first-principles calculations. Besides, the coefficients in SP models are correlated with physical meaning; therefore, it is useful to track the essential interactions. According to the approach to deriving the coefficients, the energy function is divided into three parts: (i) energy of reference structure, (ii) harmonic contributions, and (iii) anharmonic contributions. The energy of reference structure is obtained by first-principles calculations. Based on the energy and the wave functions of the RS, we derive the harmonic coefficients by DFPT. Finally, the anharmonic coefficients are obtained by data fitting on a set of training set. Since these processes are related to first-principles calculations, SP models preserve its predicting power.

We start our analysis by elucidating three AFE criteria from the microscopic perspective and examining them on PZO and CTO. First, an AFE material manifests a nonpolar ground state. PZO is *Pbam* and CTO is *Pnma* at low temperatures; therefore, both of them meet this criterion. Second, there is a polar phase, whose energy is close to the ground state. PZO and CTO satisfy the criteria. Both of them possess a polar phase, *R3c*, whose energy is near to their ground states. Finally, the energy barrier between nonpolar and polar phases is flat enough to allow the phase transition at a sufficiently large electric field. Since PZO and CTO are respectively identified as an AFE and an AFD, we could speculate that PZO meets this criterion, while CTO does not. Therefore, we target to uncover the terms in the SP model responsible for the energy barrier difference.

By comparing the curvature at the harmonic level and the energy of local minima, we deduce that in reciprocal space, the unstable antipolar and polar phonon modes are responsible for the low barrier between *Pbam* and *R3c* phases in PZO. In real space, Pb-O interactions play important roles in AFE characteristics in PZO. With adjustment of the Ca-O harmonic and anharmonic interactions, we can reproduce the phase transition path between *Pbam* and *R3c* phases in CTO. Finally, we investigate if hydrostatic pressure can be a practical way to simulate Pb-O interactions between calcium and oxygen atoms in CTO, but we find it an unfeasible method.

For the following research, we expect to use molecular dynamics to explore the nonpolar-polar phase transition path on a more complete PZO SP model. Accordingly, we can obtain the physical value of the energy barrier, and track the change in energy barrier as we tune the CTO model. Besides, it is noteworthy to follow the same scheme to compare CTO with another AFE material, PbHfO₃, whose tolerance factor (t=0.974) is close to CTO as well, and examine if Pb-O interactions are crucial for their difference. If so, we may lay down the critical role of Pb-O interactions in AFE materials.

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Appendix A

Anharmonic coefficients

Index	Representative SATs	Values
1	$\frac{(Ca_x - O1_x)^1 (Ca_x - O1_x [\bar{1}00])^1 (n_1)^1}{(Ca_x - O1_x [\bar{1}00])^1 (n_1)^1}$	-1.372E-02
2	$(Ca_x - O1_x)^2 (Ca_y - O2_y)^1 (Ca_x - O1_x[\bar{1}00])^1$	6.907E-04
3	$(Ca_x - O1_x)^2 (Ca_x - O3_x [\bar{1}\bar{1}0])^2$	6.297E-04
4	$(Ca_{u} - OI_{u})^{2} (\eta_{2})^{1}$	-8.680E-03
5	$(Ca_x - O1_x)^1 (Ca_x - Ti_x[00\bar{1}])^1 (\eta_1)^1$	6.193E-03
6	$(Ca_x - O1_x)^2 (Ca_x - O3_x[\bar{1}\bar{1}0])^1 (Ca_x - Ti_x[\bar{1}\bar{1}\bar{1}\bar{1}])^1$	-1.985E-04
7	$(Ca_x - O1_x)^1 (Ca_z - Ti_z[\bar{1}\bar{1}0])^1 (\eta_5)^1$	-8.483E-03
8	$(Ca_x - O1_x)^1 (Ca_x - O2_x)^1 (Ca_x - O2_x[0\bar{1}0])^1 (Ca_x - O2_x[0\bar{1}\bar{1}])^1$	4.865 E-04
9	$(Ca_x - O1_x)^2 (Ca_z - O1_z)^2$	2.307 E-03
10	$(Ca_x - O1_x)^1 (Ca_x - Ti_x)^1 (Ca_x - O2_x[0\bar{1}\bar{1}])^2$	-8.472E-04
11	$(Ca_x - O1_x)^1 (Ca_x - O2_x)^1 (Ca_x - Ti_x[0\bar{1}\bar{1}])^1 (Ca_x - Ti_x[\bar{1}\bar{1}\bar{1}])^1$	1.256E-03
12	$(Ca_x - O1_x)^1 (Ca_y - O2_y)^1 (\eta_1)^1$	-1.100E-02
13	$(Ca_x - O1_x)^1 (Ca_y - O2_y)^1 (Ca_x - O3_x)^1 (Ca_x - O1_x[\bar{1}0\bar{1}])^1$	-1.020E-04
14	$(Ca_x - O1_x)^1 (Ca_z - O1_z)^1 (Ca_z - Ti_z[00\bar{1}])^1$	1.636E-03
15	$(Ca_x - O1_x)^1 (Ca_x - O2_x)^1 (Ca_x - O2_x[00\bar{1}])^1 (Ca_x - Ti_x[\bar{1}\bar{1}0])^1$	-8.134E-04
16	$(Ca_x - O1_x)^1 (Ca_y - O2_y)^1 (Ca_y - O3_y)^1 (Ca_z - O1_z[00 - 1])^1$	-4.939E-04
17	$(Ca_x - O1_x)^1 (Ca_x - Ti_x)^1 (Ca_y - Ti_y[\bar{1}0\bar{1}])^1 (\eta_1)^1$	-1.622E-02
18	$(Ca_x - O1_x)^1 (Ca_x - O2_x)^2 (Ca_y - O2_y)^1$	1.495E-03
19	$(Ca_x - O1_x)^1 (Ca_x - Ti_x)^1 (Ca_x - O2_x)^1 (Ca_y - O2_y)^1$	-1.191E-05
20	$(Ca_x - O1_x)^1 (Ca_y - O2_y)^1 (Ca_y - Ti_y)^2$	9.245E-05
21	$(Ca_x - O1_x)^2 (Ca_x - O2_x)^1 (Ca_y - O2_y)^1$	-1.121E-03
22	$(Ca_x - O1_x)^1 (Ca_z - O2_z)^1 (Ca_y - O3_y)^1$	-1.574E-03
23	$(Ca_x - O1_x)^1 (Ca_x - O1_x[00\bar{1}])^1 (\eta_1)^1$	-1.075E-03
24	$(Ca_x - O1_x)^1 (Ca_y - Ti_y[\bar{1}00])^1 (Ca_x - Ti_x[\bar{1}\bar{1}\bar{1}])^1 (\eta_3)^1$	-2.701E-02
25	$(Ca_x - O1_x)^2 (\eta_1)^1$	-2.600E-03
26	$(Ca_x - O1_x)^2 (Ca_z - O1_z)^1 (Ca_x - O1_x[\bar{1}0\bar{1}])^1$	1.139E-03
27	$(Ca_x - O1_x)^1 (Ca_y - O3_y)^1 (Ca_z - Ti_z)^1$	9.489E-04
28	$(Ca_y - O1_y)^2 (Ca_y - Ti_y)^1$	2.872E-02

Table A.1: Anharmonic terms of CTO model, the vectors indicate the position of unit cell. If it is not labeled, the position of unit cell is [000].

Continued on next page

29	$(Ca_y - O1_y)^1 (Ca_y - Ti_y)^2$	-2.813E-02
30	$(Ca_x - Ti_x)^3$	8.566E-03
31	$(Ti_x - O1_x)^2 (Ti_y - Ti_y[010])^1$	3.706E-03
32	$(Ti_x - O1_x)^1 (Ti_x - O2_x)^2 (Ti_x - O2_x [100])^1$	6.911E-03
33	$(Ti_y - O1_y)^2 (\eta_2)^1$	-4.047E-01
34	$(Ti_x - O1_x)^1 (Ti_y - O2_y)^1 (Ti_x - O2_x[100])^1 (Ti_y - O1_y[010])^1$	1.269E-02
35	$(Ti_x - O1_x)^1 (Ti_x - Ti_x[010])^1 (\eta_1)^1$	1.602 E-02
36	$(Ti_x - O1_x)^1 (Ti_y - O1_y)^1 (Ti_x - Ti_x [100])^1$	-8.588E-04
37	$(Ti_x - O1_x)^2 (Ti_y - O1_y)^2$	-1.274E-02
38	$(Ti_x - O1_x)^3 (Ti_y - O2_y)^1$	-9.896E-04
39	$(Ti_x - O1_x)^2 (Ti_y - O2_y)^1 (Ti_y - Ti_y [010])^1$	-3.613E-03
40	$(Ti_x - O1_x)^2 (Ti_z - O3_z)^1$	2.721E-03
41	$(Ti_x - O1_x)^2 (Ti_x - O2_x)^1$	2.188E-03
42	$(Ti_x - O1_x)^2 (Ti_z - O1_z)^1 (Ti_y - O3_y)^1$	-8.673E-04
43	$(Ca_x - Ti_x)^2 (Ca_y - Ti_y)^1$	1.456E-03
44	$(Ca_x - Ti_x)^1 (Ca_y - Ti_y)^1 (Ca_z - Ti_z)^1$	5.780 E-03
45	$(Ti_x - O1_x)^2 (\eta_3)^1$	-7.652E-04
46	$(Ti_y - O1_y)^1 (Ti_y - O1_y[010])^1 (\eta_2)^1$	8.356E-02
47	$(Ti_x - O1_x)^1 (Ti_z - O1_z)^1 (\eta_5)^1$	-1.645E-03
48	$(Ti_y - O1_y)^1 (Ti_x - O2_x)^1 (\eta_1)^1$	-2.145E-01
49	$(Ti_x - O1_x)^1 (Ti_x - O1_x[010])^1 (Ti_y - O1_y[010])^1$	-1.102E-02
50	$(Ti_x - O1_x)^1 (Ti_x - O3_x)^1 (\eta_4)^1$	2.562 E-03
51	$(Ti_x - O1_x)^1 (Ti_z - O2_z)^1 (Ti_z - O1_z[010])^1 (\eta_1)^1$	7.238E-03
52	$(Ti_x - O1_x)^1 (Ti_x - O1_x[010])^1 (Ti_y - O1_y[010])^2$	4.931E-03
53	$(Ti_x - O1_x)^2 (Ti_y - O2_y)^1 (eta_3)^1$	1.017E-01
54	$(Ti_x - O1_x)^1 (Ti_x - O2_x)^1 (Ti_y - O2_y)^1$	-2.932E-03
55	$(Ti_x - O1_x)^1 (Ti_x - O3_x)^1 (Ti_z - Ti_z[001])^1$	2.730E-03
56	$(Ti_x - O1_x)^1 (Ti_x - O3_x)^1 (Ti_z - O3_z)^1$	-3.607E-03
57	$(Ti_x - O1_x)^2 (Ti_y - O3_y)^1$	-1.068E-03
58	$(Ti_y - O1_y)^4$	1.440E-02
59	$(Ti_x - O1_x)^2 (Ti_y - O1_y)^1 (Ti_y - O3_y)^1$	2.724E-03
60	$(Ti_x - O1_x)^2 (Ti_x - O2_x)^1 (Ti_x - O1_x[010])^1$	1.104E-03

Table A.1: Anharmonic terms of CTO model, the vectors indicate the position of unit cell. If it is not labeled, the position of unit cell is [000]. (Continued)

Table A.2: Anharmonic terms of PZO model, the vectors indicate the position of unit cell. If it is not labeled, the position of unit cell is [000].

Index	Representative SATs	Values
1	$(Pb_y - O1_y)^4$	3.430E-02
2	$(Pb_y - O1_y)^1 (Pb_y - O1_y[0\overline{1}0])^1 (\eta_2)^1$	-4.447E-03
3	$(Pb_y - O1_y)^2 (Pb_z - O1_z)^2$	1.697 E-04
4	$(Pb_x - Zr_x)^1 (Pb_x - Pb_x[010])^1 (\eta_2)^1$	-1.791E-03
5	$(Zr_y - O1_y)^1 (Zr_y - O1_y[100])^1 (\eta_2)^1$	-0.297E-02

Continued on next page

6	$(O1_z - O2_z)^2 (O1_z - O1_z[001])^2$	1.576E-05
7	$(Pb_x - O1_x)^1 (Pb_x - O2_x)^2 (Pb_z - O2_z)^1$	-4.832E-04
8	$(Pb_y - O1_y)^2 (\eta_3)^1$	-4.274E-03
9	$(Zr_y - O1_y)^2 (\eta_1)^1$	3.851E-02
10	$(Pb_y - O1_y)^1 (Pb_z - O1_z)^1 (\eta_4)^1$	-4.481E-03
11	$(Pb_x - O1_x)^1 (Pb_x - O2_x[\bar{1}0\bar{1}])^1 (\eta_1)^1$	-3.847E-03
12	$(Pb_x - O1_x)^1 (Pb_y - Zr_y[\bar{1}0\bar{1}])^1 (Pb_z - Zr_z[\bar{1}0\bar{1}])^1$	2.577 E-03
13	$(Pb_y - O1_y)^2 (O1_z - O2_z)^1 (O1_z - O1_z[010])^1$	1.048E-04
14	$(Pb_y - O1_y)^1 (Pb_z - O1_z)^1 (Pb_z - Zr_z[\bar{1}0\bar{1}])^1$	1.071E-03
15	$(Pb_y - O1_y)^2 (Pb_x - Zr_x)^1 (Pb_z - O2_z[\bar{1}0\bar{1}])^1$	3.445 E-04
16	$(Pb_x - Zr_x)^1 (Pb_x - Zr_x[00-1])^1 (\eta_2)^1$	-3.004E-02
17	$(Pb_x - O1_x)^1 (Pb_x - Zr_x[\bar{1}0\bar{1}])^1 (Pb_y - Zr_y[\bar{1}0\bar{1}])^1$	1.793E-03
18	$(Pb_x - O1_x)^1 (Zr_x - O1_x)^1 (\eta_1)^1$	-6.679E-03
19	$(Pb_y - O1_y)^1 (Pb_z - O1_z[00 - 1])^1 (Pb_z - Pb_z[001])^2$	4.079 E-04
20	$(Pb_x - Pb_x[100])^1 (Pb_x - Pb_x[010])^1 (\eta_2)^1$	-3.921E-03
21	$(Pb_y - O1_y)^2 (O1_x - O2_x)^2$	2.729E-04
22	$(Zr_x - O1_x)^1 (Zr_z - O2_z)^2$	3.736E-03
23	$(Pb_y - O1_y)^1 (Pb_x - O2_x)^1 (Pb_x - O3_x[\bar{1}\bar{1}0])^1$	3.138E-05
24	$(Zr_y - O1_y)^1 (O1_x - O2_x[\bar{1}10])^1 (\eta_6)^1$	1.181E-02
25	$(Pb_y - O1_y)^1 (Pb_y - O1_y[00\bar{1})^1 (Pb_y - O1_y[0\bar{1}0])^1 (Pb_y - O1_y[0\bar{1}\bar{1}])^1$	7.036E-04
26	$(Pb_y - O1_y)^3 (Pb_z - O1_z)^1$	1.811E-03
27	$(O1_x - O2_x)^1 (O1_z - O2_z)^2 (O1_y - O1_y[001])^1$	1.405E-04
28	$(Pb_y - O1_y)^1 (Pb_z - Zr_z)^1 (\eta_4)^1$	-2.068E-03
29	$(Pb_y - O1_y)^2 (Pb_x - Zr_x)^1 (Pb_z - O1_z)^1$	3.479E-04
30	$(Pb_y - O1_y)^2 (Pb_z - Zr_z[\bar{1}\bar{1}\bar{1}])^1 (Pb_z - Pb_z[00\bar{1}])^1$	1.763E-04
31	$(Zr_y - O1_y)^2 (Zr_x - O2_x)^2$	1.329E-03
32	$(O1_z - O2_z)^2 (O1_y - O1_y[010])^1$	2.222E-04
33	$(Pb_y - O1_y)^1 (Pb_z - O1_z[00\bar{1}])^1 (\eta_2)^1$	9.590 E-03
34	$(Pb_y - O1_y)^1 (Pb_y - Zr_y[\bar{1}\bar{1}\bar{1}\bar{1}])^1 (\eta_2)^1$	-8.041E-04
35	$(Pb_x - O1_x)^1 (Pb_x - O2_x)^1 (Pb_y - O1_y[0\bar{1}0])^1 (Pb_x - O2_x[\bar{1}0\bar{1}])^1$	5.209E-05
36	$(Zr_x - O1_x)^1 (Zr_y - O1_y)^1 (Zr_x - O2_x)^1$	-2.705E-03
37	$(Pb_y - O1_y)^1 (Pb_x - O2_x)^1 (Pb_y - Pb_y[010])^1 (\eta_3)^1$	5.398E-03
38	$(Pb_x - Zr_x)^1 (Pb_x - Zr_x[\bar{1}\bar{1}\bar{1}])^1 (\eta_2)^1$	1.932E-02
39	$(Zr_y - O1_y)^2 (O1_x - O1_x[100])^2$	-6.723E-03
40	$(Pb_x - Zr_x)^3$	-8.861E-04
41	$(Pb_y - O1_y)^2 (Pb_z - O2_z)^1 (\eta_4)^1$	-3.024E-03
42	$(Zr_x - O1_x)^1 (O1_x - O2_x)^1 (O1_z - O2_z)^2$	7.976E-04
43	$(Pb_y - O1_y)^2 (Pb_y - Pb_y[010])^2$	9.056E-05
44	$(Zr_x - O1_x)^2 (\eta_1)^1$	-1.337E-01
45	$(Pb_y - O1_y)^2 (Pb_z - O2_z)^1$	7.507 E-05
46	$(Zr_y - O1_y)^2 (Zr_y - O3_y)^2$	9.738E-04
47	$(Zr_y - O1_y)^2 (Zr_x - O2_x)^1 (Zr_x - Zr_x[\bar{1}00])^1$	-2.757E-03
48	$(Pb_x - O1_x)^1 (Pb_y - O1_y)^1 (Pb_x - O2_x)^1 (Pb_x - Zr_x[00\overline{1}])^1$	-3.633E-04

Table A.2: Anharmonic terms of PZO model, the vectors indicate the position of unit cell. If it is not labeled, the position of unit cell is [000]. (Continued)

Continued on next page

49	$(Pb_x - Zr_x)^1 (Pb_x - Zr_x[\overline{1}00])^1 (\eta_1)^1$	1.445E-02
50	$(Pb_y - O1_y)^1 (Pb_x - Zr_x)^1 (Pb_z - O2_z[\bar{1}0\bar{1}])^1$	$7.662 ext{E-} 05$
51	$(Pb_y - O1_y)^4 (Pb_z - O1_z)^2$	5.598E-05
52	$(Pb_x - O1_x)^2 (Pb_x - O2_x[\bar{1}0\bar{1}])^2 (\eta_1)^2$	1.577 E-02
53	$(Pb_x - O1_x)^2 (Pb_x - Zr_x[\bar{1}0\bar{1}])^2 (Pb_y - Zr_y[\bar{1}0\bar{1}])^2$	-4.831E-04
54	$(Pb_x - O1_x)^2 (Pb_x - Zr_x[\bar{1}0\bar{1}])^2 (Pb_y - Zr_y[\bar{1}0\bar{1}])^4$	7.833E-04
55	$(Pb_y - O1_y)^2 (Pb_x - O2_x)^2 (Pb_y - Pb_y[010])^2$	-3.415 E - 05
56	$(Pb_y - O1_y)^2 (Pb_z - O2_z[\bar{1}0\bar{1}])^2 (Pb_y - Pb_y[001])^2$	-1.789E-05

Table A.2: Anharmonic terms of PZO model, the vectors indicate the position of unit cell. If it is not labeled, the position of unit cell is [000]. (Continued)



Figure A.1: Energy gains of (meta) stable phases on the establishing PZO SP model. The ground state is inaccurately at R3c phase, but the energy gains are close to the first-principles calculations (green crosses).