

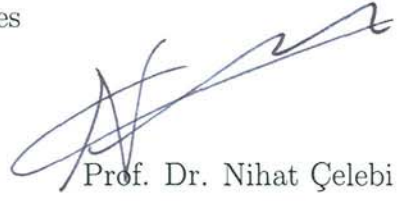
AB INITIO PRESSURE-DEPENDENT LATTICE DYNAMICS AND
ELASTIC PROPERTIES OF CHALCOPYRITE SEMICONDUCTOR
 CuAlSe_2 AND OXIDES, HYDRIDES AND BORIDES OF RARE-EARTHS

by
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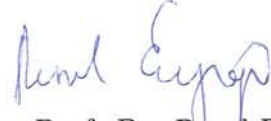
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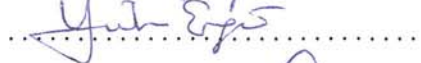
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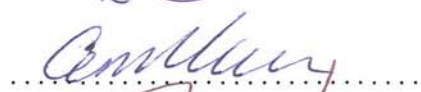
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ABSTRACT

AB INITIO PRESSURE-DEPENDENT LATTICE DYNAMICS AND
ELASTIC PROPERTIES OF CHALCOPYRITE SEMICONDUCTOR
CuAlSe₂ AND OXIDES, HYDRIDES AND BORIDES OF RARE-EARTHS

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Theoretical investigation of the physical properties of materials from first-principles (*ab initio*), today, is a very popular and powerful method in condensed matter physics and also in many other disciplines. First-principles here means that there is no experimental value used in the calculations as an input parameter. In this thesis we have performed an *ab initio* study of pressure-dependent structural, elastic and lattice dynamical properties of chalcopyrite semiconductor CuAlSe₂ and oxides, hydrides and borides of rare-earths. The calculations have been carried out by using the density-functional and density-functional perturbation theory within the local density approximation using norm conserving and optimized pseudopotentials and a plane-wave basis. Structural properties such as equilibrium lattice constants, bulk modulus, elastic constants, compressibilities and their pressure dependencies are calculated from the ground-state density functional theory. Born effective charge tensors, dielectric permittivity tensors, the phonon dispersion curves and their mode Grüneisen parameters and phonon

density of states are calculated using density functional perturbation theory. In addition to these properties the temperature dependent lattice constant, bulk modulus, volume expansion, entropy and specific heat of LaB_6 and CeB_6 are investigated by performing the quasiharmonic approximation for the free energy. The calculated results agree well with the experiments. In the case of CuAlSe_2 , we compare the mode Grüneisen parameters of the calculated quantities with those of zinc-blende type materials and find similar trends. The calculated elastic stiffness constants of CuAlSe_2 show pseudocubic behaviour. We have also found that treating the 4f electrons of cerium as valence states is crucial for a satisfactory description of the lattice dynamical properties of CeO_2 . In the study of cerium hydrides, it has been observed that while the mode Grüneisen parameters for acoustic modes of CeH_2 are calculated mostly negative throughout the Brillouin zone, they are found positive in the case of CeH_3 . Thermodynamical properties of LaB_6 and CeB_6 obtained from quasi-harmonic approximation are in a good agreement with the available experimental data.

Keywords: density functional perturbation theory, lattice dynamics, dielectric-properties, thermodynamics, pressure-dependence, rare-earth compounds, chalcopyrite semiconductors

ÖZET

KALKOPİRİT YARIİLETKEN CuAlSe_2 'NİN VE NADİR-TOPRAK OKSİT, HİDRİT VE BORATLARININ BASINÇ-BAĞIMLI ÖRGÜ DİNAMİKSEL VE ELASTİK ÖZELLİKLERİNİN AB INITIO YÖNTEMLERLE İNCELENMESİ

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Materyallerin fiziksel özelliklerinin temel-prensiplerden (*ab initio*) kuramsal olarak incelenmesi günümüzde hem yoğun madde fiziğinde hem de diğer birçok bilim dallarında çok yaygın ve etkili olarak kullanılan bir yöntemdir. Buradaki "temel-prensip" ifadesi hesaplamalarda hiçbir deneysel verinin girdi parametresi olarak kullanılmadığını belirtmektedir. Bu tezde kalkopirit yarı-iletken CuAlSe_2 'nin ve nadir-toprak oksit, hidrit ve boratların basınç-bağımlı yapısal, elastik ve örgü dinamiksel özellikleri *ab initio* yöntemler kullanılarak incelendi. Hesaplamalar yerel yoğunluk yaklaşımı ile yoğunluk-fonksiyoneli ve yoğunluk fonksiyoneli tedirginme kuramları çerçevesinde optimize ve norm-korunumlu sanal-potansiyeller ile düzlem-dalga tabanı kullanılarak hesaplandı. Denge örgü sabiti, hacim modülü, elastik sabitleri gibi yapısal özellikler taban-durum yoğunluk-fonksiyoneli kuramı ile elde edildi. Born etkin yük tensörleri, dielektrik geçirgenlik tensörü, fonon dağılım eğrileri ve bunların mod Grüneisen parametreleri ve fonon durum yoğunlukları ise yoğunluk fonksiyoneli tedirginme kuramı ile hesaplandı. Bunlara

ek olarak LaB_6 ve CeB_6 bileşiklerinin sıcaklığa bağlı örgü sabiti, hacim modülü, hacim genişmesi, entropi ve özgül ısı değerlerini elde etmek için serbest enerji için olan yarı-harmonik yaklaşımı kullanıldı. Hesaplanan sonuçların deneylerle iyi bir uyum içinde olduğu gözlemlendi. CuAlSe_2 için bakıldığında, hesaplanmış olan niceliklerin mod Grüneisen parametreleri çinko-blende tipi materyaller ile karşılaştırıldı ve benzer eğilimler bulundu. Aynı bileşiğin hesaplanmış elastik sertlik sabitlerinin sanal-kubik davranış içinde olduğu gözlemlendi. CeO_2 bileşiğinin örgü dinamiksel özelliklerinin açıklanmasında seryum atomunun 4f elektronlarının değerlik durumunda bulunmasındaki önemi vurgulandı. Seryum hidritler ile ilgili olan çalışmada akustik modların Brillouin bölgesi boyunca olan Grüneisen parametrelerinin CeH_2 için çoğunlukla negatif bulunurken bu değerler CeH_3 için pozitif olduğu gözlemlendi. LaB_6 ve CeB_6 bileşiklerinin yarı-harmonik yaklaşım ile elde edilen termodinamiksel özelliklerin mevcut bulunan deneysel veriler ile iyi bir uyum içinde olduğu gözlemlendi.

Anahtar Kelimeler: yoğunluk fonksiyoneli tedirginme kuramı, örgü dinamiği, dielektrik özellikler, termodinamik, basınç bağımlılığı, nadir-toprak bileşikleri, kalkopirit yarıiletkenler

Babama

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CHAPTER 1

INTRODUCTION

The rapid development of the technology in the last century thanks to the deep research activities on matter. New techniques such as molecular beam epitaxy (MBE) have been developed for device fabrication to be able to produce wide variety of devices that perform various and complicated tasks. The demand of smaller, faster and efficient devices require a well knowledge of the basic properties of the materials. Experimental research is an essential tool to obtain the fundamental properties of materials and their behavior under different situations. In the last few decades measurement techniques have also been improved such as development of lasers, more sensitive detectors and charged couple devices (CCD). However, explanation of most behaviors and responses of the solids under different situations would be incomplete without a theoretical investigation. It should be also mentioned that construction of the artificial structures needs a very strong theoretical support before and during the experimental processes. In parallel to the development of the new devices and the increasing measurement techniques, powerful theoretical methods have also been developed in order to explain various physical properties.

Theoretical investigation of the matter at microscopic level orients someone to the world of ions and electrons. Physical properties of the solids can be predicted by solving an appropriate Schrödinger equation in the framework of quantum mechanics. Since the number of the interacting particles in a solid is huge ($\simeq 10^{23}$), the exact solution is impossible. Fortunately, the dramatic increase of the computing power, recently developed efficient algorithms and useful approximations allow one to study many properties of real materials.

This thesis is a contribution to study some physical properties of several mate-

materials theoretically by using density-functional and density-functional perturbation theory (DFT, DFPT) within local-density approximation (LDA) which are, today, very popular and powerful methods in condensed matter physics and also in many other disciplines. These methods are being numerously applied to many different structures successfully such as atoms, molecules, crystals and surfaces. Main goal of the DFT is to perform calculations from first-principles which means that there is no experimental value used in the calculations as an input parameter. This makes the comparison of the theoretical results with experimental ones much more efficient and meaningful.

Basically DFT provides a theoretical framework to calculate the ground-state total energy and the charge density of a system. This method has been developed in mid 1960s by Hohenberg and Kohn [1] and Kohn and Sham [2]. In Ref. [1] it has been shown that the ground state total energy of a system of electrons in an external potential (such as atomic nuclei) can be defined as an universal functional of electron density $n(r)$. Then Kohn and Sham [2] showed that it is possible to replace the many electron problem by an exactly equivalent set of self consistent one-electron equations. These equations are called Kohn-Sham equations and can be solved in a reasonable computer time by the help of some methods (using suitable basis sets and self-consistency cycle methods) and some approximations that describes the electron-electron and ion-electron interactions. LDA approximates the non-classical electron-electron interactions and it is successful for most cases. Pseudopotential approximation[3] describes the ion-electron interactions in a different manner to reduce the computing time.

Since the total ground state energy of a solid is determined, many physical properties of solids can be obtained. For example by calculating the total energies at different values of the volume, one can get the theoretical equilibrium lattice constant at the lowest value of the total energy. The bulk modulus B_0 and its pressure derivative B'_0 can be obtained by fitting the data to an equation of state.

It is also possible to get the electronic band structure from the Kohn-Sham

scheme (mainly called Kohn-Sham band structure). Electronic band structure is an important property for solids, especially for semiconductors. The energy difference between the lowest unoccupied (conduction) band and the highest occupied (valence) band is called as band-gap and it is mostly underestimated in the DFT-LDA picture. There is a successful *GW* approximation which allows us to calculate the self-energy correction to the LDA energies and this approximation gives nice results to many systems.[4]

There exists many other physical properties that are related not only to ground-state total energy of the system but also to its first- and second-derivatives with respect to small perturbations. For instance the minus first derivative of the total energy with respect to a nuclei displacement gives the force exerted on the corresponding nuclei. If we investigate the minus first-derivative of the total energy with respect to a homogeneous electric field in this case we get the dipole moment of a molecule. The knowledge of the second derivatives of the total energy with respect to various perturbations such as atomic displacements, electric fields or strain perturbations (or mixture of them) allows us to calculate phonon dispersion relations, Born effective charges, dielectric permittivity tensors and elastic constants.

There are mainly two types of methods for calculating the second-derivatives of the energy. There is a direct approach called frozen-phonon method allows us to calculate interatomic force constants by considering a small finite perturbation frozen in the system. The second type approach is a perturbative approach called density functional perturbation theory which is a nice and powerful theoretical technique to calculate physical properties related to second-derivatives. This theory allows us to calculate the response of periodic systems to electric field perturbations which is not possible in the frozen-phonon method. Moreover, one of the main advantage of DFPT is to calculate phonon responses at arbitrary wave-vector which frozen-phonon method needs very large computational effort because of the usage of supercells.

Although there exists numerous sources in the literature (for example Ref. [5]), for the completeness of the thesis, basic definitions of the DFT and its implementations to a periodic crystal are briefly given in Chapter 2. In order to get the second-derivative of the total energy with respect to some perturbation, main aspects of density functional perturbation theory are given in Chapter 3.

It is also possible to investigate the behavior of structural, elastic and lattice dynamical properties of materials under hydrostatic pressure. Pressure dependence of lattice dynamical properties, such as effective charges, phonon frequencies, and low frequency dielectric constants provide crucial information about the structure of the material. The investigation of the pressure dependent phonon frequencies delineate the symmetry assignments of the zone center modes as well as to give an understanding of the structural phase transitions at elevated pressures.

Chapter 4 is entirely devoted for pressure dependent structural, elastic and lattice dynamical properties of ternary chalcopyrite semiconductor CuAlSe_2 . The ternary I-III-VI₂ chalcopyrites form a large group of semiconductors with diverse structural, electrical, and optical properties. Cu-based ternary chalcopyrite semiconductors have been a subject of investigation for possible solar energy and nonlinear optical applications. For example, CuInSe_2 and CuInS_2 are considered as one of the most promising materials for the solar applications, partly because of their strong absorption under sunlight. Solar conversion efficiencies of 19% and 12% have been achieved with CuInSe_2 and CuInS_2 , respectively. One way of improving the efficiency of these solar-cells is the use of tandem structures. CuGaSe_2 - CuInSe_2 structure with high band gap (E_g) CuGaSe_2 ($E_g=1.68$ eV) on top of low gap CuInSe_2 ($E_g=1.0$ eV) would form an ideal couple for tandem photovoltaic applications. The CuInS_2 system is also of technical interest owing to its perfect lattice matching with Si. One of this class of materials, CuAlS_2 , is the widest band gap semiconductor ($E_g=3.49$ eV at 300 K) and is an important candidate for blue-to-ultraviolet light emitting device applications.

Among these compounds, CuAlSe_2 , with a bandgap of 2.67 eV, is promising

as an emitting layer of blue light photoluminescent devices as well as a window in heterostructure photovoltaic devices. Structural, electronic, and lattice dynamical properties of these chalcopyrite materials have been widely studied for the last three decades by a number of experimental and theoretical methods. However, there are still inconsistencies among the reported experimental results especially concerning the lattice dynamical properties. The aim of the work in Chapter 4 is to use a first principles linear response approach to study the lattice dynamical properties, such as Brillouin zone center phonon frequencies, Born effective charge and dielectric permittivity tensors and elastic compliance tensor of chalcopyrite CuAlSe_2 under hydrostatic pressure.

The other compounds studied in this thesis are the rare-earth compounds namely CeO_2 , CeH_2 , CeH_3 , CeB_6 and LaB_6 . Most of cerium compounds have numerous applications in technology and show different properties. For instance CeO_2 is a large band-gap insulator while CeH_2 and CeB_6 are metals. Interestingly, CeH_3 is reported in the literature as a semi-metal or semi-conductor. Since there exists a 4f electron in the cerium element, it is difficult to calculate physical properties from first principles because 4f electrons require expensive computing time. So generating useful and "less energy-cutoff required" cerium pseudopotentials is an essential tool to study those cerium compounds. In this thesis we have used several types of pseudopotentials exist in the literature. We have also generated new efficient pseudopotentials for cerium, lanthanum, boron and hydrogen elements to decrease the computing time in the calculations.

The rest of the thesis is organized as follows. In Chapter 5 we have calculated structural, elastic, dielectric and lattice dynamical properties of CeO_2 and obtained very good agreement with the available experimental data. Chapter 6 is the investigation of the cerium hydrides for their structural, elastic and lattice dynamical properties including phonon density of states. Chapter 7 is a nice example for the usage of the full spectrum of phonon dispersions. In this chapter we have calculated the thermodynamical properties of LaB_6 and CeB_6 such as vi-

brational free energy and entropy, temperature dependence of bulk modulus and its pressure derivative, constant volume and constant pressure specific heat and thermal volume expansion in quasiharmonic approximation. Chapter 8 concludes the thesis with a summary of the results.

CHAPTER 2

DENSITY FUNCTIONAL THEORY

2.1 Overview

Theoretical determination of many physical properties of a system from the standpoint of quantum mechanics is the study of solving an appropriate Schrödinger equation. For example, a crystal is a system of nuclei and electrons which are interacts via Coulomb forces. Solving such a system of N-body problem is impossible due to the large number of degrees of freedom. So, to obtain the physical properties of a system in the quantum mechanics scheme, one must attempt many approximations and simplifications. There are some number of *ab initio* methods to calculate physical properties of materials with only the knowledge of the ion specification by their atomic number. Among them, density functional theory (DFT) is one of the most popular, widely studied and applied method in the last three decades which has a powerful ability to predict the total energy of a system of electrons. The knowledge the total energy and its derivatives of a crystal allows us to calculate some physical properties.

In practice, to calculate the ground-state total energy of a system in the framework of DFT requires some approximations (local density approximation), representations (pseudopotentials, plane-waves) and direct minimization techniques (conjugate gradient algorithm). This chapter aims to review them briefly.

This chapter is organized as follows: In the next section a brief review of the main aspects of density functional theory is given. Section 2.3 is aimed to describe the many-body effects of electrons(exchange and correlation) within local density approximation. Section 2.4 is devoted to plane-wave representation and in section 2.5, we describe the pseudopotential theory which models the ion-electron interactions.

2.2 Density functional theory

Consider a real quantum mechanical system of electrons and nuclei interacting through Coulombic forces. Despite the large difference in mass between electrons and nuclei, these forces are in the same order of magnitude due to their electric charges. In this case, electrons move very fast according to the nuclei. In other words, under the motion of nuclei, electrons move instantaneously to relax to their ground-state configuration. This instantaneous motion of electrons with respect to nuclei is called as "adiabatic motion". So, from these points of view one can assume that the nuclei is stationary and the problem of the many-body system reduces to the dynamics of the electrons under a fixed nuclear configuration. The separation of the motion of the nuclei and electrons are called as "Born-Oppenheimer approximation" or "adiabatic approximation".[6]

Let us consider a system of N interacting electrons under the influence of external ionic potential in the framework of Born-Oppenheimer approximation (so the nuclei is in a fixed configuration). Then the eigenvalue equation of the many-body system is written as:

$$\hat{H}\Psi(\mathbf{r}_1, \dots, \mathbf{r}_N) = E\Psi(\mathbf{r}_1, \dots, \mathbf{r}_N) \quad (2.1)$$

where $\hat{H}$ is the Hamiltonian:

$$\hat{H} = -\sum_{i=1}^N \frac{\hbar^2}{2m} \nabla_i^2 + \sum_{i=1}^N V_{ext}(\mathbf{r}_i) + \frac{e^2}{2} \sum_{i \neq j} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}. \quad (2.2)$$

Here $\mathbf{r}_i$ is the position of the i th electron and V_{ext} is the external potential acts on the electrons caused by nuclei. In practice, the solution of Eq. 2.1 for many-electron systems is not possible due to the very large numbers of degrees of freedom.

In 1964, Hohenberg and Kohn [1] presented an approach that the total energy of an interacting system can be expressed as a functional of the charge density. The minimum value of the total energy functional is then the ground state energy

of the system with corresponding ground state charge density. The total energy of a system under fixed nuclear configuration can be written as:

$$E_{crystal} = E_{el}[n(\mathbf{r})] + E_{ion}. \quad (2.3)$$

Here E_{ion} is the Coulombic potential energy associated with interactions among ions and expressed as:

$$E_{ion} = \frac{e^2}{2} \sum_{\alpha, \beta} \frac{Z_{\alpha} Z_{\beta}}{|\mathbf{R}_{\alpha} - \mathbf{R}_{\beta}|} \quad (2.4)$$

where summation is over all atoms with positions $\mathbf{R}$ and Z s are the atomic number of corresponding atoms. Since the Coulomb interaction is very long ranged, the sum in Eq. 2.4 converges very slowly. This problem can be handled by the technique called Ewald summation. [7] The remaining term $E_{el}[n(\mathbf{r})]$ in Eq. 2.3 is the total energy of electronic part with energy functionals:

$$E_{el}[n(\mathbf{r})] = F[n(\mathbf{r})] + V[n(\mathbf{r})] \quad (2.5)$$

with

$$F[n(\mathbf{r})] = T[n(\mathbf{r})] + U[n(\mathbf{r})] \quad (2.6)$$

where $T[n(\mathbf{r})]$ is the kinetic energy functional and $U[n(\mathbf{r})]$ is the energy functional of electron-electron interactions of the interacting system. $V[n(\mathbf{r})]$ is the interaction energy of the electronic system defined as

$$V[n(\mathbf{r})] = \int d\mathbf{r} n(\mathbf{r}) V_{ext}(\mathbf{r}) \quad (2.7)$$

where $V_{ext}(\mathbf{r})$ is the external potential that describes the effect of ions and in some cases external sources such as electric field.

$F[n(\mathbf{r})]$ is called *universal functional* because it is independent from external potential $V_{ext}(\mathbf{r})$ and also from the system under study. But $V[n(\mathbf{r})]$ is dependent on $V_{ext}(\mathbf{r})$ so it is non-universal. If one knows the system configuration it is not

so difficult to calculate $V[n(\mathbf{r})]$.

The exact form of the functionals $T[n(\mathbf{r})]$ and $U[n(\mathbf{r})]$ are unknown because of the many-body effects of the interacting electron system. These functionals include energy of non-classical electron-electron interactions and true kinetic energy of the interacting electron gas which can not be determined exactly.

In 1965, Kohn and Sham [2] has introduced a method to avoid the complexity of the universal energy functionals $T[n(\mathbf{r})]$ and $U[n(\mathbf{r})]$. They redefined the total electronic energy of Eq. 2.5 as:

$$E_{el}[n(\mathbf{r})] = T_0[n(\mathbf{r})] + U_H[n(\mathbf{r})] + E_{xc}[n(\mathbf{r})] + V[n(\mathbf{r})] \quad (2.8)$$

where the new functionals $T_0[n(\mathbf{r})]$ is the non-interacting part of kinetic energy functional, $U_H[n(\mathbf{r})]$ is the classical part electrostatic energy named as Hartree energy of electron-electron interactions and given by:

$$U_H = \frac{e^2}{2} \int \int d\mathbf{r} d\mathbf{r}' \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}. \quad (2.9)$$

$E_{xc}[n(\mathbf{r})]$ is called as exchange-correlation energy which contains the non-classical part of the electron-electron interactions and the difference between the kinetic energies of interacting and non-interacting electron gas. By definition one can state that $E_{xc}[n(\mathbf{r})]$ contains the differences ($E_{xc}[n(\mathbf{r})] = T[n(\mathbf{r})] - T_0[n(\mathbf{r})] + U[n(\mathbf{r})] - U_H[n(\mathbf{r})]$). The exact form of the exchange-correlation energy $E_{xc}[n(\mathbf{r})]$ is unknown but there are several approximations to predict this energy which give surprisingly good results. One of them called local density approximation(LDA) is discussed in the next section.

From this point, Kohn and Sham [2] introduced a simple method that replaces the many-body interacting problem into an auxiliary system of non-interacting electrons subject to an effective potential. Consider a system of non-interacting electrons under an effective potential called V_{eff} . Then the Schrödinger equation

of this one-electron system can be written as

$$\left(-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial \mathbf{r}^2} + V_{eff}(\mathbf{r})\right)\psi_i(\mathbf{r}) = \epsilon_i\psi_i(\mathbf{r}) \quad (2.10)$$

with single-particle states $|\psi_i\rangle$ with the constraints $\langle\psi_i|\psi_j\rangle = \delta_{ij}$ and energy eigenvalues ϵ_i . Index i reads to $N/2$ for the spin-degeneracy.

Here $V_{eff}(\mathbf{r})$ is given as

$$V_{eff}(\mathbf{r}) = V_H(\mathbf{r}) + V_{ext}(\mathbf{r}) + v_{xc}(\mathbf{r}) \quad (2.11)$$

with $V_H(\mathbf{r})$ is the Hartree potential

$$V_H(\mathbf{r}) = \int d\mathbf{r}' \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \quad (2.12)$$

and $v_{xc}(\mathbf{r})$ is the functional derivative of the exchange-correlation energy with respect to the electronic charge density

$$v_{xc}(\mathbf{r}) = \frac{\delta E_{xc}[n(\mathbf{r})]}{\delta n(\mathbf{r})}. \quad (2.13)$$

Equation 2.10 is called as Kohn-Sham Equations. Although these equations are a set of single-particle problem they still include many-body effects introducing the exchange-correlational functional.

All the terms in V_{eff} in Eq. 2.11 depend upon the charge density $n(\mathbf{r})$ and it is necessary to solve the Kohn-Sham equations of Eq. 2.10 self-consistently. One make a guest for the form of the density and solve the Kohn-Sham equations to obtain the set of states $\psi_i(\mathbf{r})$. Then the density constructs from these states with the equation:

$$n(\mathbf{r}) = 2 \sum_{i=1}^{N/2} |\psi_i(\mathbf{r})|. \quad (2.14)$$

This procedure is repeated until the input and output densities become same. Having obtained the one-electron states $\psi_i(\mathbf{r})$ one can calculate the non-interacting

kinetic energy $T_0[n(\mathbf{r})]$ with relation:

$$T_0[n(\mathbf{r})] = -2 \sum_{i=1}^{N/2} \int d\mathbf{r} \psi_i^*(\mathbf{r}) \left(\frac{\hbar^2}{2m} \frac{\partial^2}{\partial \mathbf{r}^2} \right) \psi_i(\mathbf{r}). \quad (2.15)$$

The total energy of the non-interacting system is the total of Kohn-Sham eigenvalues

$$\begin{aligned} 2 \sum_{i=1}^{N/2} \epsilon_i &= T_0[n(\mathbf{r})] + \int d\mathbf{r} n(\mathbf{r}) V_{eff}(\mathbf{r}) \\ &= T_0[n(\mathbf{r})] + e^2 \int \int d\mathbf{r} d\mathbf{r}' \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + \int d\mathbf{r} n(\mathbf{r}) v_{xc}(\mathbf{r}) + \int d\mathbf{r} n(\mathbf{r}) V_{ext}(\mathbf{r}) \end{aligned} \quad (2.16)$$

and

$$T_0[n(\mathbf{r})] = 2 \sum_{i=1}^{N/2} \epsilon_i - e^2 \int \int d\mathbf{r} d\mathbf{r}' \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} - \int d\mathbf{r} n(\mathbf{r}) v_{xc}(\mathbf{r}) - \int d\mathbf{r} n(\mathbf{r}) V_{ext}(\mathbf{r}). \quad (2.17)$$

Inserting Eq. 2.17 to Eq. 2.8 gives

$$E_{el}[n(\mathbf{r})] = 2 \sum_{i=1}^{N/2} \epsilon_i - \frac{e^2}{2} \int \int d\mathbf{r} d\mathbf{r}' \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + E_{xc}[n(\mathbf{r})] - \int d\mathbf{r} n(\mathbf{r}) v_{xc}(\mathbf{r}). \quad (2.18)$$

As can be seen from Eqns. 2.16 to 2.18, Kohn-Sham eigenvalues do not represent the real system as defined auxiliary. The negative terms in Eq. 2.18 involves sum of single-particle energies and known as double-counting corrections. The ground-state total energy and ground-state charge density are the only physical observables of DFT.

2.3 Local-density approximation

Before making attempts to solve the problem of single-particle Kohn-Sham equations (Eq. 2.10), an explicit expression of the exchange-correlation energy is required. This is the major problem of the DFT because it is the only component in the theory that the exact definition is unknown. But exchange-correlation en-

ergy part of the total energy is relatively small and can be approximated. Kohn and Sham [2] has proposed an assumption for the exchange-correlation energy $E_{xc}[n(\mathbf{r})]$ to provide an accurate and practically applicable approximation. They assumed that the exchange-correlation energy of each small volume of an homogeneous electron gas is equal to the same exchange-correlation energy of an inhomogeneous electron gas that both homogeneous and inhomogeneous gases at that small volume has same charge density. This approximation is known as *local-density approximation* (LDA).

So with this assumption the exchange-correlation correlation energy functional can be written as:

$$E_{xc}[n(\mathbf{r})] = \int d\mathbf{r} \, \varepsilon_{xc}(\mathbf{r})n(\mathbf{r}) \quad (2.19)$$

where $\varepsilon_{xc}(\mathbf{r})$ is equal to the exchange-correlation energy per electron in a homogeneous electron gas that has the same charge density $n(\mathbf{r})$ at point $\mathbf{r}$. Then the exchange-correlation potential $v_{xc}(\mathbf{r})$ can be obtained by

$$v_{xc}(\mathbf{r}) = \frac{\delta E_{xc}[n(\mathbf{r})]}{\delta n(\mathbf{r})} = \frac{\partial [n(\mathbf{r})\varepsilon_{xc}(\mathbf{r})]}{\partial n(\mathbf{r})} \quad (2.20)$$

with

$$\varepsilon_{xc}(\mathbf{r}) = \varepsilon_{xc}^{\text{hom}}[n(\mathbf{r})]. \quad (2.21)$$

The LDA is exact for a uniform electron gas and is expected to be valid for slowly varying charge density distributions. Since the definition of the local-density approximation is very simple and approximated inexactly, results of calculations give much good results than expected.

To obtain a good form for $\varepsilon_{xc}(\mathbf{r})$ Ceperley and Alder [8] has performed nearly exact Quantum Monte Carlo calculations for the homogeneous electron gas. This numerical results have been parameterized by several studies [9–11] which yield similar results.

There have been several attempts to improve the LDA functionals like using gradient expansions [12] but they did not show much improvements for infinite

systems.

2.4 Plane-waves

The many-body problem has been mapped into an effective single-particle problem by introducing Kohn-Sham equations (Eq. 2.10) as mentioned in the previous section. These equations can be solved in a periodic solid by expanding the wave-functions in a complete set of known functions. However solving these equations is still a formidable task because of infinite number of electrons moving in the static field of infinite number of ions. Each infinite number of the electronic wave-functions must be calculated and the basis set of the functions is also infinite because each wave-function extends over the entire solid.

In a perfect crystal, ions are arranged periodically so that the effective potential (V_{eff}) felt by electrons will also be periodic. This periodicity will be same as the length ($\mathbf{R}_\mu$) of the unit cell of the crystal. So,

$$V_{eff}(\mathbf{r}) = V_{eff}(\mathbf{r} + \mathbf{R}_\mu). \quad (2.22)$$

Electrons that move in a periodic potential are known as *Bloch electrons* and this periodic potential allows us to use the *Bloch's theorem* [13]. By the use of this theorem, it will be possible to reduce the infinite number of one-electron wave-functions to a finite number of electrons which stand in the unit cell of the crystal (or half of that number with considering the spin degeneracy). According to Bloch's theorem, the wave-function in a periodic potential can be written as the product of a wavelike part and a cell periodic part

$$\psi_{i\mathbf{k}}(\mathbf{r}) = \exp[i\mathbf{k}\cdot\mathbf{r}]u_i(\mathbf{r}) \quad (2.23)$$

where $\mathbf{k}$ is a vector inside the first Brillouin zone of the reciprocal lattice and

$u_i(\mathbf{r})$ is a periodic function with the periodicity of the direct lattice:

$$u_i(\mathbf{r} + \mathbf{R}_\mu) = u_i(\mathbf{r}). \quad (2.24)$$

The cell periodic part of the wave function can be expressed by expanding it in terms of a discrete plane-wave basis set:

$$u_i(\mathbf{r}) = \sum_{\mathbf{G}} c_{i,\mathbf{G}} \exp[i\mathbf{G} \cdot \mathbf{r}] \quad (2.25)$$

where $\mathbf{G}$ is the reciprocal lattice vector and the $c_{i,\mathbf{G}}$ are plane-wave expansion coefficients. Then inserting Eq. 2.25 into Eq. 2.23 gives the electronic wave-function in terms of linear combination of the plane-waves

$$\psi_{i\mathbf{k}}(\mathbf{r}) = \sum_{\mathbf{G}} c_{i,\mathbf{k}+\mathbf{G}} \exp[i(\mathbf{k} + \mathbf{G}) \cdot \mathbf{r}]. \quad (2.26)$$

Plane-wave representation is one of the most widely used implementation in density functional theory because of its conceptual simplicity and computational efficiency. Due to the lattice periodicity plane-waves are natural basis and unbiased by atomic positions so it has same accuracy for different crystal structures. Furthermore, the accuracy of the expansion can be systematically checked and improved simply by increasing the size of plane-wave basis set.

By the use of Bloch's theorem, instead of calculating an infinite number of electronic wave-functions, now the problem changes to calculate a finite number of electronic wave-functions at an infinite number of $\mathbf{k}$ points. At each $\mathbf{k}$ point, only a finite number of the available energy levels will be occupied. Although there are infinite number of $\mathbf{k}$ points, one does not need to consider all of them. The wave-functions at $\mathbf{k}$ points that are very close together will be almost identical. So, one can represent the wave-functions over a region of reciprocal space by considering the wave-function at a single $\mathbf{k}$ point. There are very accurate methods [14–16] that appropriately sample the Brillouin zone at special sets of $\mathbf{k}$ points. One of

them, the method of Monkhorst and Pack [16] is used in this thesis. Amount of $\mathbf{k}$ points is important for the error in total energy of the system and a convergence test should be done by increasing the number of $\mathbf{k}$ points.

In principle, the series in Eq. 2.26 should be infinitive but in practice the series should be truncated to handle it computationally. The coefficients $(c_{i,\mathbf{k}+\mathbf{G}})$ each has kinetic energy $\frac{\hbar^2}{2m} |\mathbf{k} + \mathbf{G}|^2$, and plane-waves that have low kinetic energy is more important than those have high kinetic energy. Choosing an appropriate energy cut-off reduces the basis set to a finite size. It should be noted that by increasing the cutoff energy the magnitude of the error decreases and cutoff energy should be increased until the calculated total energy has converged.

Finally, substituting Eq. 2.26 into Eq. 2.10 gives,

$$\sum_{\mathbf{G}'} \left[\frac{\hbar^2}{2m} |\mathbf{k} + \mathbf{G}|^2 \delta_{\mathbf{G}\mathbf{G}'} + V_H(\mathbf{G} - \mathbf{G}') + V_{ext}(\mathbf{G} - \mathbf{G}') + V_{xc}(\mathbf{G} - \mathbf{G}') \right] \times c_{i,\mathbf{k}+\mathbf{G}'} = \varepsilon_i c_{i,\mathbf{k}+\mathbf{G}} \quad (2.27)$$

where the potentials are described in terms of their Fourier components and reciprocal space representation of kinetic energy is diagonal. Kohn-Sham equations are now taken on the particularly simple and appealing form. Eq. 2.27 is a secular equation now and a Hamiltonian matrix $(H_{\mathbf{k}+\mathbf{G},\mathbf{k}+\mathbf{G}'})$ whose matrix elements are given in brackets above could be solved by usual diagonalisation methods. The size of the matrix is determined by the energy cutoff. There has been different attempts to develop computationally efficient iterative algorithms to handle large matrices. Among them, in this thesis, we have used a method in our calculations that directly minimizes the Kohn-Sham total energy functional with a conjugate gradient algorithm. The details of this approach can be found in Ref. [5].

2.5 Pseudopotential Theory

Although it has been introduced an energy cutoff to reduce the number of plane-waves from infinite size to a finite size, the number of plane-waves required for the

calculations are still enormous because the wave-functions of the orbitals oscillate rapidly near the nuclei region. An all-electron calculation would be computationally very expensive because it includes both core and valence electrons. Pseudopotential approximation [3],[5] allows us to reduce the number of the plane-waves to a reasonable amount while expanding the electronic wave-functions.

It is well known that in most molecular and solid state systems, it is possible to separate atomic states into *valence* and *core* states. Valence states are responsible for most of physical properties and chemical bonding in molecules and solids. In contrast, core states are tightly bounded, frozen in their atomic configuration, chemically inert and independent from environment. Therefore, the pseudopotential approximation is introduced that maps the all-electron frozen core problem onto an equivalent problem involving valence electrons only. In the pseudopotential approximation core electrons and strong ionic potential are removed and replaced by an effective pseudopotential which is much weaker and replaces the valence wave-functions which oscillate rapidly in the core region by pseudo-wave-functions which vary smoothly in the core region. Schematic illustration of the all-electron and pseudo-electron potentials and their corresponding wave functions have been given in Fig. 2.1. As can be seen from figure the all-electron wave-functions oscillate rapidly near the core region because that region is occupied by core electrons and wave-functions of the valence electrons must oscillate rapidly to provide orthogonality. A pseudopotential is constructed such a way that pseudo wave-functions has no radial nodes in the core region and pseudo wave-functions and pseudopotentials agree with true wave-functions and potential outside some cut-off radius, r_{cut} . Pseudopotentials whose pseudo wave-functions coincide with all-electron wave-functions outside a cut-off radius r_{cut} are called *norm-conserving pseudopotentials*.

The pseudopotentials are designed in such a way that it must preserve the atomic properties of the elements. Therefore there are some common requirements that pseudopotentials must satisfy.

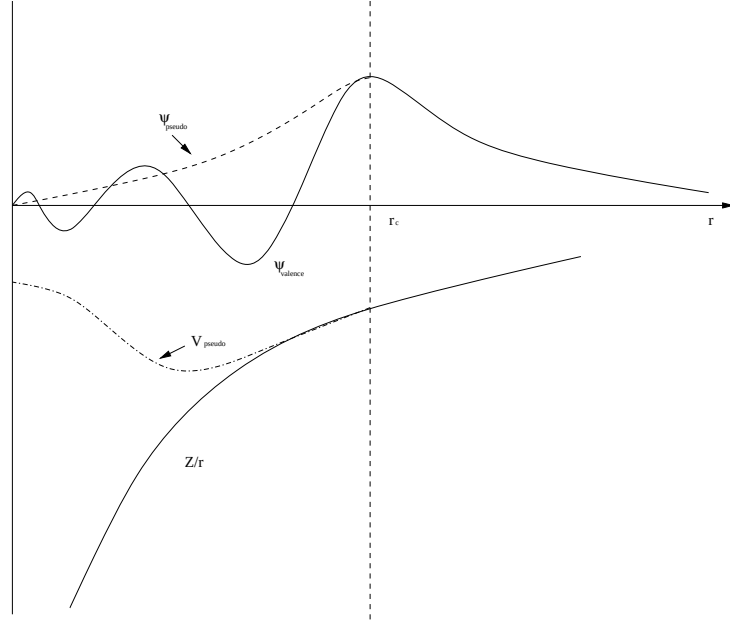


Figure 2.1: Schematic illustration of a pseudopotential.

- A core radius must be defined that the pseudo wave-function matches the all-electron wave-function beyond this radius. (the norm-conserving condition)
- Scattering properties or phase shifts for pseudo wave-functions must be identical with all-electron wave-functions and this means that pseudopotentials must be different for each angular momentum. Pseudopotentials with angular momentum dependence are called non-local pseudopotentials.
- The valence all-electron and pseudopotential eigenvalues must be equal.
- The core charge produced by both pseudo wave-functions and the all-electron wave-functions must be the same.
- In the core region the pseudo wave-function must be nodeless and pseudopotentials must be as smooth as possible.
- The first and second derivatives of pseudo wave-functions must be continuous and non-oscillatory.

An ionic pseudopotential consists sum of two terms: Coulomb attractive term and

a short-range term. The first term is the local term and given by atomic valence. The nonlocal second term must be able to represent the effect of core electrons on valence electrons correctly because of the orthogonality condition and also must include the effect of electrostatic potential and exchange-correlation between core and valence states. The most general form of a non-local pseudopotential is:

$$V_s(\mathbf{r}) = V_s^{loc}(r) + \sum_{l=0}^{l_{max}} V_{s,l}^{nl} P_l \quad (2.28)$$

where the index s denote the atom and P_l is a projector defined by

$$P_l f(\mathbf{r}) = \sum_{m=-l}^{m=l} f_{lm}(r) Y_l^m(\theta, \phi) \quad (2.29)$$

where Y_l^m is a spherical harmonic of angular momentum l and f_{lm} are the expansion coefficients of the function $f(\mathbf{r})$.

Non-local norm conserving pseudopotentials which are sufficiently smooth in the core region can be efficiently used in a plane-wave basis set. They are good at describing the scattering properties of an ion at various environments. This property increases the accuracy and transferability of non-local norm conserving pseudopotentials. Generation of pseudopotentials are not unique and there exists many studies[17–21] which have introduced pseudopotentials that work extremely well.

2.6 Conclusion

In this chapter we have briefly give some information about basics of density functional theory without any proof. Kohn-Sham formulation of the many-body problem is a very useful approach which allows us to calculate the correct ground-state electronic energy and electron density. We have also investigated the approximations and methods that are allow us to calculate accurate results.

CHAPTER 3

DENSITY FUNCTIONAL PERTURBATION THEORY

3.1 Overview

In Chapter 2 we have investigated the ground-state properties of a periodic system within the framework of density functional theory. Ground-state properties can provide many information about the physics of a system such as total energy, charge-density, equilibrium lattice-constants and bulk modulus. However, many other physical quantities that are accessible experimentally are directly related to various *responses* of the system to the application of small external perturbations. Among these perturbations, small atomic displacements, strain perturbations and applied macroscopic electric fields have a particular significance for molecular systems and these perturbations are the main interest of this work. Many physical properties are then associated with the derivatives of the total energy of the system with respect to these perturbations. For example, the force exerted on a nuclei is related to the first derivative of the energy with respect to atomic displacements and the first derivative of the energy with respect to homogeneous electric field gives the dipole moment of a molecule. Formulation of many other physical quantities such as dielectric tensor, Born effective charge tensors, elastic constants and phonon dispersion spectra are directly related to the second derivatives of the total energy.

There are basically two methods exist for the determination of the quantities mentioned above within the framework of density functional theory. The first one is a direct-method known as *frozen-phonon technique*[22] which calculates simply the total energy of the solids for the unperturbed and perturbed cases and determine the energy derivatives numerically. Then one can construct the dynamical matrix to obtain phonon frequencies. The main practical advantage

of this technique is simply requires ground-state calculations. But this method can not handle perturbations incommensurate with periodic lattice. It is also impossible to obtain quantities of the system under the homogeneous electric field because of its linear potential in space. If one attempts to calculate the phonon frequencies away from the Brillouin zone center ($\mathbf{q} \neq \mathbf{0}$) within frozen-phonon approach, the use of the supercells required and this results the increase of the computing time.

The second method is the use of the perturbation theory to evaluate the response functions directly within the density functional framework. There are two formalisms for this perturbative approach. In the Baroni, Giannozzi and Testa (BGT) formalism [23, 24], a series of equations, so-called Sternheimer equations, are obtained which can be solved self-consistently to calculate the linear responses. Gonze formalism [25–28] is basically the consideration of the perturbation theory applied to a variational principle. This method states that the first-order wave-functions can be derived from a minimization of a variational expression of second order energy derivatives. Both BGT and Gonze formalisms allow us to calculate the phonon dispersion at any arbitrary wave-vector without using supercells and with a reasonable computer time. These perturbative techniques are, in the linear-response theory, within the framework of DFT, referred as *density functional perturbation theory* (DFPT).

This chapter is organized as follows: In Section 3.2 we briefly review some basics of DFPT. The following sections 3.3 and 3.4 are adapted for the Sternheimer approach and variational approach, respectively.

3.2 Basics of Perturbation Theory

In the previous chapter, we have investigated the formulation of the DFT for the calculation of the ground-state properties of an unperturbed periodic solid, such as total energy, wave functions and charge-density. From now on, we assume that all these ground state properties are known. In order to obtain the derivatives of

the total energy with respect to an applied small perturbation characterized by the parameter λ , we describe the new problem by Schrödinger equations as:

$$H(\lambda)|\psi_n(\lambda)\rangle = E(\lambda)|\psi(\lambda)\rangle. \quad (3.1)$$

The external potential v_{ext} that depend on the parameter λ , can be expanded to a Taylor series and it is supposed to be known to all orders:

$$v_{\text{ext}}(\lambda) = v_{\text{ext}}^{(0)} + \lambda v_{\text{ext}}^{(1)} + \lambda^2 v_{\text{ext}}^{(2)} + \dots \quad (3.2)$$

Since we are interested the changes of physical quantities (total energy, wave-functions, electronic charge density or Hamiltonian) due to the perturbation of the external potential (Eqn. 3.2) these perturbed quantities $X(\lambda)$ can be expanded with the same form of $v_{\text{ext}}(\lambda)$,

$$X(\lambda) = X^{(0)} + \lambda X^{(1)} + \lambda^2 X^{(2)} + \dots \quad (3.3)$$

Let us consider the hamiltonian $H(\lambda)$ in Eqn. 3.1 is supposed to be known in the first-order:

$$H(\lambda) = H^{(0)} + \lambda H^{(1)} \quad (3.4)$$

and writing wave function $\psi_n(\lambda)$ and energy $\varepsilon_n(\lambda)$ as power series like Eqn. 3.3, respectively;

$$\psi_n(\lambda) = \psi_n^{(0)} + \lambda \psi_n^{(1)} + \lambda^2 \psi_n^{(2)} + \dots \quad (3.5)$$

and

$$\varepsilon_n(\lambda) = \varepsilon_n^{(0)} + \lambda \varepsilon_n^{(1)} + \lambda^2 \varepsilon_n^{(2)} + \dots \quad (3.6)$$

Inserting Eqns. 3.4, 3.5, and 3.6 to Eqn. 3.1 we get:

$$\begin{aligned} & H^{(0)} |\psi_n^{(0)}\rangle + \lambda \left(H^{(1)} |\psi_n^{(0)}\rangle + H^{(0)} |\psi_n^{(1)}\rangle \right) + \lambda^2 \left(H^{(1)} |\psi_n^{(1)}\rangle + H^{(0)} |\psi_n^{(2)}\rangle \right) + \dots \\ &= \varepsilon_n^{(0)} |\psi_n^{(0)}\rangle + \lambda \left(\varepsilon_n^{(1)} |\psi_n^{(0)}\rangle + \varepsilon_n^{(0)} |\psi_n^{(1)}\rangle \right) + \lambda^2 \left(\varepsilon_n^{(2)} |\psi_n^{(0)}\rangle + \varepsilon_n^{(1)} |\psi_n^{(1)}\rangle + \varepsilon_n^{(0)} |\psi_n^{(2)}\rangle \right) + \dots \end{aligned} \quad (3.7)$$

If we take $\lambda = 0$ in Eqn. 3.7 we get the unperturbed equation:

$$H^{(0)} \left| \psi_n^{(0)} \right\rangle = \varepsilon_n^{(0)} \left| \psi_n^{(0)} \right\rangle \quad (3.8)$$

with no surprise and supposed to be calculated from DFT described in previous chapter. Derivation of Eqn. 3.7 with respect to λ and then taking $\lambda = 0$ we get first-order perturbation of Schrödinger equation;

$$H^{(1)} \left| \psi_n^{(0)} \right\rangle + H^{(0)} \left| \psi_n^{(1)} \right\rangle = \varepsilon_n^{(1)} \left| \psi_n^{(0)} \right\rangle + \varepsilon_n^{(0)} \left| \psi_n^{(1)} \right\rangle \quad (3.9)$$

and if we differentiate Eqn. 3.7 with respect to λ two times and then take $\lambda = 0$ we get second-order of perturbation:

$$H^{(1)} \left| \psi_n^{(1)} \right\rangle + H^{(0)} \left| \psi_n^{(2)} \right\rangle = \varepsilon_n^{(2)} \left| \psi_n^{(0)} \right\rangle + \varepsilon_n^{(1)} \left| \psi_n^{(1)} \right\rangle + \varepsilon_n^{(0)} \left| \psi_n^{(2)} \right\rangle. \quad (3.10)$$

To obtain first derivative of the energy $\varepsilon_n^{(1)}$ we can premultiply Eqn. 3.9 by $\langle \psi_n^{(0)} |$,

$$\langle \psi_n^{(0)} | H^{(1)} \left| \psi_n^{(0)} \right\rangle + \langle \psi_n^{(0)} | H^{(0)} \left| \psi_n^{(1)} \right\rangle = \varepsilon_n^{(1)} \langle \psi_n^{(0)} | \psi_n^{(0)} \rangle + \varepsilon_n^{(0)} \langle \psi_n^{(0)} | \psi_n^{(1)} \rangle. \quad (3.11)$$

Since $H^{(0)}$ is hermitian, it is possible to write

$$\langle \psi_n^{(0)} | H^{(0)} \left| \psi_n^{(1)} \right\rangle = \langle \psi_n^{(0)} | \varepsilon_n^{(0)} \left| \psi_n^{(1)} \right\rangle = \varepsilon_n^{(0)} \langle \psi_n^{(0)} | \psi_n^{(1)} \rangle \quad (3.12)$$

and using $\langle \psi_n^{(0)} | \psi_n^{(0)} \rangle = 1$, from Eqn. 3.11, we obtain the equation for first-order energy :

$$\varepsilon_n^{(1)} = \langle \psi_n^{(0)} | H^{(1)} \left| \psi_n^{(0)} \right\rangle. \quad (3.13)$$

This theorem is the fundamental result of first-order perturbation theory and first derivative of the energy can be obtained by only the knowledge of the unperturbed ground-state wave functions of the system and the perturbation hamiltonian $H^{(1)}$. We do not need to calculate first-order wave functions $\psi_n^{(1)}$.

To obtain the second derivative of the energy, starting from second-order Schrödinger equation (3.10) we premultiply by $\langle \psi_n^{(0)} |$ and get

$$\varepsilon_n^{(2)} = \langle \psi_n^{(0)} | H^{(1)} - \varepsilon_n^{(1)} | \psi_n^{(1)} \rangle \quad (3.14)$$

where we have used the relation

$$\langle \psi_n^{(0)} | H^{(0)} | \psi_n^{(2)} \rangle = \langle \psi_n^{(0)} | \varepsilon_n^{(0)} | \psi_n^{(2)} \rangle. \quad (3.15)$$

We do now need the first-order wave functions $\psi_n^{(1)}$ to get second-order energy derivative $\varepsilon_n^{(2)}$.

The first-order wave functions $\psi_n^{(1)}$ are generally expanded in terms of a sum over unperturbed wave functions[29, 30],

$$| \psi_n^{(1)} \rangle = \sum_{m \neq n} C_{mn}^{(1)} | \psi_m^{(0)} \rangle \quad (3.16)$$

where the expansion coefficient $C_{mn}^{(1)}$ is given by

$$C_{mn}^{(1)} = \frac{\langle \psi_m^{(0)} | H^{(1)} | \psi_n^{(0)} \rangle}{\varepsilon_n^{(0)} - \varepsilon_m^{(0)}}. \quad (3.17)$$

The evaluation of $\psi_n^{(1)}$ s in Eqn. 3.16 requires a knowledge of the full spectrum of Kohn-Sham Hamiltonian and an extensive summation over unoccupied (conduction) bands.

3.3 Sternheimer Approach

Computationally, it is convenient to avoid the sum over conduction bands in Eqn. 3.16. Baroni and his co-workers [24] have introduced a method which requires only the knowledge of the occupied states in order to calculate the first-order wave-functions of the system. The computational cost of the method is comparable to the ground-state unperturbed Kohn-Sham equations.

The first-order Schrödinger equation (Eqn. 3.9) can be gathered in terms of $|\psi_n^{(1)}\rangle$ and $|\psi_n^{(0)}\rangle$ as follows:

$$(H^{(0)} - \varepsilon_n^{(0)}) |\psi_n^{(1)}\rangle = -(H^{(1)} - \varepsilon_n^{(1)}) |\psi_n^{(0)}\rangle \quad (3.18)$$

where $\varepsilon_n^{(1)}$ is given by Eqn. 3.13 with the orthogonality condition so called *parallel transport gauge*

$$\langle \psi_n^{(0)} | \psi_m^{(1)} \rangle = 0. \quad (3.19)$$

The first-order Kohn-Sham potential in the DFT picture is given by

$$H^{(1)} = T^{(1)} + v_{\text{ext}}^{(1)}(r) + e^2 \int \frac{n^{(1)}(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' + \int \frac{\delta v_{xc}}{\delta n(\mathbf{r}')} n^{(1)}(\mathbf{r}') \quad (3.20)$$

and the first-order density can be computed from $\psi_n^{(1)}$

$$n^{(1)}(\mathbf{r}') = \sum_{n=1}^N \psi_n^{(0)*} \psi_n^{(1)} + \psi_n^{(1)*} \psi_n^{(0)}. \quad (3.21)$$

The above set equations must be solved self-consistently. First we guess a suitable $H^{(1)}$ and subsequently Eqn. 3.18 is solved to get first-order wave functions with constraints in Eqn. 3.19. Then we compute the first-order charge density in Eqn. 3.21 using these first-order wave functions. The new $H^{(1)}$ is calculated with the new first-order charge density. This process is iterated until the self-consistency achieved.

3.4 Variational approach

In the previous section first-order wave functions, which are needed to calculate the second order energy derivative ($\epsilon_n^{(2)}$), are obtained from the direct resolution of the Steinheimer equations. Alternatively, second-order energy derivatives can be obtained using the variational principle. The second order energy derivatives can be directly minimized with respect to the deviation of the first-order wave

functions which obeys a variational principle.

In the study of the two-electron systems of Hylleraas [31] in 1930, it has been shown that the $(2n+1)$ th derivative of the eigenenergies of a quantum-mechanical Hamiltonian can be calculated from the knowledge of the eigenfunction and its first n derivatives. In the same work it has also been noted that the second-order derivative of the eigenenergy expression is variational with respect to the deviations in the first-order derivative of the wave function. In 1956, an iterative procedure has been proposed by Dalgarno and Stewart [32] which gives the $(2n+1)$ th derivative of the eigenenergy of a quantum-mechanical Hamiltonian from only the knowledge of the change in the eigenfunctions up to order n . In this work Hamiltonian is considered to be changed linearly in the small perturbation parameter. Then Dupont-Bourdelet *et. al.* [33] generalized this result to Hamiltonians with a general dependence upon a small parameter. In 1961, Sinanoğlu [34] showed that it is possible to combine any variational principle with perturbation theory to yield even-order variational principles. It was not until the work of Gonze [25] that gives explicit formulas for these variational principles for an arbitrary even-order perturbation as well as for the " $2n+1$ " theorem. Here, the expressions are given both with and without constraints using Lagrange multiplier technique. Gonze has also studied [26] the treatment of adiabatic perturbations within density functional perturbation theory at arbitrary order of the perturbation expansion.

3.4.1 Variational Principle and Perturbation Theory

Let us consider one perturbation, with one small parameter λ and a general variational principle for the energy E which is a functional of wave function Φ . Variational here is meant in the sense of "lower variational bound" or "minimal principle" that is, the value of the functional for a wave function slightly different than the "correct" wave function is higher than the minimal value E_0 for the true wave function Φ_0 . Then it is possible to write

$$\forall \Phi, \quad 0 \leq E[\Phi] - E[\Phi_0] \leq K \|\Phi - \Phi_0\|^2. \quad (3.22)$$

Here the error in the functional is positive and related to the difference between the wave functions which is quadratic with some positive number K . This situation is considered for a lower variational bound and under sufficient conditions of differentiability which are always met in practice. In the following, $\hat{E}$ will denote the functional and E will be the value that this functional can take.

Let the functional $\hat{E}$ also depends on parameter λ , $\hat{E}_{(\lambda)}[\Phi]$. The wave function Φ_0 that minimizes the functional is also depend on this parameter. For λ close to zero, it is possible to define a fixed number K such that

$$\forall \Phi, \quad 0 \leq \hat{E}_{(\lambda)}[\Phi] - E_{(\lambda)}[\Phi_0(\lambda)] \leq K \|\Phi - \Phi_0(\lambda)\|^2. \quad (3.23)$$

The connection between perturbation theory and the variational principle can be investigated by considering the expansion of the exact wave function after Eqn. 3.3,

$$\Phi_0(\lambda) = \sum_{i=0}^{\infty} \lambda^i \Phi_0^{(i)} \quad (3.24)$$

and using the trial function

$$\Phi_t = \sum_{i=0}^n \lambda^i \Phi_0^{(i)} + \lambda^{n+1} \delta \Phi_t \quad (3.25)$$

one can get the $(2n + 1)$ theorem [25]

$$E_0^{(2n+1)} = \left\{ \hat{E}_{(\lambda)} \left[\sum_{i=0}^n \lambda^i \Phi_0^{(i)} \right] \right\}^{(2n+1)} \quad (3.26)$$

which gives an interesting result such that the knowledge of the wave function expansion up to order n allows us to determine the energy at order $2n + 1$.

For the even order of perturbation there exists a variational(minimum) principle as

$$E_0^{(2n)} = \min_{\delta\Phi_t} \left\{ \left(\hat{E}_{(\lambda)} \left[\sum_{i=0}^{n-1} \lambda^i \Phi_0^{(i)} + \lambda^n \delta\Phi_t \right] \right)^{(2n)} \right\} \quad (3.27)$$

where the trial n th-order wave function $\delta\Phi_t$ is equal to "correct" wave function $\Phi_0^{(i)}$ at the minimum.

In order to obtain more explicit formulas of Eqns. 3.26 and 3.27 by considering the wave function $\Phi(x)$ where x is a point in many-dimensional space and using Taylor series as well as Eqn. 3.3 after replacing either $2n$ or $2n + 1$ with m it is possible to get [25],

$$E_0^{(m)} = \sum_{k=0}^{m-1} \sum_{j=1}^{m-k} \int \cdots \int \frac{1}{j!k!} \sum_{i_1, \dots, i_j=1}^n \delta(k + i_1 + \cdots + i_j - m) \\ \times \frac{\partial^{j+k} \hat{E}}{(\partial\lambda)^k \partial\Phi(x_1) \cdots \partial\Phi(x_j)} \Phi^{(i_1)}(x_1) \cdots \Phi^{(i_j)}(x_j) dx_1 \cdots dx_j + \frac{1}{m!} \frac{\partial^m \hat{E}}{(\lambda)^m}. \quad (3.28)$$

Here the derivatives of the functional $\hat{E}$ are evaluated at $\lambda = 0$ and at the unperturbed wave function.

These are the most general equations for a functional without constraints. For the DFT calculations, which this thesis is based on, there exists a fixed particle number constraint so it is convenient to investigate how the expressions 3.26 and 3.27 change with introducing constraints.

Now if we consider the Lagrange multiplier method for the minimization of $\hat{E}[\Phi_t]$ under constraint

$$\hat{F}_\Lambda[\Phi_t] = \hat{E}[\Phi_t] - \Lambda \hat{C}[\Phi_t] \quad (3.29)$$

where $\hat{C}[\Phi_t]$ is the functional that places on the domain of variation of Φ_t :

$$\hat{C}[\Phi_t] = 0. \quad (3.30)$$

In this equation (3.29), Λ is called Lagrange multiplier. This parameter is chosen such that the solution Φ_t that minimizes the functional 3.29 satisfies the

constraint condition equation 3.30. This value of the Lagrange parameters is denoted by Λ_0 .

In order to investigate Eqn. 3.22 under constraint, a variational principle within Lagrange method is needed. So it is possible to show that there exists some Ω that

$$0 \leq \hat{F}_{\Lambda_0}[\Phi] - \hat{F}_{\Lambda_0}[\Phi_0] + \Omega(\hat{C}[\Phi])^2 \leq K\|\Phi - \Phi_0(\lambda)\|^2 \quad (3.31)$$

for all possible Φ wave functions. One can rewrite the previous equation by using Eqn. 3.29 and considering the possibility of the λ dependency of the constraints

$$0 \leq \hat{E}_\lambda[\Phi] - \Lambda_0(\lambda)\hat{C}_{(\lambda)}[\Phi] + \Omega(\hat{C}_{(\lambda)}[\Phi])^2 - E_0(\lambda) \leq K\|\Phi - \Phi_0(\lambda)\|^2. \quad (3.32)$$

If the trial function (Eqn. 3.25) for the unconstraint variational principle is used for the present case one can get the expression of $2n + 1$ theorem as [25]

$$\begin{aligned} E_0^{(2n+1)} &= \left\{ \hat{F}_{(\lambda)} \left[\sum_{i=0}^n \lambda^i \Phi_0^{(i)} \right] \right\}^{(2n+1)} \\ &= \left\{ \hat{E}_{(\lambda)} \left[\sum_{i=0}^n \lambda^i \Phi_0^{(i)} \right] - \Lambda_0(\lambda) \hat{C}_{(\lambda)} \left[\sum_{i=0}^n \lambda^i \Phi_0^{(i)} \right] \right\}^{(2n+1)} \end{aligned} \quad (3.33)$$

and the expression for the even-orders

$$E_0^{(2n)} = \min_{\delta\Phi} \left\{ \left(\hat{F}_{(\lambda)} \left[\sum_{i=0}^{n-1} \lambda^i \Phi_0^{(i)} + \lambda^n \delta\Phi_t \right] \right)^{(2n)} \right\}, \quad (3.34)$$

$$E_0^{(2n)} = \min_{\delta\Phi} \left\{ \left(\hat{E}_{(\lambda)} \left[\sum_{i=0}^{n-1} \lambda^i \Phi_0^{(i)} + \lambda^n \delta\Phi_t \right] - \Lambda_0(\lambda) \hat{C}_{(\lambda)} \left[\sum_{i=0}^{n-1} \lambda^i \Phi_0^{(i)} + \lambda^n \delta\Phi_t \right] \right)^{(2n)} \right\} \quad (3.35)$$

where in the minimization process $\delta\Phi$ must satisfy the perturbation expansion of the constraint as

$$\left\{ \hat{C}_{(\lambda)} \left[\sum_{i=0}^{n-1} \lambda^i \Phi_0^{(i)} - \lambda^n \delta \Phi_t \right] \right\}^{(n)} = 0. \quad (3.36)$$

These equations are presented within a single constraint which can be easily translated to more than one constraint [26].

3.4.2 *Perturbative treatment of the Kohn-Sham Energy*

Functional

Before discussing the variational approach to perturbation theory for the Kohn-Sham energy functional it is convenient to write the basic equations of density functional theory. The minimization of the total energy of the electronic system under the orthonormality constraints $\langle \Phi_\alpha | \Phi_\beta \rangle = \delta_{\alpha\beta}$ can be done using the Lagrange multiplier method,

$$E[\Phi_\alpha] = \sum_{\alpha=1}^N \langle \Phi_\alpha | T + v | \Phi_\alpha \rangle + E_{Hxc}[n] - \sum_{\alpha,\beta=1}^N \Lambda_{\beta\alpha} [\langle \Phi_\alpha | \Phi_\beta \rangle - \delta_{\alpha\beta}] \quad (3.37)$$

where E_{Hxc} is the sum of the Hartree and exchange-correlation energies, $\Lambda_{\beta\alpha}$ are the Lagrange multipliers corresponding to the orthonormalization constraints $\langle \Phi_\alpha | \Phi_\beta \rangle = \delta_{\alpha\beta}$ and these constraints are valid for all "occupied" orbitals where N is the number of orbitals equal to the half the number of electrons if the system is spin degenerate. The corresponding Euler-Lagrange equations are

$$H|\Phi_\alpha\rangle = \sum_{\beta=1}^N \Lambda_{\beta\alpha} |\Phi_\beta\rangle \quad (3.38)$$

where the Hamiltonian

$$H = T + v_{KS} = T + v + v_{Hxc}. \quad (3.39)$$

After considering the perturbation expansion of the above equations it is possible to get [26]

$$\begin{aligned}
E^{(m)} = & \sum_{\alpha=1}^N \sum_{j=0}^n \sum_{k=0}^m \sum_{l=0}^n \delta(m-j-k-l) \langle \Phi_{\alpha}^{(j)} | (T+v)^{(k)} | \Phi_{\alpha}^{(l)} \rangle \\
& + \frac{1}{m!} \frac{d^m}{d\lambda^m} E_{Hxc} \left[\sum_{\alpha=0}^N \left(\sum_{j=0}^n \lambda^j \Phi_{\alpha}^{(j)*}(r) \right) \left(\sum_{k=0}^n \lambda^k \Phi_{\alpha}^{(k)}(r) \right) \right] \Big|_{\lambda=0} \\
& - \sum_{\alpha,\beta=1}^N \sum_{j=0}^n \sum_{k=0}^m \sum_{l=0}^n \delta(m-j-k-l) \Lambda_{\beta\alpha}^{(k)} \langle \Phi_{\alpha}^{(j)} | \Phi_{\beta}^{(l)} \rangle \\
& + \sum_{\alpha,\beta=1}^N \Lambda_{\beta\alpha}^{(m)} \delta_{\alpha\beta}.
\end{aligned} \tag{3.40}$$

where $m = 2n$ or $m = 2n + 1$. Here for both cases, only wave functions up to order n are needed and for the even-orders of expansion ($m = 2n$) this functional is fully variational.

3.4.3 First and second orders of DFPT

After obtaining the most general expressions of variational density functional perturbation theory, it is now useful to specialize to the first- and second-order derivatives of the energy. These derivatives are very important for determination of quantities mentioned in the beginning of this chapter. If we consider the first order change in the electronic energy obtained from the $2n + 1$ theorem we get:

$$E^{(1)} = \sum_{\alpha=1}^n \langle \Phi_{\alpha}^{(0)} | (T+v)^{(1)} | \Phi_{\alpha}^{(0)} \rangle + \frac{d}{d\lambda} E_{Hxc}[n^{(0)}] \Big|_{\lambda=0}. \tag{3.41}$$

In this equation there is no need to know the perturbed wave functions. The last part will be zero if the Hartree and exchange-correlation energies do not have an explicit dependence on the perturbing parameter, λ . If the kinetic and interacting energies do not explicitly depend on the perturbation we get

$$E^{(1)} = \sum_{\alpha=1}^n \langle \Phi_{\alpha}^{(0)} | v^{(1)} | \Phi_{\alpha}^{(0)} \rangle. \tag{3.42}$$

This equation is the familiar Hellmann-Feynman theorem derived from density-functional formalism.

The second order energy is given by

$$\begin{aligned}
E^{(2)} = & \sum_{\alpha=1}^n [\langle \Phi_{\alpha}^{(1)} | (T + v)^{(1)} | \Phi_{\alpha}^{(0)} \rangle + \langle \Phi_{\alpha}^{(1)} | (H - \varepsilon_{\alpha})^{(0)} | \Phi_{\alpha}^{(1)} \rangle + \langle \Phi_{\alpha}^{(0)} | (T + v)^{(2)} | \Phi_{\alpha}^{(0)} \rangle \\
& + \langle \Phi_{\alpha}^{(0)} | (T + v)^{(1)} | \Phi_{\alpha}^{(1)} \rangle] + \frac{1}{2} \int \int \frac{\delta^2 E_{Hxc}[n^{(0)}]}{\delta n(\mathbf{r}) \delta n(\mathbf{r}')} n^{(1)}(\mathbf{r}) n^{(1)}(\mathbf{r}') d\mathbf{r} d\mathbf{r}' \\
& + \int \frac{d}{d\lambda} \frac{\delta E_{Hxc}[n^{(0)}]}{\delta n(\mathbf{r})} \Bigg|_{\lambda=0} n^{(1)}(\mathbf{r}) d\mathbf{r} + \frac{1}{2} \frac{d^2}{d\lambda^2} E_{Hxc}[n^{(0)}] \Bigg|_{\lambda=0}
\end{aligned} \tag{3.43}$$

where

$$n^{(1)}(\mathbf{r}) = \sum_{\alpha=1}^N \Phi_{\alpha}^{(0)*}(\mathbf{r}) \Phi_{\alpha}^{(1)}(\mathbf{r}) + \Phi_{\alpha}^{(1)*}(\mathbf{r}) \Phi_{\alpha}^{(0)}(\mathbf{r}) \tag{3.44}$$

and Eqn. 3.43 must be minimized with respect to first-order wave functions $\Phi_{\alpha}^{(1)}$ and under constraints:

$$\langle \Phi_{\alpha}^{(0)} | \Phi_{\beta}^{(1)} \rangle + \langle \Phi_{\alpha}^{(1)} | \Phi_{\beta}^{(0)} \rangle = 0 \tag{3.45}$$

and we have

$$\langle \Phi_{\alpha}^{(0)} | \Phi_{\beta}^{(1)} \rangle = 0 \tag{3.46}$$

in the parallel-transport gauge.

The Euler-Lagrange equations applied to this functional are given as [26]:

$$P_c(H^{(0)} - e_{\alpha}^{(0)})P_c|\Phi_{\alpha}^{(0)}\rangle = -P_c H^{(1)}|\Phi_{\alpha}^{(0)}\rangle \tag{3.47}$$

which is the Sternheimer equation. This result ensures the connection between the Green's function method[23].

3.5 Conclusion

In this chapter we give a very brief and general information for the density functional perturbation theory to which allows us to calculate second-derivative of the

total energy with respect to some perturbation such as collective displacement of atoms, homogeneous static electric fields or strains. After giving some basics of perturbation theory we have focused on the two main approaches namely Sternheimer and Variational approaches. In the section of variational approach the connection between the variational principle and the perturbation theory is described and the first- and second-order derivatives of the energy are given in the framework of the density functional perturbation theory.

CHAPTER 4

AB INITIO VOLUME-DEPENDENT ELASTIC AND LATTICE DYNAMICAL PROPERTIES OF CHALCOPYRITE CuAlSe_2

4.1 Introduction

The ternary I-III-VI₂ chalcopyrites form a large group of semiconductors with diverse structural, electrical and optical properties [35, 36] and here attracted important attention for a long time because of their large potential in photovoltaic and nonlinear optical applications. Among these compounds, CuAlSe_2 , with a band gap of 2.67 eV [37] is promising as emitting layer of blue light photoluminescent devices [38] as well as a window in heterostructure photovoltaic devices [39].

Experimental determinations of phonon frequencies, elastic stiffness constants, compressibilities, and bulk moduli for a number of chalcopyrite compounds have been reported in the literature but the results are often contradictory [40, 41]. The lattice dynamical properties of CuAlSe_2 have been studied experimentally by Raman [42–46] and infrared [46–48] spectroscopic methods. The study of characteristic phonon frequencies is one of the most important methods for the characterization of strained materials [49]. Pressure dependence of lattice dynamical properties, such as effective charges, phonon frequencies and low frequency dielectric constants provide crucial information about the structure of the material. The pressure dependent phonon frequencies of these materials have been investigated to delineate the symmetry assignments of the zone center modes as well as to give an understanding of the structural phase transitions at elevated pressures. Among these studies, Gonzalez *et. al.* [50], have used ZnS as an ana-

logue of CuGaS₂ and reported pressure-dependent zone center phonons up to a pressure of 18.4 GPa. The pressure dependent of structural properties of CuAlS₂ and CuAlSe₂ were studied by an energy dispersive X-ray diffraction technique by Roa *et. al.* [51] and CuAlSe₂ was found to undergo a transition to a probable rock-salt structure at 12.4 GPa. Derollez *et. al.* [52] measured acoustic and low frequency optical modes of AgGaSe₂ by inelastic neutron scattering and found large negative Grüneisen parameters for these modes. Roa *et. al.* [45] have reported pressure Raman measurements for CuAlSe₂ up to 30 GPa and observed a structural phase transition around 12 GPa.

Elastic constants of most of the chalcopyrite family of semiconductors have not been determined experimentally because of various difficulties in growing single crystals of these compounds [41]. Attempts have been made to fill this gap in the knowledge of the elastic properties of the chalcopyrites by theoretical calculations using different approaches, but mostly the results obtained differ considerably, and in many cases no satisfactory agreement has been achieved with existing experimental data. On the other hand, the availability of reliable elastic constant data is an essential prerequisite for any calculation or analysis of the influence of pressure, stress and strain on the properties of crystals and thin epitaxial layers.

In this chapter, we present extensive first principles studies of the elastic, structural and lattice dynamical properties of chalcopyrite CuAlSe₂ under hydrostatic pressure. In Section 4.2 we briefly review the underlying method and the parameters of the calculations. In the following section, the results are compared to experiments and tetrahedral binary compounds. Section 4.4 concludes the chapter with a brief review of the main results.

4.2 Computational Details

The present results have been obtained using the ABINIT code [53], that is based on pseudopotentials and planewaves. It relies on an efficient Fast Fourier Trans-

form algorithm [54] for the conversion of wavefunctions between real and reciprocal space, on the adaptation to a fixed potential of the band-by-band conjugate gradient method [5] and on a potential-based conjugate-gradient algorithm for the determination of the self-consistent potential [55]. The exchange-correlation energy is evaluated in local density approximation (LDA), using Perdew-Wang parametrization [10] of Ceperley-Alder electron-gas data [8].

The pseudopotentials have been generated with FHI98PP code [56]. The details of choice of pseudopotentials were reported before for calculations of CuInSe₂ [57], CuGaS₂ [58] and CuInS₂ [59]. The kinetic energy cutoff needed to obtain a convergence better than 0.01 eV for total energy is found to be equal to 45 Ha. Changing cutoff from 40 to 45 Ha changes response quantities less than 1 %. The Brillouin zone is sampled by 12 special k points, which is found to be enough for convergence of static as well as response calculations.

The ground state properties in the pressure free case are obtained by minimization of total energy with respect to the unit cell volume V . This is done by calculating the total energy for a number of fixed η values. For each η u is determined by minimizing the force on the atoms. The equilibrium volume, bulk modulus and its pressure derivatives are calculated by fitting to a third-order Vinet equation of state [60]. The hydrostatic pressure is simulated by a uniform decrease in lattice constants a and c . For each compressed volume, the equilibrium value of u is recalculated from the force considerations.

Elastic and lattice dynamical properties are calculated within the framework of density functional perturbation theory. Technical details of the computation of responses to strain perturbations, atomic displacements and homogeneous electric fields can be found in Ref. [27] and [61], while Ref. [28] presents the subsequent computation of dynamical matrices, Born effective charges, dielectric permittivity tensors, and interatomic force constants. The details of the calculation of elastic constants in linear response framework is given in Ref. [61].

Table 4.1: Calculated structural parameters of CuAlSe₂ compared to experimental data (a in $a.u.$, η and u are dimensionless.)

	This work	Ref.[62]	Ref.[63]	Ref.[51]	Ref.[64]
a	10.400	10.590	10.595	10.604	10.605
η	1.985	1.954	1.956	1.957	1.943
u	0.257	0.269	0.261	-	-

4.3 Results

4.3.1 Atomic structure and lattice properties

The body-centered tetragonal chalcopyrite structure (space group D_{2d}^{12} , No. 122) can be derived from the cubic zinc-blende structure (space group T_d^2) by populating one of the face centered cubic sublattice with group VI atoms and other one with equal amounts of group I and III atoms in a regular fashion. Since, generally, I-VI and III-VI bond lengths, denoted by d_{I-VI} and d_{III-VI} , respectively, are not equal, mentioned substitution results in two different structural deformations: First one is the relocation of anions in the $x - y$ plane which is characterized by parameter $u = 0.25 + (d_{I-VI}^2 - d_{III-VI}^2) / a^2$. Here, a is the lattice constant in the x or y direction. The second consequence of differing anion-cation bond lengths is a deformation of the unit cell to a length c which is generally different from $2a$. This tetragonal distortion is characterized by the quantity $\eta = c/a$.

The zero pressure lattice structural properties are obtained by energy and force minimization and compared to available experimental values in Table 4.1. Considering the fact that the zero-point motion and thermal effects are not taken into account, the calculated a , η and u values agree with the experimental values quite well. The bulk modulus and its pressure derivative calculated by fitting to a third-order Vinet equation of state [60] are found to be 79.12 GPa and 4.55 which are in good agreement with available experimental bulk modulus values (85 ± 2 [51], and 85 ± 8 [64] GPa) as well as model calculations (71.16 [65] and 89.78 [66]) of CuAlSe₂.

Table 4.2: Independent elastic stiffness tensor components of CuAlSe₂ in units of GPa.

		C ₁₁	C ₁₂	C ₁₃	C ₃₃	C ₄₄	C ₆₆
CuAlSe ₂	This work	102.9	63.4	65.7	104.5	42.8	41.5
CuInSe ₂	This work	96.8	60.9	63.2	97.0	39.1	37.9
CuInSe ₂	Ref. [69](Exp.)	97.0	59.7	86.0	108.9	36.2	31.6
CuInSe ₂	Ref. [70](Theo.)	71.0	45.3	45.3	63.3	45.5	47.4

Under pressure tetrahedrally coordinated chalcopyrite compounds undergo transformation to a denser phase with octahedral coordination [67], probably rock-salt structure. The phase transition pressure for CuAlSe₂ is around 12 GPa [51]. This pressure corresponds to a volume reduction of 15 % if we use our calculated B_0 and B'_0 values in Vinet equation of state. Our calculations are done for the volume compression range (up to 10 %) which is away from the phase transition point.

4.3.2 Elastic constants

There are a number of ways to calculate the elastic coefficients of a material from first principles. Until recently, the most widely used method was to deform the crystal from its equilibrium shape by a set of tetragonal and sheer deformations of various sizes and compute the resulting stress by using quantum mechanical definition of stress [68]. Relationships between the applied strain and the calculated stress components provides a set of over-determined linear system which are solved by singular value decomposition to obtain sought elastic stiffness constants. Recently, Hamann *et. al.* [61] developed a reduced coordinate metric tensor method for linear response formulation of strain type perturbations which could be calculated in density functional perturbation theory (DFPT). The elastic constants reported in this section are obtained by the method of Ref. [61] as implemented in Abinit.

The elastic stiffness tensor of chalcopyrite compounds has six independent components because of the symmetry properties of D_{2d}^{12} space group:, namely

C_{11} , C_{33} , C_{44} , C_{66} , C_{12} , C_{13} in Young notation. The elastic compliance tensor elements of CuAlSe₂ which are calculated by using the method of metric tensor formulation of Hamann *et. al.* [61] are displayed in Table 4.2. Elastic stiffness tensor components must satisfy certain relations known as Born stability criteria [6] which for the tetragonal chalcopyrite lattice requires that $C_{11}, C_{33}, C_{44}, C_{66} > 0$, $C_{11} > |C_{12}|$, $C_{11}C_{33} > C_{13}^2$, $(C_{11} + C_{12})C_{33} > 2C_{13}^2$. The values reported in Table 4.2 satisfy all of these constraints. Since the experimental values are not available for CuAlSe₂, to give an idea about the expected experimental-theoretical spread, we display experimental, theoretical and our calculated values for CuInSe₂ in the same table. Except for C_{13} ($\approx 25\%$ underestimated) and C_{66} ($\approx 20\%$ overestimated), the agreement between the calculated and experimental values is very good. The results obtained in this work seems to be much closer to the experimental values compared to those reported in Ref. [70]. The main ingredients of calculations in this work and Ref. [70] are similar, namely pseudopotential LDA-DFT. Although the method of elastic constant calculations are different, results should converge to a common value. The pronounced difference in the results of these two sets of calculations might be due to lack of enough convergence in the calculations reported in Ref. [70]. Elastic constants reported in Table 4.2 shows that CuAlSe₂, also, displays pseudocubic elastic behavior: for cubic crystals $C_{11}/C_{33} = C_{44}/C_{66} = C_{12}/C_{13} = 1$, from Table 4.2 we find $C_{11}/C_{33} = 0.99$, $C_{44}/C_{66} = 1.03$, $C_{12}/C_{13} = 0.97$ for CuAlSe₂. A similar behavior, which is an expected result because of the u and η deformations being so small, was found for other Cu based chalcopyrites in Ref. [70].

One can define linear compressibilities for the pressure response of lattice constants a (κ_a) and c (κ_c) axis of chalcopyrite structure [41]. κ_a and κ_c can be expressed in terms of elastic stiffness constants as:

$$\begin{aligned}\kappa_a &= -\frac{1}{a} \frac{\partial a}{\partial p} = \frac{C_{33} - C_{13}}{C_{33}(C_{11} + C_{12}) - 2C_{13}^2} \\ \kappa_c &= -\frac{1}{c} \frac{\partial c}{\partial p} = \frac{C_{11} + C_{12} - 2C_{13}}{C_{33}(C_{11} + C_{12}) - 2C_{13}^2}\end{aligned}$$

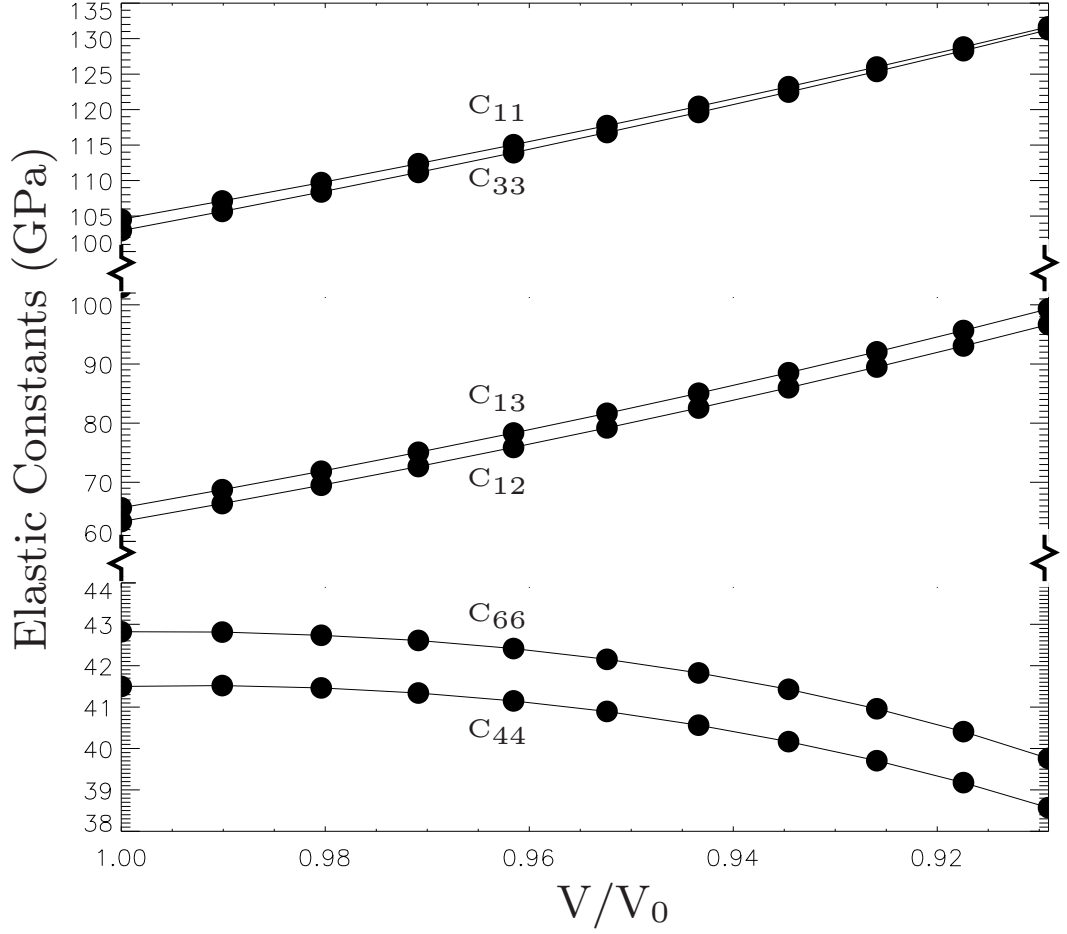


Figure 4.1: Volume dependence of the components of elastic stiffness components of CuAlSe₂.

Our calculated κ_a and κ_c are close with values 4.4 and 4.0 TPa⁻¹, respectively. This finding partly justifies treating the effect of hydrostatic pressure on the lattice as uniform contraction of both a and c axis. Volume compressibility, which is defined as $\kappa = 2\kappa_a + \kappa_c$, is equal to 12.8 TPa⁻¹ which is similar to that reported for other chalcopyrite compounds [41].

The volume dependence of elastic constants is displayed in Fig. 4.1. As can be seen from the figure, C_{44} and C_{66} decreases linearly (nonlinearly) at low (high) pressures values while the other components increase with the compression of the lattice. Although the pressure dependence of elastic constants of CuAlSe₂ is not available experimentally, elastic constants of a similar compound CdGaAs₂ show similar properties at low pressures [41]. Volume dependence of κ_a and κ_c are displayed in Fig. 4.2 along with the volume dependence of the bulk modulus. Both

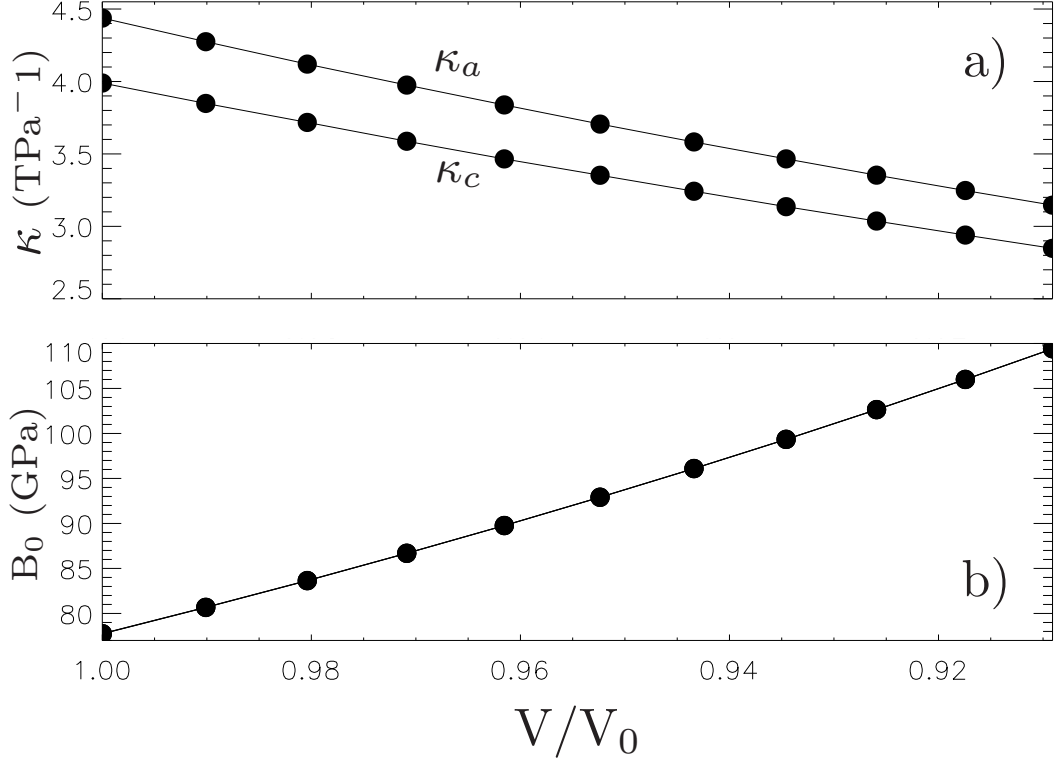


Figure 4.2: Volume dependence of (a) linear compressibilities (κ_a and κ_c) and (b) the bulk modulus of CuAlSe₂

compressibilities (bulk modulus) decrease (increase) uniformly with increasing pressure.

4.3.3 Born Effective Charges

For insulators, the Born effective charge is a measure of the change in electronic polarization due to ionic displacements. For atom κ , $Z_{\kappa,\beta\alpha}^*$, quantifies, to linear order, the polarization per unit cell, created along the direction β when the atoms of sublattice κ are displaced along the direction α , under the condition of zero electric field. Computationally, its the mixed second derivative of the total energy with respect to macroscopic field component E_α and β component of the displacement of κ th particle.

In Table 4.3, we display dynamical effective charge tensors, eigenvalues of symmetric parts of these tensors and Grüneisen parameters of these eigenvalues,

Table 4.3: Calculated Born effective charges of CuAlSe₂. The eigenvalues, λ of the symmetric part of Z^* are given in brackets. The last column is the Grüneisen parameter, γ^* for the effective charge.

		λ	γ^*
Z_{Cu}^*	$\begin{pmatrix} 0.75 & 0.09 & 0.00 \\ -0.09 & 0.75 & 0.00 \\ 0.00 & 0.00 & 0.69 \end{pmatrix}$	$\begin{bmatrix} 0.75 \\ 0.75 \\ 0.69 \end{bmatrix}$	$\begin{bmatrix} -3.25 \\ -3.25 \\ -3.23 \end{bmatrix}$
Z_{Al}^*	$\begin{pmatrix} 2.45 & 0.02 & 0.00 \\ -0.02 & 2.45 & 0.00 \\ 0.00 & 0.00 & 2.59 \end{pmatrix}$	$\begin{bmatrix} 2.45 \\ 2.45 \\ 2.59 \end{bmatrix}$	$\begin{bmatrix} -0.08 \\ -0.08 \\ -0.32 \end{bmatrix}$
$Z_{\text{Se}_1}^*$	$\begin{pmatrix} -1.50 & 0.00 & 0.00 \\ 0.00 & -1.71 & 0.62 \\ 0.00 & 0.65 & -1.64 \end{pmatrix}$	$\begin{bmatrix} -2.31 \\ -1.50 \\ -1.04 \end{bmatrix}$	$\begin{bmatrix} -0.71 \\ -0.69 \\ -1.47 \end{bmatrix}$
$Z_{\text{Se}_3}^*$	$\begin{pmatrix} -1.71 & 0.00 & 0.62 \\ 0.00 & -1.50 & 0.00 \\ 0.65 & 0.00 & -1.64 \end{pmatrix}$	$\begin{bmatrix} -2.31 \\ -1.50 \\ -1.04 \end{bmatrix}$	$\begin{bmatrix} -0.71 \\ -0.69 \\ -1.47 \end{bmatrix}$

γ^* which is defined as

$$\gamma^* = -\frac{d \ln \lambda}{d \ln V} \quad (4.1)$$

where V is the unit cell volume and λ is the eigenvalue of the symmetric part of relevant effective charge tensor. The effective charge tensors are also displayed graphically in Fig. 4.3.

Because of finite k-point sampling there is a deviation from charge neutrality which is less than 0.01 electron for the unit cell. The first thing to consider from Table 4.3 is that if Cu, Al, and Se in CuAlSe₂ are considered as +1, +3 and -2 ions, the dynamical charges show no anomalous behavior which is expected because such anomalous effective dynamical charges are observed for ferroelectrically unstable semiconductors as well as near metallic and strongly-correlated electronic systems [71] and CuAlSe₂ has none of these properties.

The form of effective charge tensor for the constituents is determined by the site symmetry of the ions. Z^* of cations, which have same site symmetry (they are located at $4a$ and $4b$ Wyckoff positions) are almost diagonal with an anisotropy

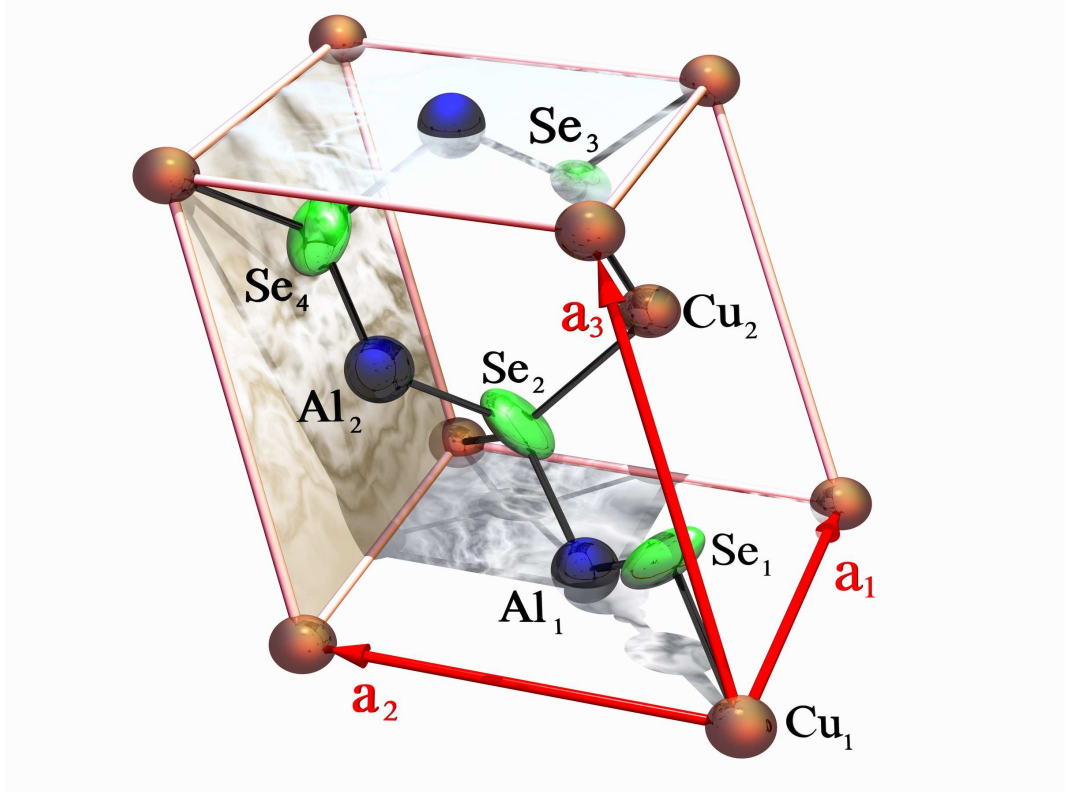


Figure 4.3: Dynamical Born effective charges of chalcopyrite CuAlSe_2 . Here, for each atom the unit sphere is transformed by the effective charge tensor of that atom. Al and Se spheres are further scaled by $1/3$ and $1/2$, respectively for visual clarity.

of $\approx 9\%$ for Cu and $\approx -5\%$ for Al. These anisotropies are higher than those seen in CuAlS_2 [72], but still low enough that the shapes of Cu and Al in Fig. 4.3 are almost spherical. The shape of Z^* for Se ion is markedly different from that of cations as can be seen from Table 4.3 and Fig. 4.3. Se ions are located at lower symmetry sites ($8d$ positions) and as a result their effective charge tensors have nonequivalent diagonal components as well as sizable off-diagonal components. The tetrahedral shifting of anion atoms creates four different configurations for these atoms and the resulting effective charge tensor elements can be divided into two classes according to the direction of the tetrahedral shifting being along x or y direction. $Z_{\text{Se},zz}^* = -1.64$ for all anions while $Z_{\text{Se},xx}^*$ and $Z_{\text{Se},yy}^*$ take the value -1.50 or -1.71 depending on the direction of u . Also, depending on the u distortion being along x or y direction, the off-diagonal components $Z_{\text{Se},zx}^*$, $Z_{\text{Se},xz}^*$ or $Z_{\text{Se},yz}^*$, $Z_{\text{Se},zy}^*$ are different than zero. Hence, the shape of effective charge tensor

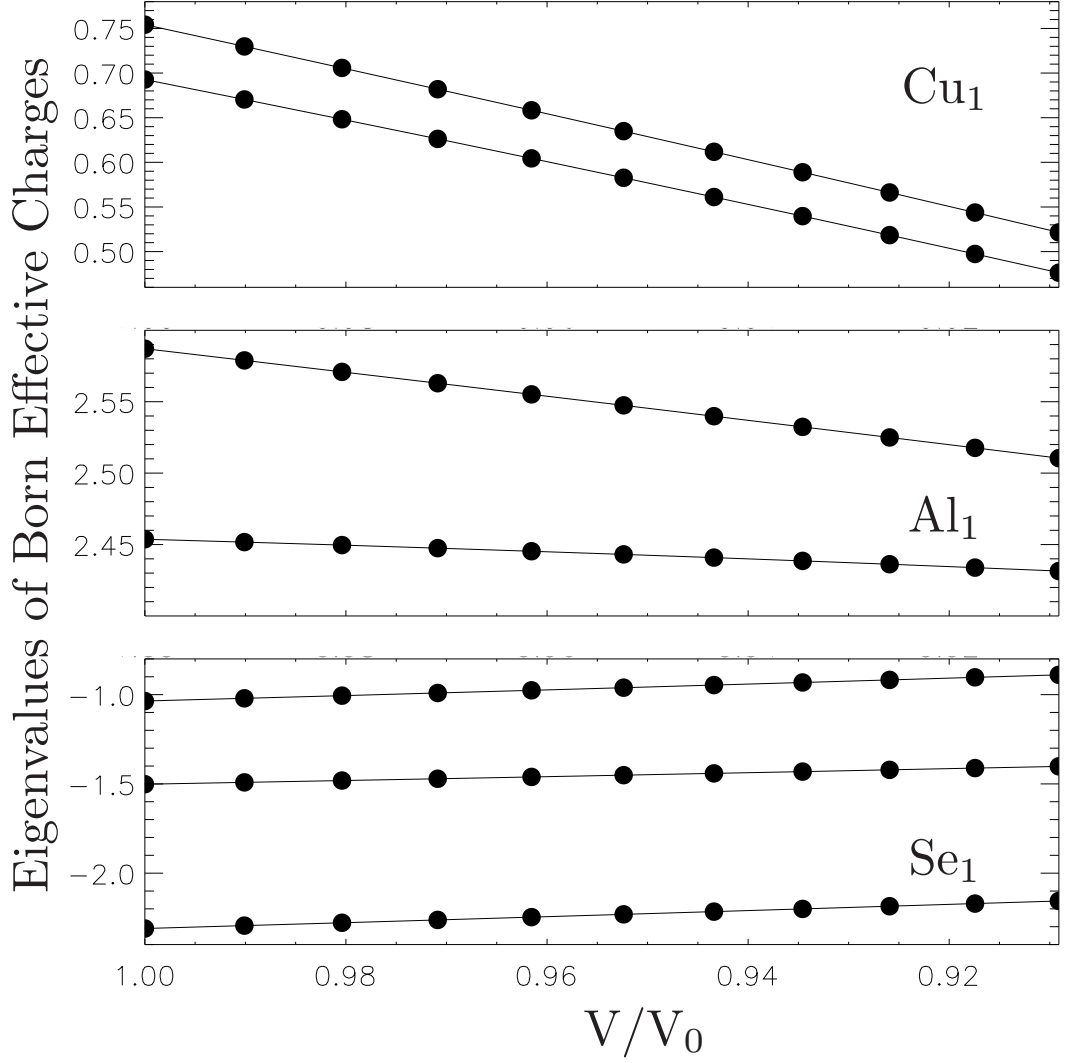


Figure 4.4: Volume dependent Born effective charges of CuAlSe₂.

for anions is far from being spherical, which also has been observed for other members of the Cu-based chalcopyrite family of semiconductors.

As can be seen from the Table 4.3, the Grüneisen parameter for the dynamical effective charges of all the ions are negative, which indicate that Z^* decreases with increasing pressure. The eigenvalues of the symmetric part of the effective charge tensors are displayed as function of the volume in Fig. 4.4. The most important conclusion from the effective charge Grüneisen parameters in Table 4.3 and the graphs in Fig. 4.4 is that the Born effective charges decrease linearly with pressure in the considered pressure range. Pressure induced reduction of effective charges indicates a charge redistribution in comparison with zero pressure situation is found to be the case for almost all zinc-blende materials, except SiC [73].

Table 4.4: Static and high frequency dielectric tensor components of CuAlSe₂.

	$\epsilon_{\infty}^{\parallel}$	$\epsilon_{\infty}^{\perp}$	ϵ_{∞}	$\epsilon_0^{\parallel}$	$\epsilon_0^{\perp}$	ϵ_0
This work	8.07	8.22	8.17	9.99	9.74	9.82
Ref. [48]	5.2	6.0	5.7	6.67	8.28	7.74
Ref. [74]	6.0	6.2	6.1	8.4	8.6	8.5

4.3.4 Dielectric Permittivity Tensors

The form of the dielectric tensor is determined by the symmetry of the crystal. Our calculated electronic (ϵ_{∞}) and static (ϵ_0) dielectric tensors have two independent components $\epsilon^{\parallel}$ and $\epsilon^{\perp}$ along and perpendicular to the c axis, respectively. While electronic dielectric tensor is almost isotropic, ϵ_0 has a small ($\approx 2.5\%$) anisotropy, which is consistent with the fact that for CuAlSe₂ tetragonal distortion is very small ($\eta = c/a \approx 2$).

We display our calculated dielectric tensor components along with model calculations of Ref. [74] and experimentally available values in Table 4.4. The averages of ϵ_{∞} and ϵ_0 , obtained from the expression ϵ_{∞} (or ϵ_0) = $(2\epsilon_{\infty}^{\perp} + \epsilon_{\infty}^{\parallel})/3$ are also shown in this table.

The infrared data for the electronic part of the dielectric tensor of CuAlSe₂ are similar and around 5, but for the static dielectric tensor components there are up to 30 % difference between $\epsilon_0^{\perp}$ reported in Ref. [48] and Ref. [74]. It is well known that the density functional theory (DFT) overestimates the high-frequency dielectric constants, this is a well-known problem related to underestimation of the band-gap in DFT [75–77]. Our calculated ϵ_{∞} values are somewhat higher than expected overestimation. The agreement for the component of ϵ_0 is better.

One can define a Grüneisen parameter

$$\gamma^{\epsilon} = -\frac{d \ln \epsilon}{d \ln V} \quad (4.2)$$

for the pressure dependence of the dielectric constants. We have found that the Grüneisen parameters of the electronic part of both perpendicular and parallel

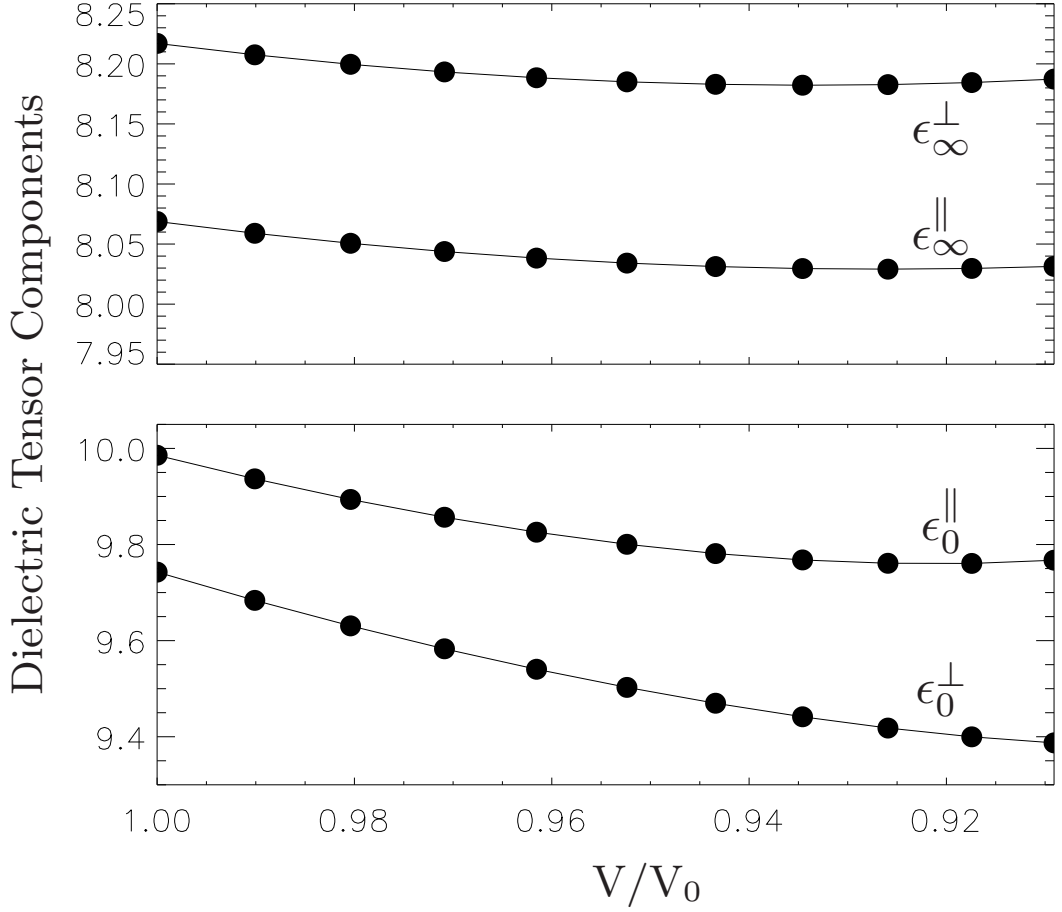


Figure 4.5: Volume dependent static and high frequency dielectric tensor components of CuAlSe₂.

components of dielectric tensor to be negative with similar magnitude ($\gamma^{\epsilon_{\infty}^{\perp}} = -0.126$ and $\gamma^{\epsilon_{\infty}^{\parallel}} = -0.132$) which are somewhat lower than the values found for zinc-blende compounds [73]. The static constants show a similar trend with markedly higher Grüneisen parameters ($\gamma^{\epsilon_0^{\perp}} = -0.64$ and $\gamma^{\epsilon_0^{\parallel}} = -0.52$). It should be noted that the relative difference between the $\gamma^{\epsilon_0^{\perp}}$ and $\gamma^{\epsilon_0^{\parallel}}$ (0.19) is higher than that for $\gamma^{\epsilon_{\infty}^{\perp}}$ and $\gamma^{\epsilon_{\infty}^{\parallel}}$ (-0.05).

Figure 4.5 displays our calculated volume-dependent static and high frequency dielectric tensor components. All of the components decrease under pressure; the volume dependence of static (high-frequency) components is slightly (highly) nonlinear, especially at higher pressures, which is similar to what has been found for the most tetrahedrally coordinated semiconductors.

4.3.5 Zone Center Phonons

Since the body-centered tetragonal unit cell of the chalcopyrite structure has eight atoms, there are a total of 24 modes of vibration. A detailed discussion of group theoretical properties of chalcopyrite zone center phonons can be found in Refs. [58] and [78]. The irreducible representation at the center of the Brillouin zone is

$$\Gamma_{\text{opt}} = 1\Gamma_1 \oplus 2\Gamma_2 \oplus 3\Gamma_3 \oplus 3\Gamma_4 \oplus 6\Gamma_5$$

for optical modes, and

$$\Gamma_{\text{aco}} = 1\Gamma_4 \oplus 1\Gamma_5$$

for acoustic modes.

In Table 4.5 our calculated zone center phonon frequencies, their symmetry assignments and mode Grüneisen parameters are displayed and compared with infrared [46–48] and Raman [42–46] spectroscopic measurements. The most striking thing about the experimentally available data in Table 4.5 is that except Γ_1 and the highest frequency Γ_4 and Γ_5 modes, there are very large differences among all phonon mode frequencies. The zone center phonon frequencies of Cu-based chalcopyrite semiconductors, generally, are clearly grouped into three branches: low, medium and high frequency. IR data reported by Ref. [48] is at odds with this trend and its low frequency Γ_4 and intermediate frequency Γ_5 modes are either overtones or comes from a modification of the chalcopyrite structure. Our calculated results agree best with the Raman and IR measurements reported by Ref. [46] with an average relative root-mean square deviation of around nine percent, which is within the range of expected accuracy of DFT response calculations.

The Grüneisen parameter γ_i for phonon mode i is defined as

Table 4.5: Frequencies of phonons and mode Grüneisen parameters at the Γ point (ω in cm^{-1}).

Mode	Ab initio		Experiment							γ_i	
	Present	IR[47]	IR[48]	IR[46]	R[42]	R[43]	R[44]	R[45]	R[46]	Present	Ref.[45]
Γ_1	192				186	189	185	185	187	1.5	1.4
Γ_2	218									1.2	
Γ_2	181									1.6	
Γ_3	381					233	207	311	~315	1.2	1.5
Γ_3	191				213		124	214	214	1.9	1.1
Γ_3	96						87	60	124	0.02	1.5
$\Gamma_{4\text{TO}}^{\text{LO}}$	389	375	401	382		373			384	1.3	
	358	350	370	340	358		389		342	1.5	
$\Gamma_{4\text{TO}}^{\text{LO}}$	204		349	193				264		2.2	
	200		342	186			360			2.3	0.5
$\Gamma_{4\text{TO}}^{\text{LO}}$	90		260	84	85	89		93	89	-0.5	-0.1
	89		252	84	60		60	88		-0.6	0.1
$\Gamma_{5\text{TO}}^{\text{LO}}$	398	395	396	398		388		395	398	1.1	
	373	360	393	366	395		394		366	1.2	0.8
$\Gamma_{5\text{TO}}^{\text{LO}}$	361	350	382	350		266		367	351	1.5	
	359	340	354	346			364		347	1.6	1.0
$\Gamma_{5\text{TO}}^{\text{LO}}$	200		348	186		197		344		2.5	
	198		343	184	342		343			2.5	1.1
$\Gamma_{5\text{TO}}^{\text{LO}}$	171		237	164		165		245		2.2	
	170		229	161	161		162		161	2.3	0.6
$\Gamma_{5\text{TO}}^{\text{LO}}$	106		159	111		112		160		-0.8	0.6
	106		156	110			112	159	113	-0.8	2.4
$\Gamma_{5\text{TO}}^{\text{LO}}$	65		80			67		81	61	-1.9	0.04
	65		79				106	78		-1.9	0.1
rms relative deviations											
		0.035	0.332	0.053	0.232	0.232	0.371	0.265	0.094		

$$\gamma_i = -\frac{d \ln \omega_i}{d \ln V} \quad (4.3)$$

where ω_i the frequency of the mode i and V is the unit cell volume of the crystal. γ_i expresses the change in phonon frequency under hydrostatic pressure. In Table 4.5 we also display and compare our calculated mode Grüneisen parameters with experimental values reported in Ref. [45]. One of the interesting properties of phonons of tetrahedrally coordinated semiconductors of diamond and zinc-blende structure is the pressure softening of their transverse acoustic (TA) modes. Mode Grüneisen parameter for TA modes of Group IV, III-V and II-VI compounds that crystallize in diamond and zinc-blende structure are all negative towards the Brillouin zone boundaries [79]. As the chalcopyrite structure is obtained by doubling and deforming the zinc-blende structure, the first Brillouin Zone (BZ) of chalcopyrite is formed by folding the zinc-blende BZ. The correspondence between the chalcopyrite zone center phonon modes and modes in zinc-blende structure has

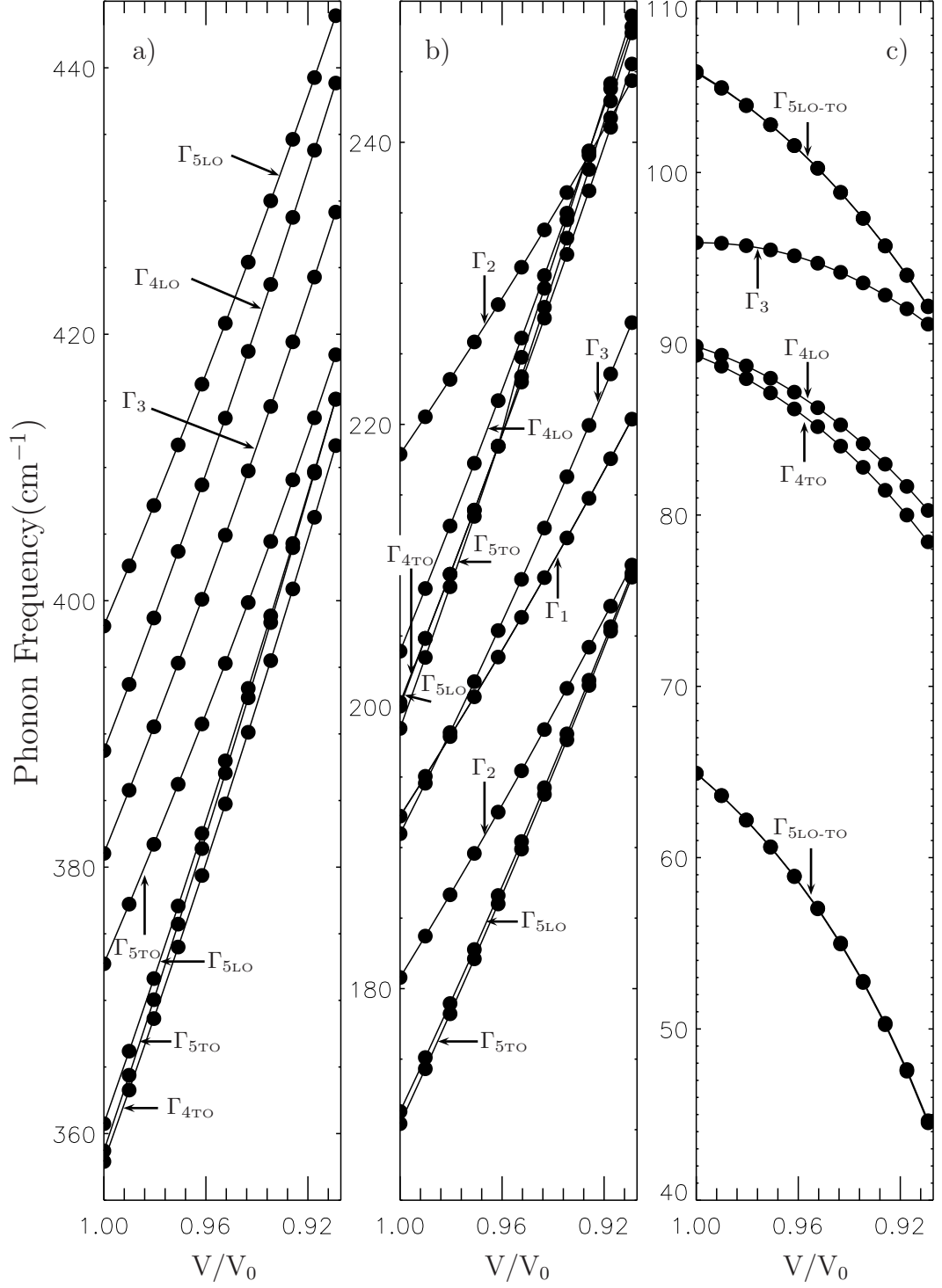


Figure 4.6: Volume dependence of phonon frequencies for CuAlSe₂ at the Γ point.

been given in Refs. [78, 80–82]. We have found three negative mode Grüneisen parameters for CuAlSe₂, which are two low frequency optical Γ_5 and one low frequency Γ_4 modes. These modes originate from X_{5ac} , W_{4ac} and W_{2ac} modes of zinc-blende structure, respectively. γ for the X_{5ac} -originated mode is similar in

magnitude and sign to values reported for zinc-blende structures [83–86]. Frequency and mode Grüneisen parameters at W point for zinc-blende materials are, unfortunately, not as well known as those at X point. From the available data [83] we would expect a smaller, but still negative Grüneisen parameter. Experimental γ for these two modes seem to be very small but positive.

For zinc-blende materials, the mode Grüneisen parameter for longitudinal optical phonon modes (γ_{TO}) is generally higher than that of transverse optical mode (γ_{LO}) [83], which is interpreted as reflection of a decrease in ionicity with increasing pressure. We have found a similar relationship for CuAlSe₂ for the polar modes (the highest frequency Γ_5 and Γ_4 modes) originating from the zone-center polar mode (Γ_{15}) of zinc-blende structure.

The volume dependent zone center phonon frequencies of CuAlSe₂ are shown in Fig. 4.6. High and intermediate frequency modes, which are displayed in Fig. 4.6a and Fig. 4.6b respectively, show a similar volume dependence; their frequency increase linearly with pressure at different rates. The volume dependence of low frequency branch, which is displayed in Fig. 4.6c, is completely different compared to the intermediate and high frequency branch. Two Γ_{5LO-TO} and Γ_{4LO-TO} modes decrease with volume reduction as expected from their negative mode Grüneisen parameter, in addition Γ_3 mode frequency starts decreasing after a volume reduction to 97%. Furthermore the volume dependence of these modes is far from linear, especially for Γ_4 mode.

4.4 Conclusion

We have investigated the pressure dependent lattice dynamical properties, such as Born effective charge tensor, Brillouin zone center phonon frequencies, and static and high frequency dielectric tensors and elastic compliance tensors of ternary semiconductor CuAlSe₂ within the density functional perturbation theory framework. We have found that the pressure dependence of these quantities show similar trends with binary tetrahedrally coordinated compounds. Under

hydrostatic pressure, the dynamical effective charges decrease. The zone center modes originating from the modes with negative Grüneisen parameter in zinc-blende materials, have negative Grüneisen parameters and the ordering of $\gamma_{TO} > \gamma_{LO}$ is respected for the zone-center chalcopyrite modes that originate from the zone-center polar mode of zinc-blende structure.

CHAPTER 5

AB INITIO PRESSURE-DEPENDENT VIBRATIONAL AND DIELECTRIC PROPERTIES OF CeO_2

5.1 Introduction

Cerium oxide(CeO_2) or ceria is a rare-earth oxide which has numerous applications in technology. CeO_2 is extensively used in modern catalytic industry because of its high oxygen storage capability. It is the major component in catalytic converters to reduce harmful emissions from automobile exhausts [87]. Cubic fluorite crystal structure of CeO_2 with a small lattice constant mismatch to Si ($\sim 0.35\%$) makes it suitable for high quality epitaxy on silicon to produce the silicon-on-insulator structures [88] and stable buffer layers of high temperature superconductors in current carrying applications [89]. CeO_2 layer on silicon which has a high dielectric constant is also attractive as a high storage capacitor [90].

In spite of wide technological usage, lattice dynamical properties of CeO_2 have been investigated only by a small number of experimental and theoretical studies. On the experimental side, the Brillouin zone center(BZC) phonon frequencies have been measured and reported by using infrared (IR) reflectivity [91–93] and Raman spectroscopy [94–100] techniques. Pressure dependence of the Raman as well as IR active BZC modes are investigated by Ref. [101]. Phonon frequencies along high symmetry directions of the Brillouin zone have been determined from inelastic neutron scattering experiments by Clausen *et al.* [102] whose reported data contains only the modes with frequencies below 500 cm^{-1} . Hydrostatic pressure dependence of structural properties of CeO_2 were investigated by high-pressure Raman [101] and X-ray diffraction [103, 104] studies and it has been found that bulk CeO_2 has a phase transition from fluorite-type to αPbCl_2 -type

structure at about 31 GPa pressure. For nanocrystalline CeO₂ the transition occurs significantly at lower pressures 26.5 GPa [105] or 22.3 GPa [106].

On the theoretical side, the whole phonon dispersion curves of CeO₂ have been studied by using phenomenological models [95, 96, 102, 107, 108] only. Model calculations have two main drawbacks; the type of interactions that are taken into account might not be enough to account for the binding properties of the solid. Furthermore, the interaction parameters of the model have to be derived from a fit to experimentally measured quantities. This is a major deficiency when the experimental results are incomplete or contradictory. For example, Sato and Tateyama [107] have employed a rigid-ion model to calculate the phonon dispersions of CeO₂. Their model uses the elastic constants as part of input parameters, but since those were not available for CeO₂ at that time, Ref. [107] chose to use those of ThO₂ which were in turn found to be quite different from the experimental ones [96]. Also, LO frequency used in their calculation appears to be much higher than the value found in infrared measurements [91, 92]. Weber *et al.* [95] has also used rigid-ion model and elastic constants predicted by their model differ markedly from the experimental values [96]. The only previous ab initio study, that we are aware of, for lattice dynamical properties of CeO₂ was by Yamamoto *et al.* [109] who have calculated the dielectric constants, Born effective charges and IR-active TO phonon frequency at BZC with density functional theory, local density approximation using ultra-soft pseudopotentials and plane wave basis sets.

An important reason for the sparseness of the first principles studies on the lattice dynamical properties of ceria has been the difficulty of treating the nature of occupation and bonding of 4f electron of cerium in a DFT-LDA framework. Recent studies on structural properties suggest a valence band picture [110] which is also found to be the case for a good description of the the lattice dynamical properties. In this study, we have studied lattice dynamical properties and their pressure dependencies for CeO₂. The dispersion curves of phonon frequencies

and mode Grüneisen parameters have been obtained using density functional and density functional perturbation theory. Born effective charges, dielectric permittivity tensor and their behavior under pressure have also studied.

This chapter is organized as follows. In section 5.2 computational details of the work is briefly reviewed. In the following section, the results of our calculations are presented, discussed and compared to experiments. Section 5.4 concludes the chapter with a brief review of the main results.

5.2 Computational Details

All of the calculations reported here were performed by using ABINIT [53] implementation of density functional theory (DFT) with a plane wave basis set for the wavefunctions and periodic boundary conditions. Cerium oxide has the fluorite structure with three atoms per primitive face-centered-cubic cell; Ce is located at (0,0,0) while two oxygens are at $\pm(1/4,1/4,1/4)$ reduced positions.

The interaction between the valence electrons and nuclei and core electrons is described by using Hartwigsen-Goedecker-Hutter (HGH) pseudopotentials [21] which use local density approximation (LDA) to the exchange correlation functional. A pseudopotential DFT description of cerium is difficult because of questions related to the nature of occupation and bonding of 4f electron as well as the appreciable overlap of 5s and 6p core orbitals with the valence orbitals. First principles calculations indicate that 4f electron should be treated as valence electron in CeO_2 and as core electron in hexagonal form of ceria Ce_2O_3 [110]. We have found that, among a number of pseudopotentials that were tested (Trouillier-Martins type norm-conserving pseudopotentials of PSPNC [111] and FHI [112] variants are tested). Although the lattice constants were found to be in reasonable agreement with the experimental values, the calculated bulk modulus was more than $\approx 30\%$ higher than the experimental one.), the HGH one is the only one which is able to reproduce the lattice dynamical properties with an acceptable accuracy. Cerium HGH pseudopotential used in this study treats semicore 5s 5p

Table 5.1: Calculated equilibrium lattice parameter (a_0), bulk modulus (B_0), its pressure derivative (B'_0) and elastic constants of CeO₂ compared to other theoretical and experimental data. (a_0 in Å, B_0 and elastic constants are in GPa and B'_0 is dimensionless.) (GGA, generalized gradient approximation; FP LMTO, fullpotential linear muffin tin orbital; PP, plane-wave pseudopotential method; PAW, projector-augmented wave method; SIC, self-interaction corrected; LSD, local spin density approximation.)

a_0	B_0	B'_0	C_{11}	C_{12}	C_{44}	Method
5.366	210.1	4.4	386	124	73	This work
5.406	230	4.0				Exp. (Ref. [103])
5.411	236	4.4				Exp. (Ref. [104])
5.411	220	4.4				Exp. (Ref. [113])
	204		403	105	60	Exp. (Ref. [96])
			450	117	57	Shell Model (Ref. [102])
5.421						PP-GGA (Ref. [114])
5.405						PP-LDA (Ref. [109])
5.39	214.7					FP-LMTO (Ref. [110])
5.45	193.5					PAW-GGA (Ref. [115])
5.384	176.9					SIC-LSD (Ref. [113])

electrons and as a result require extremely high kinetic energy cutoff; $E_{\text{cutoff}}=160$ Ha was found to be adequate for the convergence of the total energy at 1 meV level.

The Brillouin zone integrations were tested for $4 \times 4 \times 4$ and $8 \times 8 \times 8$ Monkhorst-Pack grids [16] and the $4 \times 4 \times 4$ grid was found to be enough for the convergence of elastic as well as the dynamical properties.

Lattice dynamical and elastic properties are calculated within the framework of density functional perturbation theory [24]. Technical details of the computation of responses to strain perturbations, atomic displacements and homogeneous electric fields can be found in Ref. [27] and [61], while Ref. [28] presents the subsequent computation of dynamical matrices, Born effective charges, dielectric permittivity tensors, and interatomic force constants. The details of the calculation of elastic constants in the linear response framework is given in Ref. [61].

5.3 Results

5.3.1 Atomic structure and lattice properties

Calculated equilibrium lattice parameter(a_0), bulk modulus(B_0), pressure derivative of bulk modulus(B'_0) and the elastic stiffness constants of CeO_2 are displayed in Table 5.1 along with some data in the literature. Equilibrium lattice parameter a_0 obtained by energy and force minimization has only a discrepancy of 0.8% with the experimental value. The bulk modulus and its pressure derivative is calculated by fitting to a third-order Vinet equation of state [60]. Considering the fact that the zero-point motion and thermal effects are not taken into account [116], the calculated B_0 and B'_0 values agree with the experimental values reasonably well [96, 103, 104, 113]. In the framework of DFT-LDA, our calculated values of elastic constants are compatible to experimental data of Nakajima *et al.* [96] which are obtained from Brillouin scattering measurements.

5.3.2 Born effective charges and dielectric constants

For insulators, the Born effective charge is a measure of the change in electronic polarization due to ionic displacements. For atom κ , $Z_{\kappa,\beta\alpha}^*$, quantifies, to linear order, the polarization per unit cell, created along the direction β when the atoms of sublattice κ are displaced along the direction α , under the condition of zero electric field. Computationally, its the mixed second derivative of the total energy with respect to macroscopic field component E_α and β component of the displacement of κ th particle. The form of Z^* for a particular atom depends on the symmetry of the site occupied by that atom. In CeO_2 , cerium and oxygens reside at $4a$ and $8c$ Wyckhoff positions, respectively. The point symmetry of these positions are O_h and T_d . So one would expect the effective charge tensor for both atomic species to be isotropic. The Born effective charges of cerium and oxygen are calculated to be $Z_{\text{Ce}}^* = 5.5762$ and $Z_{\text{O}}^* = -2.7881$, respectively. The calculation for the effective charges is very well converged as can be seen

Table 5.2: Calculated static and high frequency dielectric constants and zone-center infrared active phonon frequencies(in units cm^{-1}).

	ϵ_∞	ϵ_0	ω_{TO}	ω_{LO}	Ref.
Calc.	6.23	23.0	301	579	This Work
Calc.	7.5	24.3	305		[109]
Calc.	2.85	16.6			[102]
Exp.	5.31	≈ 24.5	272	595	[91]
Exp.	4.7	35.3	218	597	[92]
Exp.	6	23	283		[93]

from the fulfillment of acoustic sum rule ($\sum Z^* = 0$). The calculated values are in close agreement with those calculated by Yamamoto *et al.* [109] ($Z_{\text{Ce}}^* = 5.712$, $Z_{\text{O}}^* = -2.856$) who used a similar pseudopotential PW-LDA method.

The pressure dependence of Born effective charges can reveal important information about the bonding structure of the material. Hydrostatic pressure dependence of Z^* can be analyzed by defining a charge Grüneisen parameter γ^* as $\gamma^* = -\frac{d \ln Z^*}{d \ln V}$ where V is the unit cell volume. Grüneisen parameters of Born effective charges are found 0.37 for both Z_{Ce}^* and Z_{O}^* .

The form of the dielectric tensor is determined by the symmetry of the crystal. Since CeO_2 is a cubic material its electronic (ϵ_∞) and static (ϵ_0) dielectric tensors have only one component. We display our calculated dielectric constants along with theoretical calculations and experimentally available data in Table 5.2. The experimental ϵ_∞ values range from 4.7 [92] to 6 [93] while our computed value is 6.23. It is well known that DFT-LDA calculations overestimate the value of high frequency dielectric constant because of the band-gap problem. But also comparing the theoretical ϵ_0 value computed here (23.0) with the infrared data of Ref. [93], we can say that the agreement is excellent, though probably an accidental agreement.

For the pressure dependence of the dielectric constants one can define a Grüneisen parameter as $\gamma^\epsilon = -\frac{d \ln \epsilon}{d \ln V}$. We have found that the Grüneisen parameters for the electronic and static dielectric constants are found to be $\gamma^{\epsilon_\infty} = -0.10$ and $\gamma^{\epsilon_0} = -2.66$, respectively. These numbers indicate that both constants de-

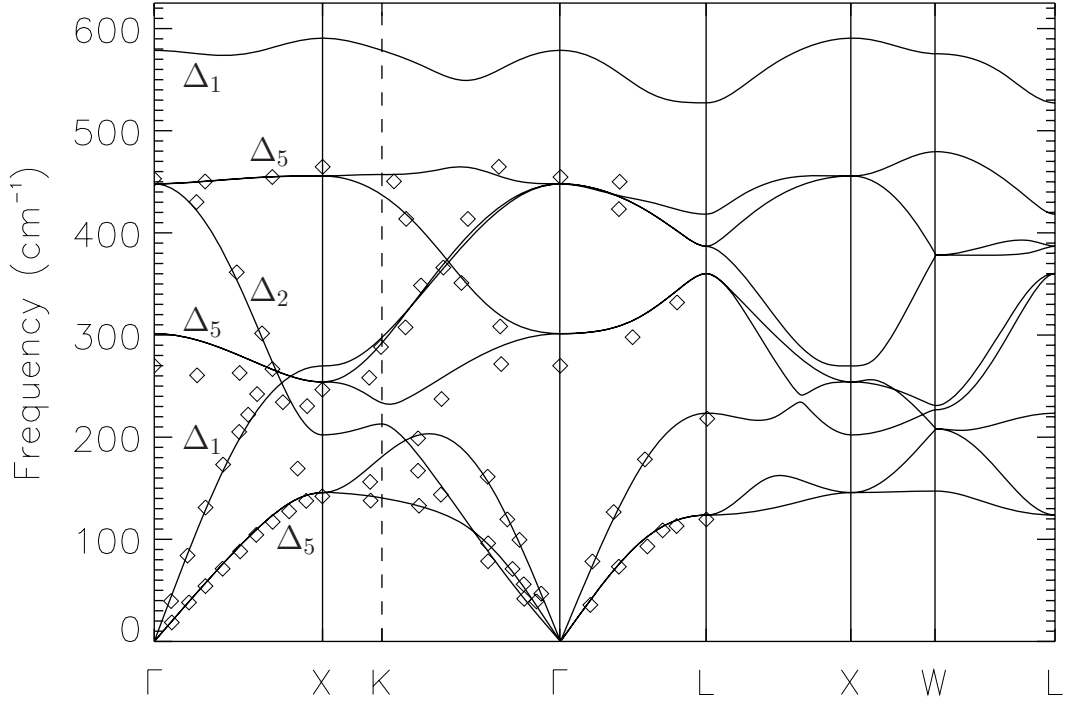


Figure 5.1: Calculated phonon dispersions of CeO₂ through high-symmetry points of Brillouin zone with neutron data(diamonds) of Ref. [102].

crease under pressure but the static part is more sensitive to pressure changes.

5.3.3 Phonons

CeO₂ has a cubic fluorite-type structure and belongs to the space group O_h^5 ($Fm\bar{3}m$). It has three atoms per primitive unit cell. Cerium atom locates at (0,0,0) and two oxygen atoms at $(\pm 0.25, \pm 0.25, \pm 0.25)$. The factor group analysis gives the decomposition of the zone center modes as $2T_{2u} + T_{1g}$. The three-fold degenerate T_{1g} mode is only Raman-active while one of T_{2u} modes is only infrared active; the other three-fold degenerate T_{2u} mode is the acoustical mode. The degeneracy of the optical T_{2u} is partially lifted by the inclusion of polarization effects which leads to LO/TO splitting.

Our calculated Γ point phonon frequencies are displayed along with several infrared data in Table 5.2. Before discussing these results, we should point out an interesting finding from the phonon calculations is the relative insensitivity of zone center phonon mode frequencies to the energy cut-off for the wavefunctions compared to the convergence of the total energy. The total energy is converged

at 1 meV level for $E_{\text{cut}} = 160$ Ha while the phonon modes seem to converge at a lower cutoff; as part of the convergence study, we have compared the Γ point vibration frequencies for $E_{\text{cut}} = 60, 100$ and 160 Ha. While there is a considerable difference between the frequencies calculated at $E_{\text{cut}} = 60$ and 100 Ha, the difference between those calculated at $E_{\text{cut}} = 100$ and 160 Ha is less than 0.5 %. The agreement between the theoretical results and experimental data is very good for the Raman and the T_{2u} LO modes. T_{2u} TO mode frequency reported by Ref. [92] seems to be too low compared to the infrared data of Refs. [91] and [93] as well as our calculated result. Compared to the frequency reported in Refs. [91] and [93], our computed T_{2u} TO frequency is $\approx 9\%$ higher. In LDA linear response calculations a difference up to 10% might be expected, but here such a large difference is seen only for one of the modes. A similar overestimation of the TO branch has been encountered in previous ab initio pseudopotential calculations of other fluorite structures such as CaF_2 [117, 118], PbF_2 [119], BaF_2 [119] and at Γ point of CeO_2 [109].

The phonon dispersions along the high symmetry directions were calculated from the interatomic force constants that were obtained from the interpolation of $4 \times 4 \times 4$ (eight irreducible q points) and $8 \times 8 \times 8$ (28 irreducible q points) grids. Overall difference between the frequencies obtained from the two grids is less than 1%. The calculated phonon dispersion relations along the Γ -X-K- Γ -L-X-W-L direction is displayed in Fig. 5.1 along with the neutron scattering data of Clausen *et al.* [102]. Overall agreement between the theoretical results and the experimental data is excellent except for the moderate disagreement mentioned in the previous paragraph. The disagreement for the T_{2u} -TO branch, which is $\approx 9\%$ around the BZ center decreases towards the zone boundary points (X and L). Another observation from the Fig. 5.1 is the near dispersionless character of the LO mode which is also found in other fluorite structures [117–119].

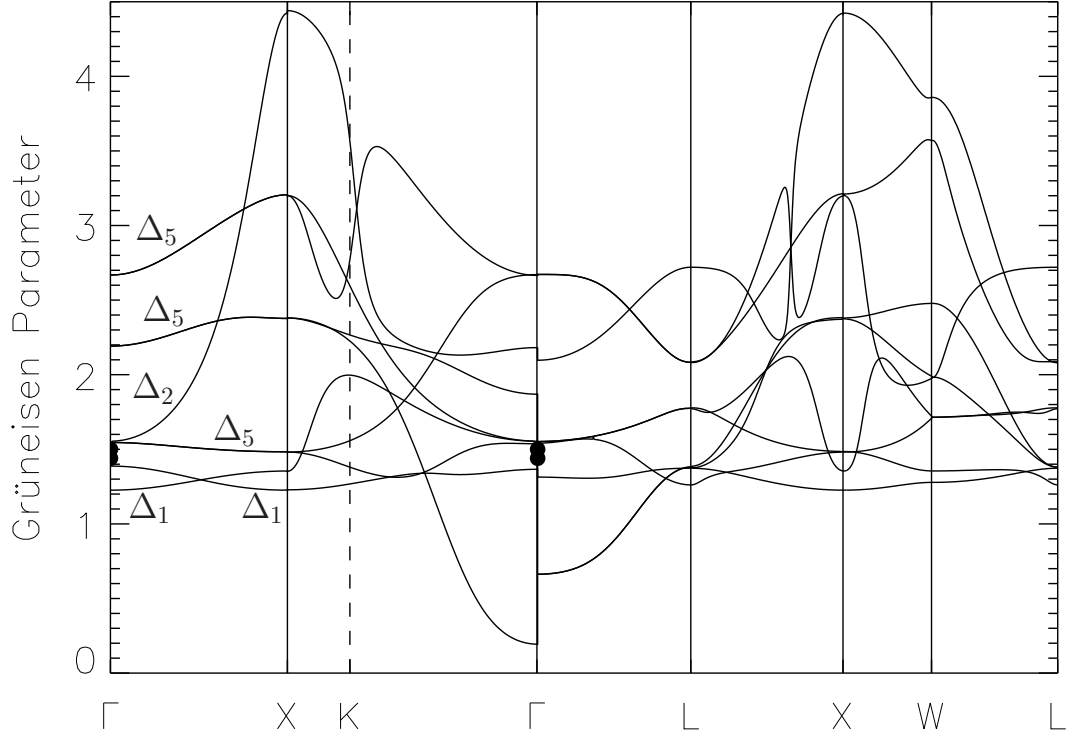


Figure 5.2: Calculated mode Grüneisen parameters of CeO₂ through high-symmetry points of Brillouin zone. Closed circles at Γ point are the experimental results of Ref. [101].

5.3.4 Mode Grüneisen parameters

The volume dependence of the phonon frequencies can be characterized by the mode Grüneisen parameters

$$\gamma_i(\mathbf{q}) = -\frac{d \ln \omega_i(\mathbf{q})}{d \ln V} \quad (5.1)$$

where $\omega_i(\mathbf{q})$ the frequency of the mode i at wave vector $\mathbf{q}$ of BZ and V is the unit cell volume of the crystal. Fig. 5.2 presents the dispersion of the mode Grüneisen parameters along the high symmetry directions of the BZ. As can be seen from the figure, γ_i s range mostly from 1 to 3 and all are positive, which indicates that all mode frequencies increase with increasing pressure. Experimental mode Grüneisen parameters of CeO₂ are available only for the zone-center modes. Kourouklis *et al.* [101] have calculated the mode Grüneisen parameters of the Raman mode ($\gamma_R = 1.44$) and infrared mode ($\gamma_{irLO} = 1.5$) of CeO₂ at zone center by using their experimental $d\omega/dP$ and bulk modulus B value from the relationship

$\gamma = (B/\omega_0)(d\omega/dP)$. Our calculated zone center mode Grüneisen parameters for T_{1g} and T_{2u} -LO modes are ($\gamma = 1.55$) and ($\gamma = 1.39$), respectively, which show a reasonably good agreement with the data reported by Ref. [101].

5.4 Conclusion

We have presented the results of first principles calculations on structural, elastic, dielectric and lattice dynamical properties of CeO_2 . Born effective charges, dielectric constants and phonon dispersion curves have been calculated by using density functional perturbation theory. Pressure dependence of these quantities have also been investigated by the determination of proper Grüneisen parameters. Our results indicate that for a proper description of these quantities one needs to take into account the semicore states of cerium and treat the 4f electron of cerium as part of valence. We have found a surprisingly good agreement between the calculated and experimental dielectric constant using the HGH pseudopotentials that possess mentioned electronic properties. Calculated phonon dispersion curves found to be in good agreement, in magnitude as well as in shape, with the neutron data throughout the high symmetry directions of the Brillouin zone except for a slight overestimation of infrared active TO mode. The overestimation of the frequency of this branch is a typical behavior in the fluorite-type materials. From the calculation of the hydrostatic pressure dependence of the phonon frequencies, we have found that all the modes have positive Grüneisen parameters, which indicates that mode frequencies increase with increasing pressure.

CHAPTER 6

VOLUME DEPENDENT VIBRATIONAL PROPERTIES OF CERIUM HYDRIDES FROM FIRST PRINCIPLES

6.1 Introduction

Hydrogen compounds of rare-earth (RE) metals have been the subject of many experimental and theoretical studies over the last 40 years. Hydrides of RE metals can form over continuous range of compositions from di- to tri-hydrides and show interesting electronic and optical properties as function of hydrogen composition; generally, the compound is metallic if the hydrogen-to-metal ratio, x , is less than ≈ 2.7 , an increase in hydrogen concentration leads to metal-insulator transition. Huiberts *et al.*[120] have shown that this transition in the hydrides of yttrium and lanthanum can be utilized to produce thin films that can be switched from a shiny mirror to a transparent window in a time on the order of seconds.

The RE-dihydrides crystallize in face-centered cubic (fcc) lattice structure with hydrogen atoms occupying the tetrahedral sites. The lattice structure of the trihydride phase is either still fcc (for LaH_3 , CeH_3 , PrH_3 and NdH_3) or hexagonal closed packed (hcp) (for YH_3 , NdH_3 , SmH_3 , ErH_3 etc.). [121] The extra hydrogens in the trihydride phase occupy the octahedral sites of the fcc or the hcp metal lattice. The hydrogen concentration dependent metal-insulator transition in RE-hydrides is not a well-understood phenomenon. The theoretical investigations in the density functional theory within the local density approximation (DFT-LDA) framework were found to be good in explaining the metallic nature of the dihydride phase. [122] The semiconducting trihydride phase proved to be more difficult to explain by using a straightforward application of the band theory. For instance, Dekker *et al.* [123] and Wang and Chou [124] have calculated

the band structure of YH_3 in a number of different geometries by using DFT-LDA scheme and found this phase to be metallic or semi-metallic with a band overlap in contrast to semiconducting phase reported by experiments. The failure to find an insulating ground state has been attributed to strong correlation effects by Ng *et al.* [125, 126] and Eder *et al.* [127] and many-body particle model calculations that take into account strong correlations among the hydrogen atoms were able to produce a band gap of 2.1 eV for LaH_3 . [125, 126] As another possible explanation of the semiconducting phase, symmetry lowering displacements of metal and hydrogen atoms were considered for the hcp YH_3 and DFT-LDA calculations were found to achieve a small band gap. [128] Since the most of the RE trihydrides are not expected to have the low symmetry structure, it is not obvious if the results of the Ref. [128] have any relevance to the electronic properties of the other RE-trihydrides. Further studies on the band structure of YH_3 and LaH_3 by using GW approximation [129–133] as well as weighted density approximation [134] (WDA) were also able to find a semiconducting phase with an optical gap of 3 eV, in close agreement with the experiments. The results of GW and WDA calculations suggest that the electronic structure of rare-earth trihydrides is similar to conventional semiconductors and the failure of DFT-LDA is related to its band-gap problem.

While the electronic and lattice dynamical properties of yttrium and lanthanum hydrides were the subject of many studies, there have been relatively less study on the properties of cerium di- and trihydrides. Lattice structure of Cerium+deuterium system have been investigated by Cheetam and Fender [135] and Titcomb *et al.* [136] by using neutron spectroscopy and by Libowitz *et al.* [137] by X-ray measurements. These studies reported a tetrahedral-octahedral substitutional disorder at non-stoichiometric compounds. The phase diagram of Ce+H system presented by Conder *et al.* [138] indicates that there are at least 10 different phases of the cerium hydride as x changes from two to three and the CeH_2 and CeH_3 both have cubic structure. The electronic structure of CeH_2 and CeH_3 was

investigated by Fujimori *et al.* [139] by using augmented plane wave method and CeH_3 was found to be semiconducting. The most complete data on the phonon dispersions of CeH_2 have been reported by Glinka *et al.* [140] and Vorderwisch *et al.* [141] measured by using inelastic neutron scattering for the non-stoichiometric $\text{CeD}_{2.12}$. Vorderwisch *et al.* [142] have, also, obtained the lattice vibrations of $\text{CeD}_{2.72}$. These experimental findings have been analyzed by phenomenological lattice dynamical model that incorporates the central force constants obtained from the fitting of measured phonon frequencies. [142] The Brillouin zone center phonons of Ce-hydrides have been investigated by IR and Raman spectroscopic techniques by Fujimori *et al.* [143] and analyzed by using a central force constant model. To the best of our knowledge, there is no first principles investigation of lattice dynamical properties of cerium hydrides.

In the present study, we aim to provide a complete set of first principles based data for the structural, elastic and lattice dynamical properties of stoichiometric form of cerium di- and tri-hydrides. We, also, report the volume dependence of these quantities which could be of use to future experimental investigations of pressure dependent studies of these compounds. The outline of the chapter is as follows: In the section 6.2 we give the details of the computational methodology and the parameters of the calculations. The calculated lattice structural parameters, elastic constants and phonon dispersions are given in the section 6.3. The volume dependence of phonon frequencies along the high symmetry directions of the Brillouin zone are discussed in section 6.3.3. Section 6.4 concludes the chapter with a brief summary of the main findings of the present study.

6.2 Computational Details

All of the calculations reported here have been obtained by using the ABINIT [53] code, which is a package that implements density functional theory with a plane wave basis set for the electronic wavefunctions and periodic boundary conditions. The interaction between the valence electrons and nuclei and core elec-

trons is described by using Troullier-Martins [20] type pseudopotentials. As the exchange-correlation potential we use the local density approximation (LDA) of Perdew-Zunger [9] functional. Both cerium and hydrogen pseudopotentials are generated using the OPIUM code. [144] The generated all electron- and pseudo-wave functions are shown in Figs. 6.1 and 6.2 for cerium and hydrogen atoms, respectively. Lattice dynamical and elastic properties are calculated within the framework of density functional perturbation theory. [24] Technical details of the computation of responses to strain perturbations and atomic displacements can be found in Ref. [27] and [61], while Ref. [28] presents the subsequent computation of dynamical matrices and interatomic force constants. The details of the calculation of elastic constants in the linear response framework is given in Ref. [61]. Cerium pseudopotential used in this study treats semicore 5p states as valence and require a kinetic energy cutoff of 60 Ha for the convergence of phonon frequencies to 0.4 meV. The Brillouin zone integrations were tested for $4 \times 4 \times 4$ and $8 \times 8 \times 8$ Monkhorst-Pack grids [16] and the $4 \times 4 \times 4$ grid was found to be enough for the convergence of elastic as well as the dynamical properties. Both CeH_2 and CeH_3 are found to be metallic in the LDA level, the Brillouin zone integrations were performed by using a Gaussian smearing with a width of 0.02 Ha. The full phonon dispersions were computed by using interatomic force constants obtained from the Fourier transform of dynamical matrices obtained on a $4 \times 4 \times 4$ $\mathbf{q}$ -grid in the fcc Brillouin zone(BZ). We extensively check the convergence of phonon frequencies with respect to the plane wave cutoff, k-point sampling of the Brillouin zone, the Fermi surface smearing parameter and $\mathbf{q}$ -point sampling for the interatomic force constants.

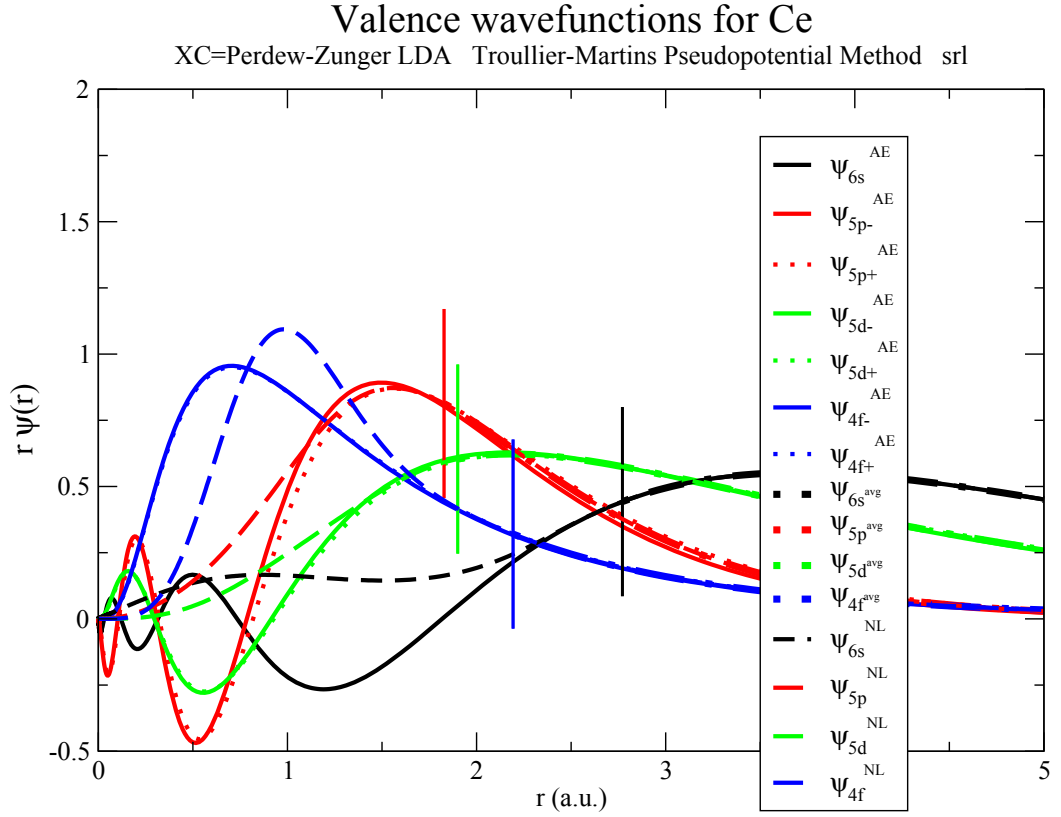


Figure 6.1: Cerium atom all electron- and pseudo-wave functions.

6.3 Results

6.3.1 Atomic structure and lattice properties

We have performed the ground-state and linear-response calculations for CeH_2 and CeH_3 to obtain the structural properties such as equilibrium lattice parameter(a_0), the bulk modulus(B_0), pressure derivative of bulk modulus(B'_0) and the elastic stiffness constants. The results are reported in Table 6.1 along with some data of other rare-earth hydrides in the literature. Equilibrium lattice parameter a_0 obtained by energy minimization has only a discrepancy of 1.3% for CeH_2 and 0.8% for CeH_3 with the experimental values. The bulk modulus and its pressure derivative is calculated by fitting to a third-order Vinet equation of state. [60] The value of CeH_3 with 83 GPa is compatible with other rare-earth trihydrides. Bulk modulus value of CeH_2 is smaller than its trihydride, so this is the case for ErH_x system.

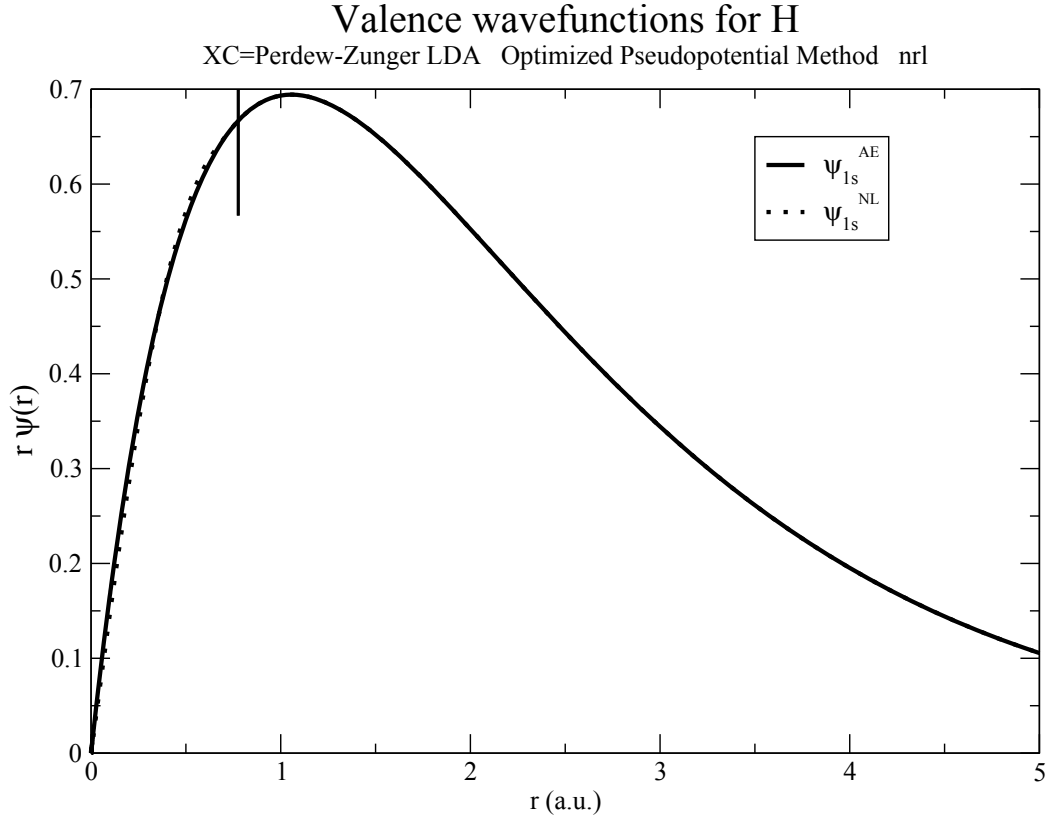


Figure 6.2: Hydrogen atom all electron- and pseudo-wave functions.

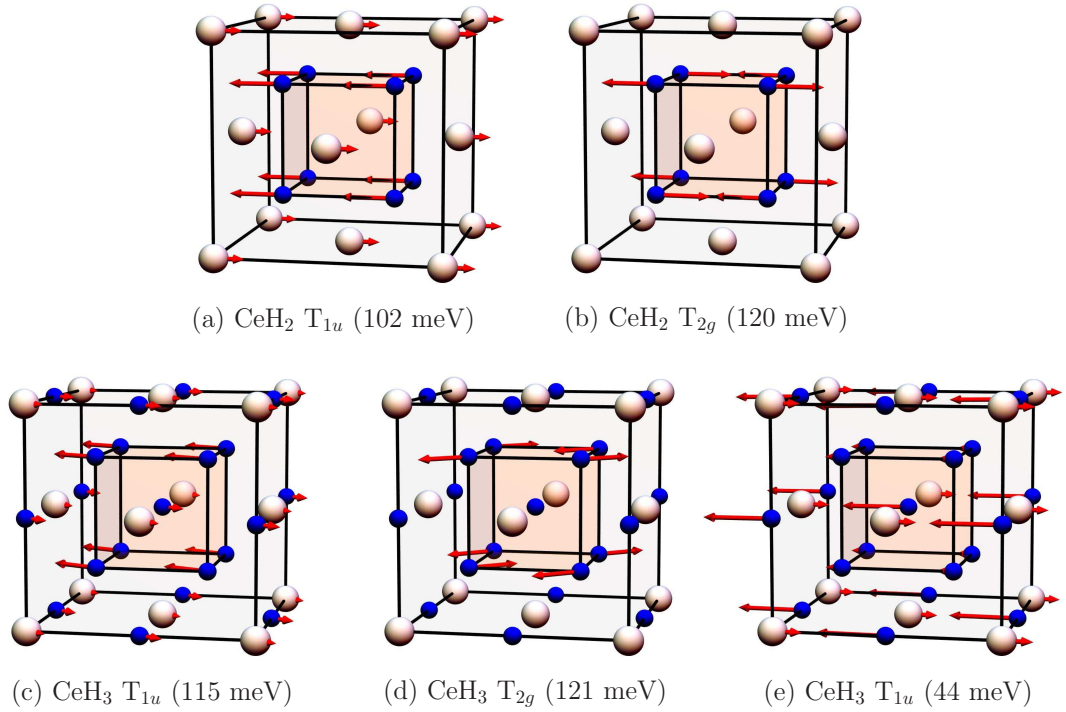


Figure 6.3: Eigendisplacements of CeH_2 and CeH_3 . Frequencies are at the zone-center.

Table 6.1: Calculated equilibrium lattice parameter (a_0), bulk modulus (B_0), its pressure derivative (B'_0) and elastic constants of CeH₂ and CeH₃ compared to available experimental data. (a_0 in Å, B_0 and elastic constants are in GPa and B'_0 is dimensionless).

	Method	a_0	B_0	B'_0	C_{11}	C_{12}	C_{44}
CeH ₂	This Work	5.655	56	4.16	75	47	65
	Expt. [145]	5.580					
CeH _{2.12}	Model [141]				87.6	43.5	52.7
CeH ₃	This Work	5.577	83	4.00	100	75	85
	Expt. [145]	5.534					
CeH _{2.72}	Model [142]				108.8	65	59.2
YH _{1.93}	Expt. [146]		95.2				
YH ₂	Expt. [147]		60.4	10.8			
ErH _{1.81}	Expt. [146]		91.1				
ErH _{1.95}	Expt. [148]		67± 3	9 fixed			
ErH _{2.091}	Expt. [148]		73± 3	8 fixed			
YH ₃	Expt. [149]		145± 5	4 fixed			
ErH ₃	Expt. [148]		81± 3	4 fixed			
GdH ₃	Expt. [150]		78± 4	4 fixed			
HoH ₃	Expt. [150]		90± 2	4 fixed			
LuH ₃	Expt. [150]		89± 4	4 fixed			
SmH ₃	Expt. [151]		80± 4	4 fixed			

Crystallographic changes upon hydridization procedure causes the materials to break up into fine powders, so it is hard to measure the elastic constants of metal- or rare-earth-hydrides. The only data that we have been able to find for the elastic constants of rare-earth-hydrides is reported by the studies of Vorderwisch *et al.* [141, 142] for non-stoichiometric CeD_{2.12} and CeD_{2.72}. In this study elastic constants are derived from the interatomic force constants which are obtained by fitting to Born-von Karman model. While the elastic constants of CeD_{2.12} reported by Ref. [141] are compatible with present results, the C_{44} value of Ref. [142] is much smaller (59.2 GPa) than our calculated value 85 GPa.

6.3.2 Phonons

CeH₂ has a cubic fluorite-type structure and belongs to the space group O_h^5 (Fm3m). The cerium atom is located at the 4a (000) Wyckoff position while

the H atoms are placed in the tetrahedral sites which are 8c (relative coordinate: (111)/4) Wyckoff position. The primitive unit cell contains three atoms. The factor group analysis gives the decomposition of the zone center phonon modes as $2T_{1u} \oplus T_{2g}$. One of the triply degenerate T_{1u} irreps form the acoustical branch while the remaining T_{1u} and T_{2g} modes are optical in character. In non-metal compounds of the same structure, the three-fold degenerate T_{2g} mode is only Raman-active while the optical T_{1u} modes is only infrared active.

CeH_3 has a BiF_3 structure with the same space group as the dihydride. The added hydrogen occupies the 4b ((111)/2) octahedral Wyckoff position. The octahedral hydrogen adds a triply degenerate T_{1u} mode to the zone center mode decomposition which becomes $3T_{1u} \oplus T_{2g}$. The new mode would be IR-active in polar materials.

We will start discussing the lattice dynamical properties of the cerium hydrides by an analysis of the zone-center modes. All the calculations reported in this section were done at the theoretical equilibrium volume. The zone-center phonon mode eigendisplacements and vibration frequencies are given in Fig. 6.3. In the mode pictures of Fig. 6.3, the cerium eigendisplacements are exaggerated by a factor of 40 compared to those of hydrogen atoms to make them visible. The T_{2g} mode in both di- and trihydride (Figs. 6.3b and d) involves the anti-symmetric breathing motion of tetrahedral hydrogen atoms and its frequency is calculated to be 120 and 121 meV for CeH_2 and CeH_3 , respectively. The calculated value of the T_{2g} mode frequency for CeH_2 is in excellent agreement with the Raman value of 119 meV reported by Zirngiebl *et al.* [152] The experimental data on T_{2g} mode of CeH_3 is more controversial. Fujimori *et al.* [143] claims this mode to be at 84 meV based on a crude linear interpolation of Raman signals from a series of non-stoichiometric cerium hydrides. Since this mode has the same pattern of tetrahedral hydrogen displacements and the trihydride phase a slightly contracted lattice constant compared to the dihydride phase, one would expect its frequency to be higher in CeH_3 than that in CeH_2 . The T_{1u} modes in both

compounds involve anti-phase motion of Ce and H atoms (Figs. 6.3a and c). Our calculated T_{1u} frequency of 102 meV for CeH_2 is in reasonable agreement with the value of 105 meV which is reported as estimation based on the IR reflectivity measurements by Fujimori *et al.* [143] The anti-phase motion of H_t against the Ce and H_o atoms forms the high frequency T_{1u} mode of CeH_3 at 115 meV, while the anti-phase displacement of the hydrogen lattice against the metal lattice (Fig. 6.3e) is the low frequency T_{1u} mode at 44 meV.

The calculated phonon density of states and dispersions along the Γ -X-K- Γ -L-X-W-L high symmetry directions of the Brillouin zone for CeH_2 and CeH_3 are displayed in Figs. 6.4 and 6.5, respectively. For comparison purposes, in Fig. 6.4, we also display the experimental inelastic neutron scattering data of Vorderwisch *et al.* [141] for $CeD_{2.12}$ and our calculated CeD_2 phonons (which are obtained by substituting the deuterium mass instead of hydrogen mass in the dynamical matrix). Similarly, neutron scattering data for $CeD_{2.72}$ of Ref. [142] is presented along with the computed dispersions of CeD_3 in Fig. 6.5. The agreement between the experimental data and computed dispersions for both of the compounds (ex-

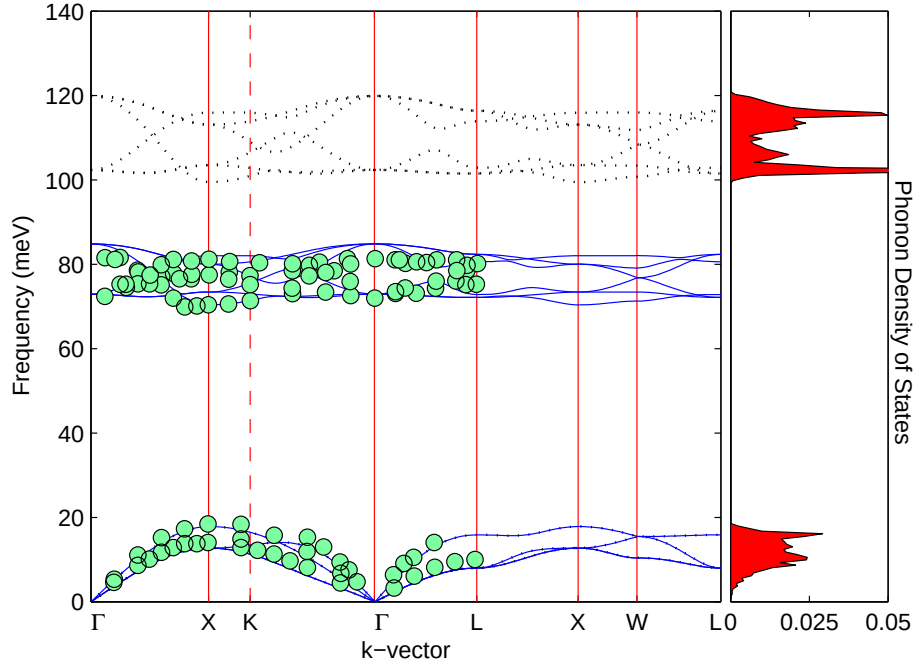


Figure 6.4: Calculated phonon dispersions and normalized DOS of CeH_2 (dotted lines) and CeD_2 (solid lines) through high-symmetry points of Brillouin zone along with the neutron data (circles) for $CeD_{2.12}$ (Ref. [141]).

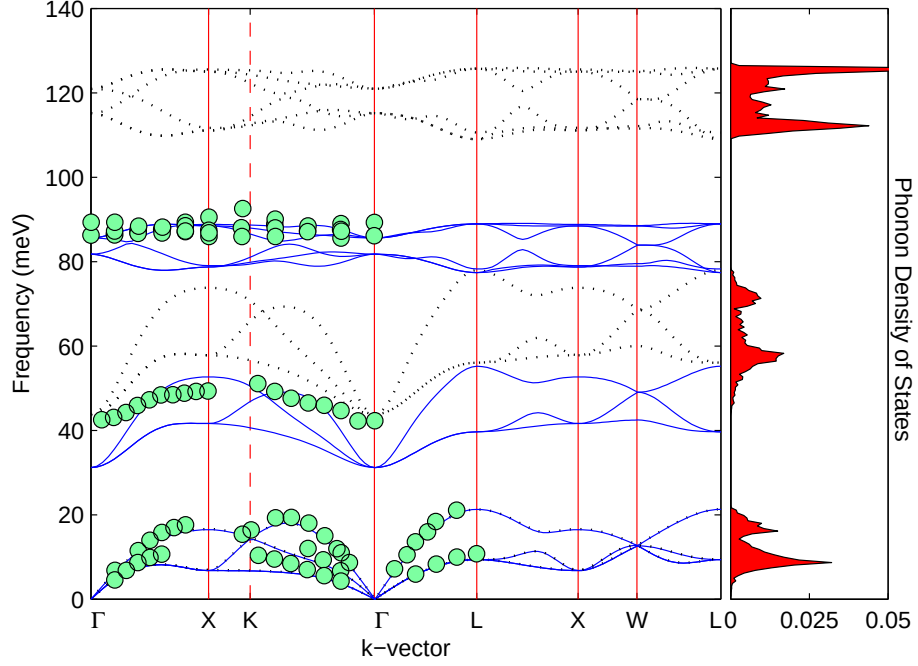


Figure 6.5: Calculated phonon dispersions and normalized DOS of CeH_3 (dotted lines) and CeD_3 (solid lines) through high-symmetry points of Brillouin zone along with the neutron data (circles) for $\text{CeD}_{2.72}$ (Ref. [142]).

cept the low frequency optical T_{1u} mode of CeH_3) is reasonable if one takes into account the fact that the experimental data is not collected for the stoichiometric compounds. Also, the experimental Ref. [142] reports instrumentation problems in measuring all the branches of low frequency optical T_{1u} phonons. The most striking feature common in Figs. 6.4 and 6.5 is the clear and wide separation of the acoustical and optical branches. This finding is inline with what one expects considering the phonon eigendisplacements discussed above and the huge mass difference between the hydrogen and cerium atoms; cerium motion dominates the acoustical branch, while optical modes are almost purely H related. The bimodal phonon DOS is common to dihydrides of other rare-earth metals also. [153–155] The main modification in the phonon dispersion as octahedral sites are filled with hydrogen seems to be shifting of the upper optical branches by approximately 8 meV to higher frequencies, and stiffening (softening) of the acoustic longitudinal (transverse) branches. This change is, at least partly, related to the reduction in the equilibrium volume. The bandwidth of all phonon branches is around 12 meV for both of the compounds. An interesting feature in the Fig. 6.5 is the disper-

sion of the low frequency optical T_{1u} mode which is very similar to the acoustical modes in shape. This finding is related to the fact that the displacement pattern of this mode involve collective motion of hydrogen lattice in the same direction while Ce atoms are almost stationary.

6.3.3 Mode Grüneisen parameters

The volume dependence of the phonon frequencies can be characterized by the mode Grüneisen parameters

$$\gamma_i(\mathbf{q}) = -\frac{d \ln \omega_i(\mathbf{q})}{d \ln V} \quad (6.1)$$

where $\omega_i(\mathbf{q})$ the frequency of the mode i at wave vector $\mathbf{q}$ of BZ and V is the unit cell volume of the crystal. Fig. 6.6 presents the dispersion of the mode Grüneisen parameters of CeH_2 for acoustic and optical modes along the high symmetry directions of the BZ. As can be seen from the figure, for optical modes $\gamma(T_{1u})$ and $\gamma(T_{2g})$ are positive with similar magnitudes for both of the modes. The γ of transverse acoustical modes (γ_{TA}) of CeH_2 are negative for most of the high-symmetry paths, except around X point; the most negative value of γ_{TA} is -3 which is at around the center of the BZ when $\mathbf{k}$ approaches Γ from the K direction. Negative transverse acoustic mode Grüneisen parameters indicate a softening of the phonon frequencies under compression of the lattice and are thought to be precursor of pressure induced structural phase transitions. No experimental data exists on the mode Grüneisen parameters of CeH_2 but negative $\gamma_i(\mathbf{q})$ are common to tetrahedrally bonded semiconductors of group IV and III-V compounds [156] and are the source of negative thermal expansion at low temperatures.

The Grüneisen parameters of CeH_3 for the high frequency T_{1u} and T_{2g} , H_o related T_{1u} and acoustical modes are displayed in Figs. 6.7a, b, and c, respectively. The most important difference between Figs. 6.6 and 6.7 is observed in the acoustical modes. The $\gamma_{ac}(\mathbf{q})$ of CeH_3 are found to be all positive which might be related to octahedral hydrogen's strengthening the lattice as is also ev-

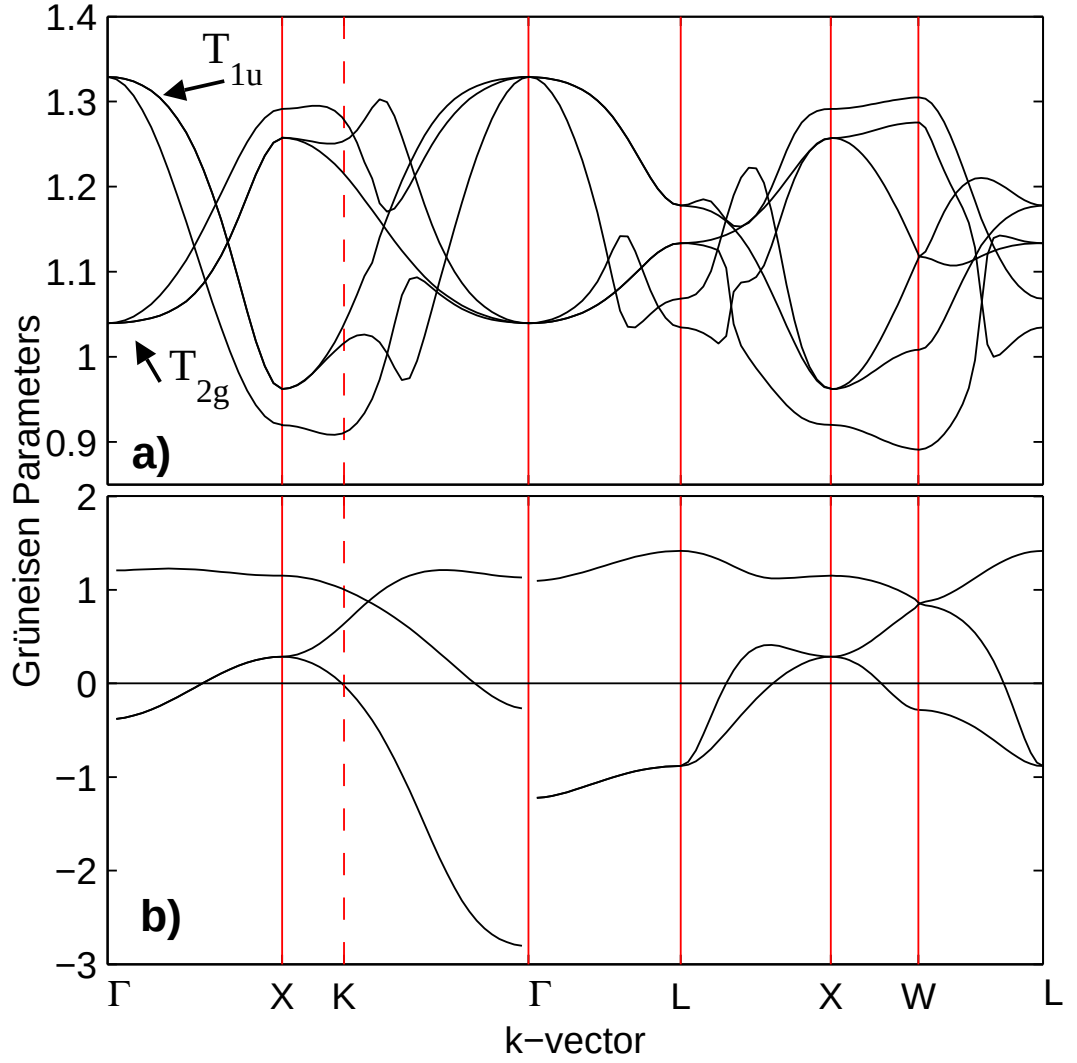


Figure 6.6: Calculated mode Grüneisen parameters of CeH_2 through high-symmetry points of Brillouin zone. a) Optical T_{1u} and T_{2g} modes b) Acoustic T_{1u} modes

identified by a shorter lattice constant for the trihydride compared to dihydride phase. The $\gamma_{ac}(\mathbf{q})$ for CeH_3 in Fig. 6.7c are zero or nearly zero at the zone center Γ and zone boundary L points while its value around X point is 8 which is a very high value for the Grüneisen parameter of any materials. The tetrahedral hydrogen related optical mode $\gamma(T_{1u})$ and $\gamma(T_{2g})$ (Fig. 6.7a) are similar to their counterparts in CeH_2 albeit with somewhat lower value for $\gamma(T_{1u})$; at the zone center $\gamma(T_{1u})=1.32$ (1.13) and $\gamma(T_{2g})=1.04$ (1.05) for CeH_2 (CeH_3). The $\gamma_{T_{1u}}(\mathbf{q})$ of octahedral hydrogen related optical mode (Fig. 6.7b) has values between ~ 2 (zone boundaries) and ~ 4 (zone center). Its shape is an inverted form of the

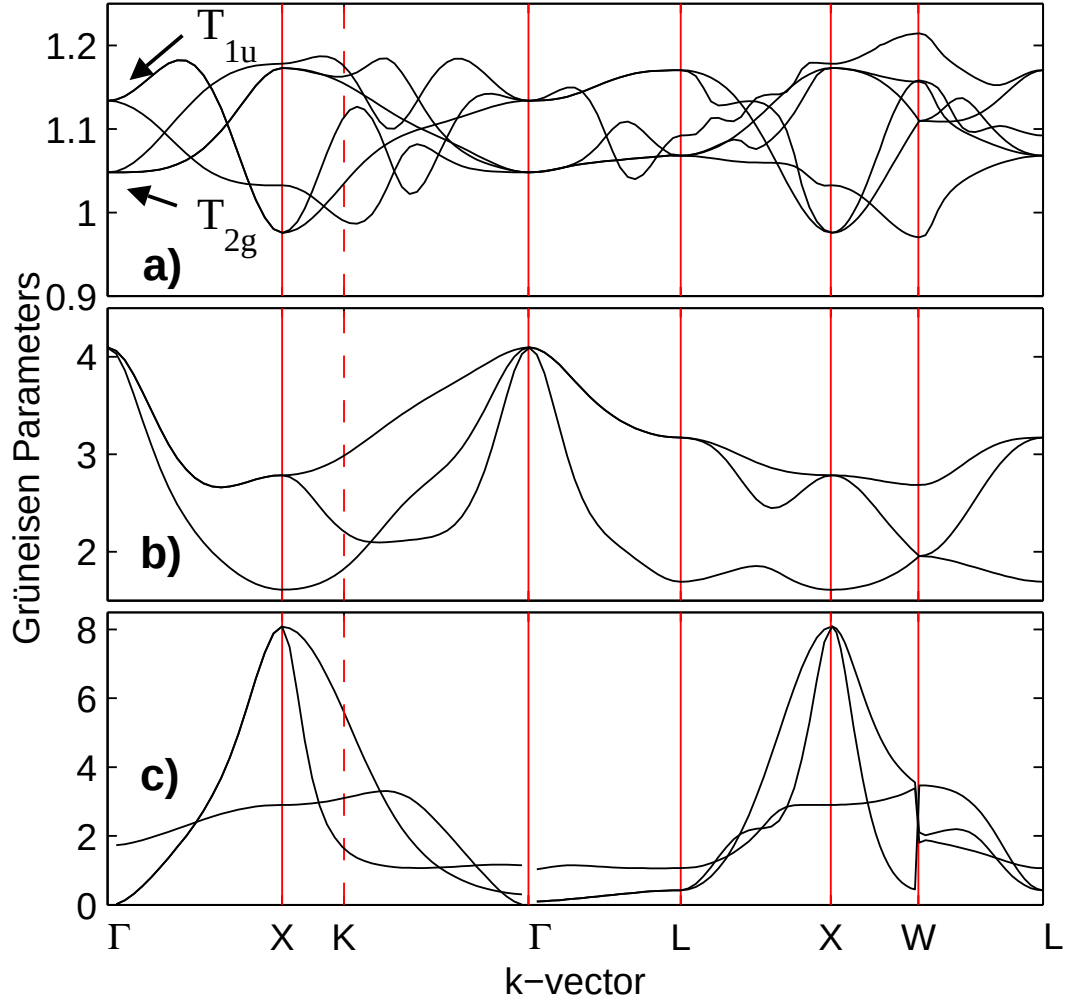


Figure 6.7: Calculated mode Grüneisen parameters of CeH_3 through high-symmetry points of Brillouin zone. a) Optical T_{1u} and T_{2g} modes b) Optical T_{1u} modes and c) Acoustic T_{1u} modes

phonon dispersion itself. At the zone center, the $\gamma(T_{1u})$ of the H_o is found to be approximately four times larger than the H_t related $\gamma(T_{1u})$. A similar ratio is found in the investigation of pressure dependent IR reflectivity of YH_3 by Ohmura *et al.* [157] and conjectured to be a manifestation of different bonding nature of octahedral and tetrahedral hydrogens with the metal.

6.4 Conclusion

We presented the results of first principles calculations on the volume dependent structural, elastic and lattice dynamical properties of di- and tri-hydrides of the rare-earth cerium metal. The calculated lattice constants are in good agreement

with the experimental data. There are no elastic constants data for the considered materials, but a comparison with the similar rare-earth hydrides and previous model calculations indicates that the calculated values are reasonable. On the structural properties, we have found that the unit cell volume decreases as the octahedral sites of the fcc lattice is filled with hydrogen to form CeH_3 from CeH_2 . This contraction with increasing H concentration is common with other rare-earth metal hydrides and is attributed to the H_o -metal hybridization. The trend in bulk modulus and the elastic stiffness constants is the opposite; B_0 and C_{ij} of CeH_3 are around 30% higher than those of CeH_2 .

We, also, have calculated and presented the phonon dispersions and their volume dependence as characterized by the mode Grüneisen parameters in the density functional perturbation theory framework. The phonon density of states are found to be in bimodal and trimodal form for CeH_2 and CeH_3 , respectively. The acoustical branch is dominated by the massive metal atoms and despite small differences exist as explained in the Section 6.3.2, the most of acoustical modes exist as a band at 15 ± 5 meV range for both of the compounds. The tetrahedral hydrogen related modes form the high frequency optical branch which is located in 100-120 meV range for CeH_2 and 110-130 meV for CeH_3 . The vibrational band related to octahedral hydrogens of CeH_3 has a wider dispersion which is centered around 60 meV with a width of 20 meV. The most important finding about the mode Grüneisen parameters is the existence of the negative transverse acoustical mode parameters for the dihydride phase. Such a negative $\gamma_{ac}(\mathbf{q})$, which is also common in tetrahedrally coordinated common semiconductors, implicates pressure dependent structural phase transition paths and low temperature negative thermal expansion coefficient which can be studied experimentally. We, also, found a relatively higher mode Grüneisen parameters for the H_o mode compared to H_t of CeH_3 .

CHAPTER 7

AB INITIO LATTICE DYNAMICS AND THERMODYNAMICS OF LaB_6 AND CeB_6

7.1 Introduction

The thermodynamical properties of a solid are determined mostly by the vibrational degrees of freedom, since, generally the electronic degrees of freedom play a noticeable role only for metals at very low temperatures [13]. Thanks to recent improvements in computing power and the development of density functional perturbation theory, a complete knowledge of the vibrational spectrum, with sufficient accuracy is within reach for a wide range of solids [24]. While in principle the temperature dependence of the phonon frequency depends on phonon anharmonic contributions as well as electronic ones, the thermodynamical properties of solids are generally studied in quasi-harmonic approximation. In the quasi-harmonic approximation [13], the crystal free energy is calculated by adding a dynamical contribution which is approximated by the free energy of a system of harmonic oscillators corresponding to the crystal vibrational modes (phonons)-to static contribution- which is accessible to standard DFT calculations. The former can be calculated by a variety of first principle methods [24]. Calculations based on various semi-empirical [158–160] as well as on the first principles methods [161–163] shows that the quasiharmonic approximation provides a reasonable description of the thermodynamical properties of many bulk materials below the melting point.

In *ab initio* quasiharmonic calculations there are two main approaches; one is to compute the temperature dependent phonon free energy from phonon frequencies calculated at different lattice constants and find the equilibrium lattice

properties by fitting an equation of state to total free energy [163–165]. Another approach is to calculate the phonon frequencies and their first and second volume derivatives at zero temperature and then calculate all thermal quantities in terms of these quantities by varying only the temperature of the thermal occupation number in the corresponding formula [84, 166].

In the last decade, specific heat, entropy, phonon contribution to the free energy and atomic temperature factors for SiO_2 in the α -quartz phase and in the high-pressure stishovite phase [167], thermal expansion coefficients of Li, Na and Al [165], thermal properties and Grüneisen parameters of Ag [164], pressure and temperature dependent thermodynamical properties of Ag [163], thermodynamic properties of Al_3Li [168], Cu [169], Al and W [166], were calculated in the DFT level within quasiharmonic approximation.

In this chapter, we apply the linear-response method to calculate the phonon dispersions and thermal properties, such as mode Grüneisen parameters, the temperature dependence of volume expansion coefficient, bulk modulus, and heat capacity of two hexaborides; LaB_6 and CeB_6 by calculating the free energy of these materials for a series of lattice constants and fitting the resulting free energy to an equation of state at several temperatures.

The chapter is organized as follows. In Sec. 7.2, a brief description of theory and technicalities of the computational procedure is given. In Sec. 7.3 we present and discuss the results we have obtained and compare them with available experimental data.

7.2 Theoretical and Computational Details

The equation of state (EOS) of a crystal at a given temperature T is constructed as [7]

$$P = - \left(\frac{\partial F}{\partial V} \right)_T \quad (7.1)$$

where F is the Helmholtz free energy. In the quasiharmonic approximation, F is given by

$$F(V, T) = E(V) + F_{\text{vib}}(\{\omega_{\mathbf{q}j}(V)\}, T) \quad (7.2)$$

where $E(V)$ is the static contribution to the internal energy at volume V and can be easily obtained from standard DFT calculations. F_{vib} is the vibrational contributions to free energy and is given by

$$F_{\text{vib}}(\{\omega_{\mathbf{q}j}(V)\}, T) = k_B T \int_0^{\omega_L} \ln \left(2 \sinh \frac{\hbar \omega}{2k_B T} \right) g(\omega) d\omega \quad (7.3)$$

where k_B is the Boltzman constant, ω_L is the largest phonon frequency, $g(\omega)$ is the phonon density of states

$$g(\omega) = \sum_{\mathbf{q}j} \delta(\omega - \omega_{\mathbf{q},j}(V)). \quad (7.4)$$

where $\omega_{\mathbf{q},j}(V)$ is the frequency of the j th phonon mode at the wave vector $\mathbf{q}$ in Brillouin zone at lattice volume V .

The specific heat capacity at constant volume in the quasiharmonic approximation is given by

$$C_v = k_B \int_0^{\omega_L} \left(\frac{\hbar \omega}{2k_B T} \right)^2 \text{csch}^2 \left(\frac{\hbar \omega}{2k_B T} \right) g(\omega) d\omega \quad (7.5)$$

Due to anharmonicity, the heat capacity at a constant pressure, C_p , is different from the heat capacity at a constant volume, C_v . At high temperatures, C_v goes to a constant which is given by classical equipartition law: $C_v \approx 3Nk_B$, where N is the number of atoms in the system, while C_p , which is what experiments determine directly, is proportional to T . C_p can be obtained from C_v by

$$C_p = C_v + \alpha_v^2 B V T \quad (7.6)$$

where α_v is the volume thermal expansion coefficient and B is the bulk modulus which is given by

$$B(T) = V \left(\frac{\partial^2 F}{\partial V^2} \right)_T \quad (7.7)$$

The vibrational contribution to the entropy of the crystal is given by

$$S = k_B \int_0^{\omega_L} \left[\frac{\hbar\omega}{2k_B T} \coth \frac{\hbar\omega}{2k_B T} - \ln \left(2 \sinh \frac{\hbar\omega}{2k_B T} \right) \right] g(\omega) d\omega \quad (7.8)$$

The present results have been obtained thanks the use of the ABINIT code [53], that is based on pseudopotentials and planewaves. It relies on an efficient Fast Fourier Transform algorithm [54] for the conversion of wavefunctions between real and reciprocal space, on the adaptation to a fixed potential of the band-by-band conjugate gradient method [5] and on a potential-based conjugate-gradient algorithm for the determination of the self-consistent potential [55]. Technical details of computation of responses to atomic displacements and subsequent computation of dynamical matrices can be found in Refs. [27] and [28].

The interaction between the valence electrons and nuclei and core electrons is described by using Troullier-Martins [20] and optimized type pseudopotentials. As the exchange-correlation potential we use the local density approximation (LDA) of Perdew-Wang [10] functional. Lanthanum, cerium and boron pseudopotentials are generated using the OPIUM code. [144] The generated all electron- and pseudo-wave functions are shown in Figs. 7.1, 7.2 and 7.3 for cerium, lanthanum and boron atoms, respectively.

Rare-earth hexaborides crystallize cubic CsCl-type structure and belongs to the space group O_h^1 (Pm3m). The rare-earth atom is located at the 1a (0, 0, 0) Wyckoff position while the octahedral boron molecule B_6 is placed in the site which is at 6f Wyckoff position with relative coordinate: (1/2, 1/2, x). The primitive unit cell contains seven atoms. For both LaB_6 and CeB_6 , sums over the BZ are found enough to perform on a mesh of a $4 \times 4 \times 4$ Monkhorst-Pack

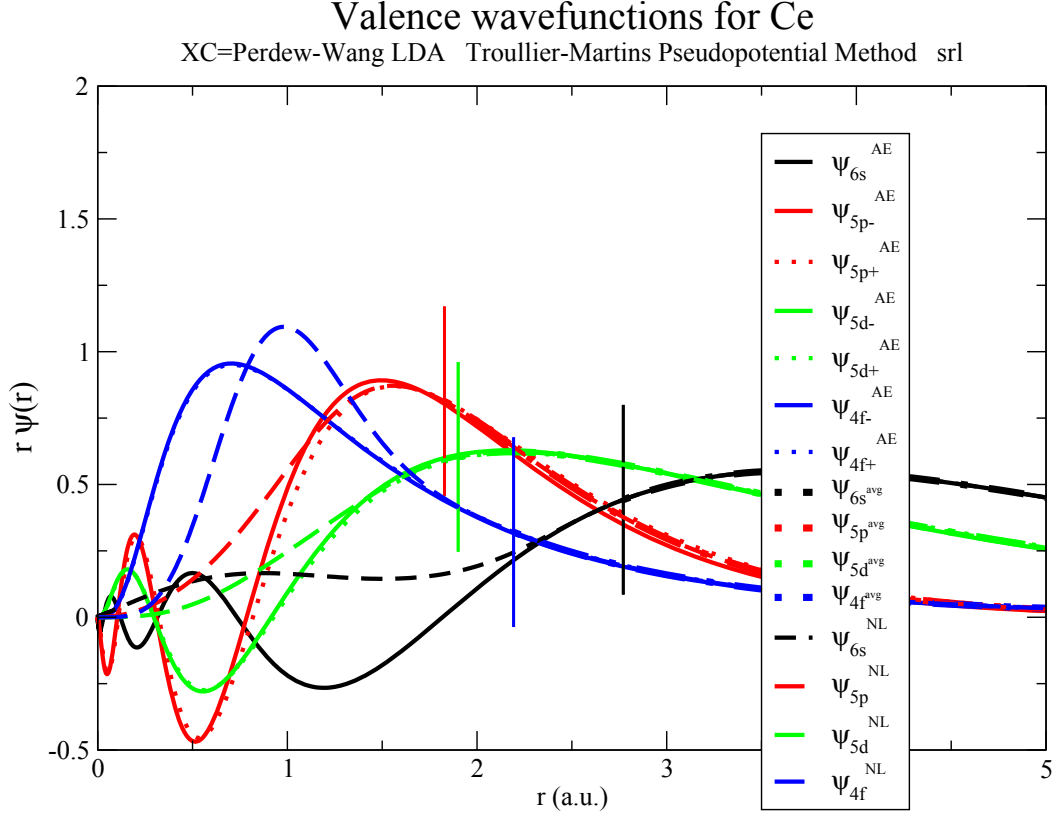


Figure 7.1: Cerium atom all electron- and pseudo-wave functions.

grid[16] which corresponds to 4 points for simple cubic structure. In order to deal with possible convergence problems for metals, Methfessel-Paxton scheme with smearing parameter $\sigma = 0.02$ Ha is used. The cutoff energies of 35 and 55 Ha were used for LaB_6 and CeB_6 calculations, respectively. Phonon dynamical matrices were computed *ab initio* for a $4 \times 4 \times 4$ $\mathbf{q}$ point mesh; Fourier interpolation was then used to obtain the dynamical matrices on a $64 \times 64 \times 64$ $\mathbf{q}$ point mesh, which is used for the calculation of all quantities that involve an integration over the phonon modes. This mesh is good for the convergence of the calculation of thermal quantities.

To summarize, the following quantities were obtained from DFT and DFPT calculations: (i) Total energies at a range of lattice constants, (ii) For each lattice constant, the dynamical matrices for the $4 \times 4 \times 4$ set of $\mathbf{q}$ points; Fourier interpolation was then used to obtain the dynamical matrices on the $64 \times 64 \times 64$ set of $\mathbf{q}$ points. This set of results was then used to calculate the thermal behavior,

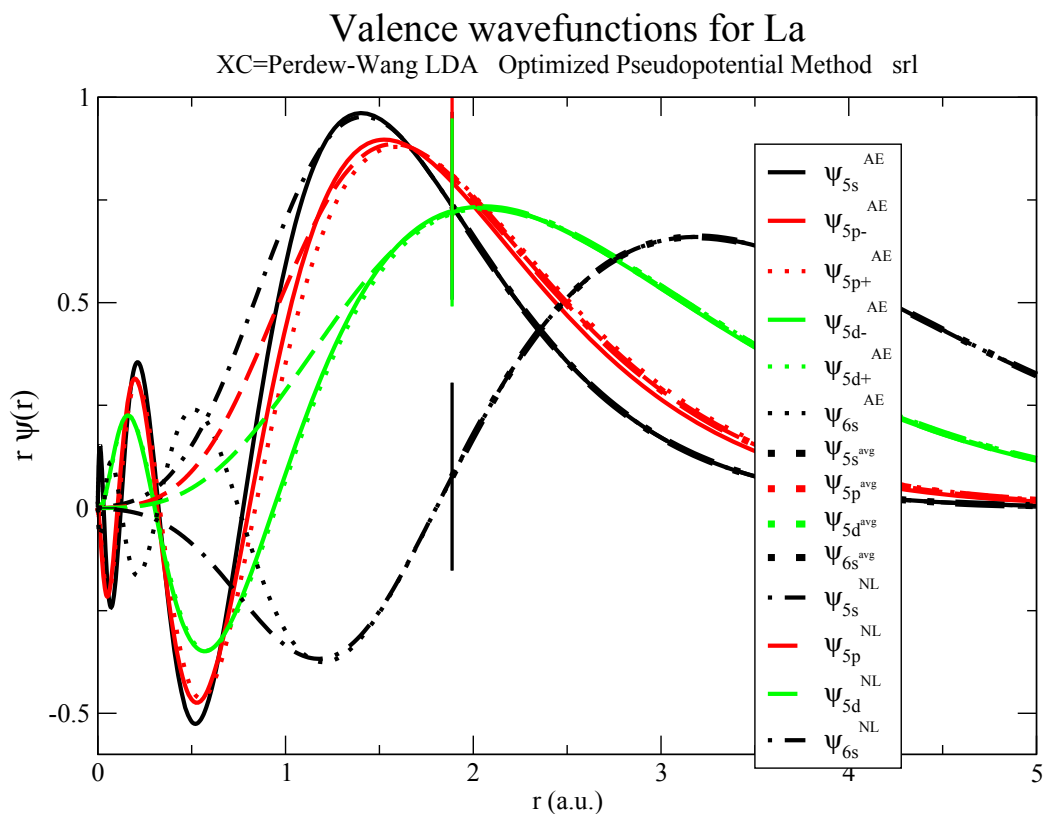


Figure 7.2: Lanthanum atom all electron- and pseudo-wave functions.

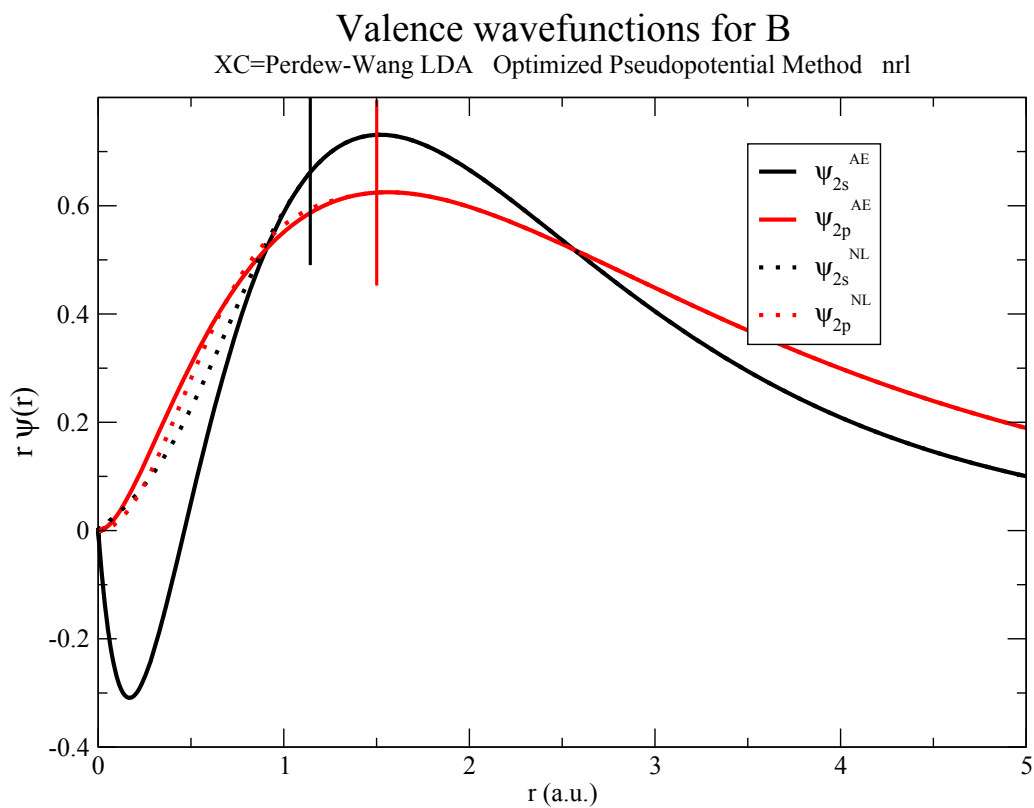


Figure 7.3: Boron atom all electron- and pseudo-wave functions.

as described below.

7.3 Results and Analysis

The static results for lattice constant a_0 , the bulk modulus B_0 and the pressure derivative of the bulk modulus B'_0 are obtained by fitting the static total energies versus lattice constant to Vinet equation of state [60].

$$E(V) = E_0 + 9B_0V_0 \left(e^{A(1-x)} \left[A^{-1}(1-x) - A^{-2} \right] + A^{-2} \right) \quad (7.9)$$

where V_0 is the equilibrium volume, $x = (V/V_0)^{1/3}$, B_0 is the bulk modulus, and $A = 3(B'_0 - 1)/2$ (B'_0 is the pressure derivative of the bulk modulus). The temperature dependent parameters of EOS (E_0 , V_0 , B_0 , and B'_0) obtained from the least square fitting procedure can be used to calculate the temperature dependent pressure-volume relations and pressure and temperature dependence of bulk modulus as

$$P(V) = \left(\frac{3(1-x)}{x^2} \right) B_0 e^{A(1-x)} \quad (7.10)$$

and

$$B(P) = -B_0 e^{(A(1-x))} \left((1-A)x^{-1} - 2x^{-2} + A \right) \quad (7.11)$$

Table 7.1 shows the equilibrium lattice parameter a_0 and positional parameter x for the materials LaB₆ and CeB₆ along with some experimental and theoretical results. The calculated quantities of the present work are in a very good agreement with the experimental ones. The calculated lattice parameter of LaB₆ has 0.6% and of CeB₆ has only 0.4% discrepancy with the measurements.

The calculated and experimental bulk modulus, its pressure derivative and elastic constants are given in Table 7.2. Experimental results given in the table show large discrepancies because of using different techniques. For LaB₆, our results are in a very good agreement with the recent study of Ref.[171] except elastic constant C_{12} which has a difference about 18%. The only available exper-

Table 7.1: Lattice Parameters for LaB₆ and CeB₆. (FP-LMTO: Full potential linear muffin-tin orbitals, PW-PP: Plane-wave pseudopotential method)

Comp.	Method	$a_0(\text{\AA})$	x_B	Method	Ref.
LaB ₆	This Work	4.1277	0.1997	PW-PP	
	Expt.	4.1527(1)	0.1993(1)	10K	[170]
	Expt.	4.1528(1)	0.1994(1)	100K	[170]
	Expt.	4.1542(1)	0.1994(1)	200K	[170]
	Expt.	4.1561(1)	0.1995(1)	300K	[170]
	Expt.	4.1565			[171]
	Calc.	4.130		FP-LMTO	[171]
CeB ₆	This Work	4.1542	0.2002	PW-PP	
	Expt.	4.1397(2)	0.19923(6)	298K	[172]
	Expt.	4.1323(7)	0.19909(11)	100K	[172]
	Expt.	4.1396(4)	0.19925(14)		[173]
	Calc.	4.098	0.200	PW-PP	[114]

Table 7.2: Bulk Modulus and Elastic Constants

Comp.	Method	$B_0(\text{GPa})$	$B'_0(a.u.)$	C_{11}	C_{12}	C_{44}	Method	Ref.
LaB ₆	This Work	180	3.79	466	37	88	PW-PP	
	Expt.	172	-1					[175]
	Expt.	163		453.3	18.2	90.1		[176]
	Expt.	142±15						[177]
	Expt.	184		463	45	89		[171]
	Calc.	185					FP-LMTO	[171]
CeB ₆	This Work	173	3.91	452	34	98	PW-PP	
	Expt.	166	3.15					[178]
	Expt.			406	-93	78		[174]

imental elastic constants study [174] reports a negative C_{12} value which is not achieved in our calculations. Our calculated elastic constants of LaB₆ and CeB₆ are compatible each other.

The experimental [179, 180] and calculated phonon dispersions along high symmetry directions of the Brillouin zone for LaB₆ and CeB₆ are displayed in Figs. 7.4 and 7.5, respectively. The phonon frequencies in Figs. 7.4 and 7.5 are calculated at the static theoretical lattice constant. For both LaB₆ and CeB₆ experimental phonon dispersion frequencies are available only up to 60 meV and

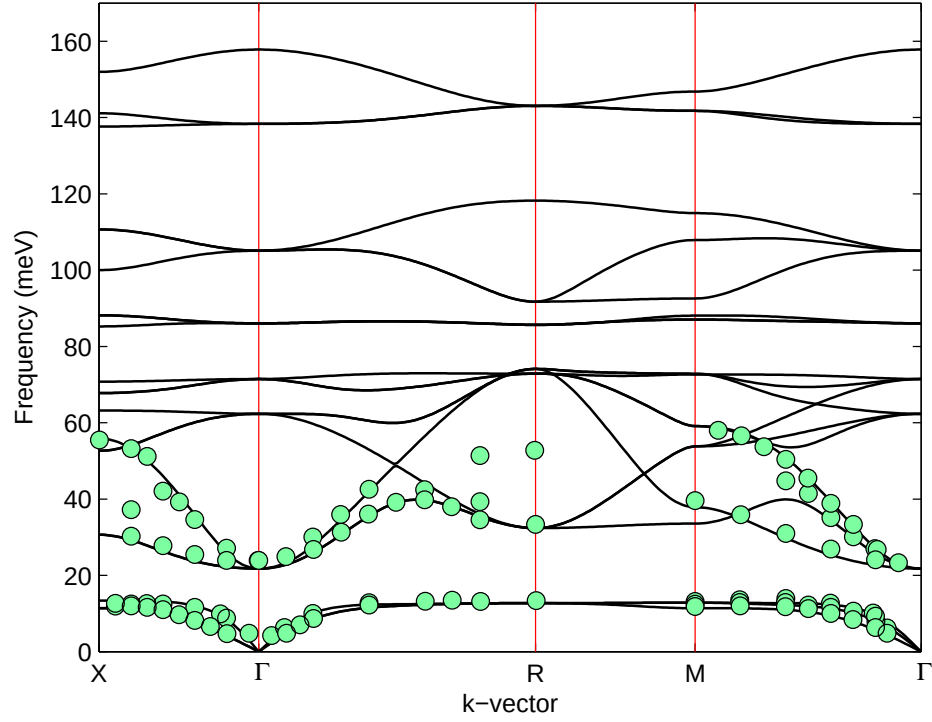


Figure 7.4: Phonon dispersions for LaB_6 . Experimental values (dotted) are from Ref. [179].

have a good agreement with the calculated results.

The anharmonicity of the vibrations can be examined by computing the mode Grüneisen parameters, defined by

$$\gamma_{\mathbf{q}\lambda} = -\frac{V}{\omega_{\mathbf{q}\lambda}(V)} \frac{\partial \omega_{\mathbf{q}\lambda}(V)}{\partial V} \quad (7.12)$$

where V is the volume of the unit cell. The mode Grüneisen parameters of LaB_6 and CeB_6 are found to be positive throughout the high symmetry points of the Brillouin zone which are displayed in Figures 7.6 and 7.7 respectively. Since the acoustic branches vanish linearly with a slope depending on the direction of approach to the Brillouin zone center, the corresponding Grüneisen mode parameters are discontinuous at the Γ point.

The details of the calculation of phonon density of states and thermodynamical quantities are explained in Ref. [167]. Phonon density of states is obtained by a root sampling (or histogram) method. Sampling a $64 \times 64 \times 64$ Monkhorst-Pack

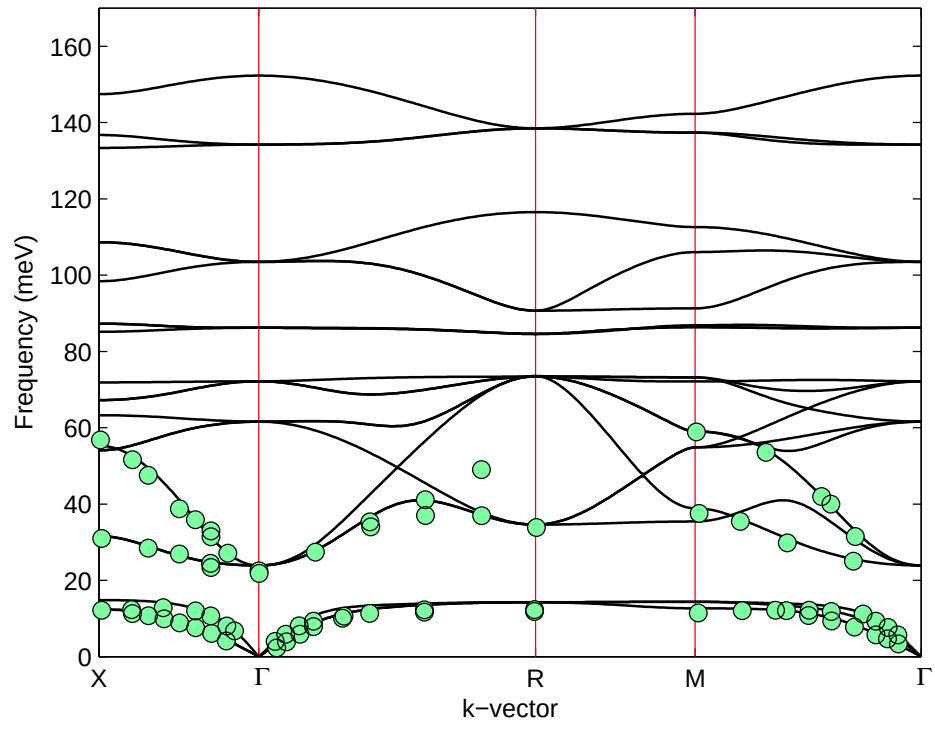


Figure 7.5: Phonon dispersions for CeB₆. Experimental values (dotted) are from Ref. [180].

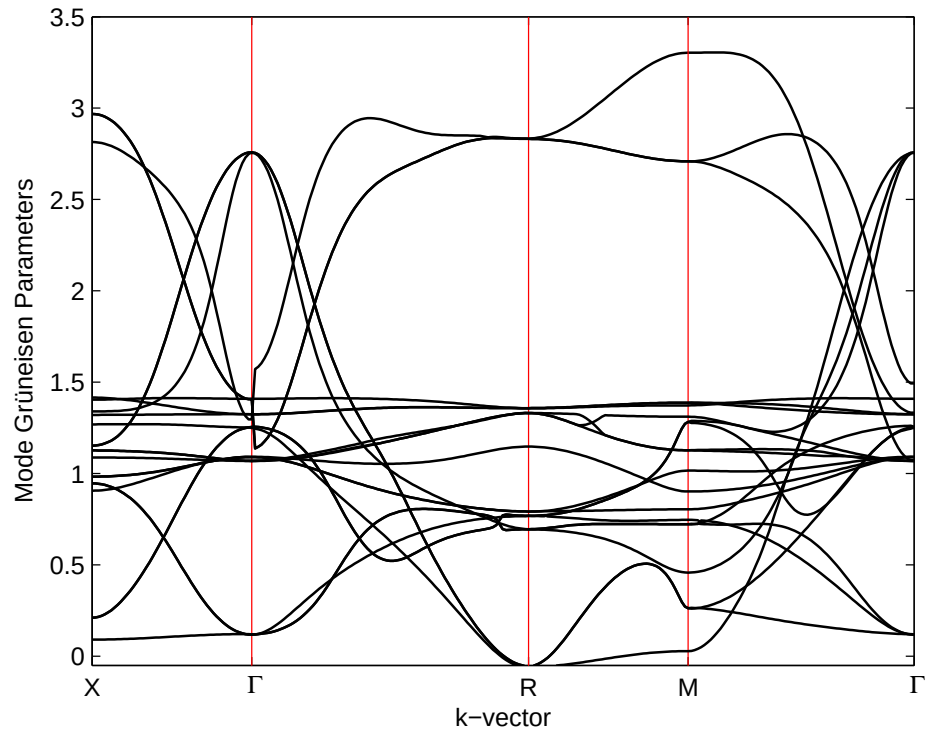


Figure 7.6: The mode Grüneisen parameters of LaB₆.

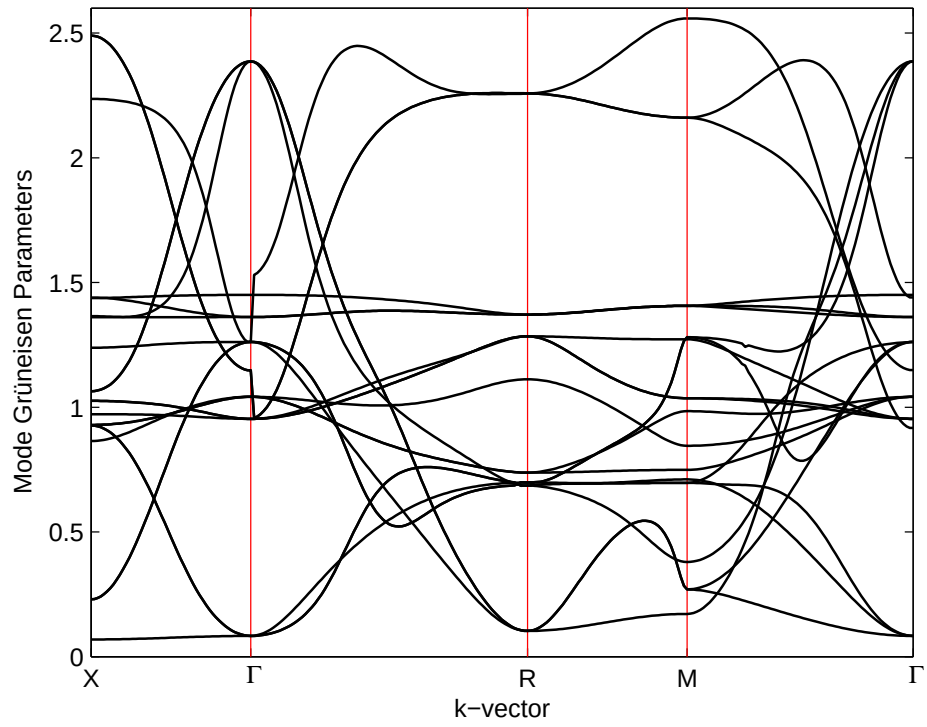


Figure 7.7: The mode Grüneisen parameters of CeB_6 .

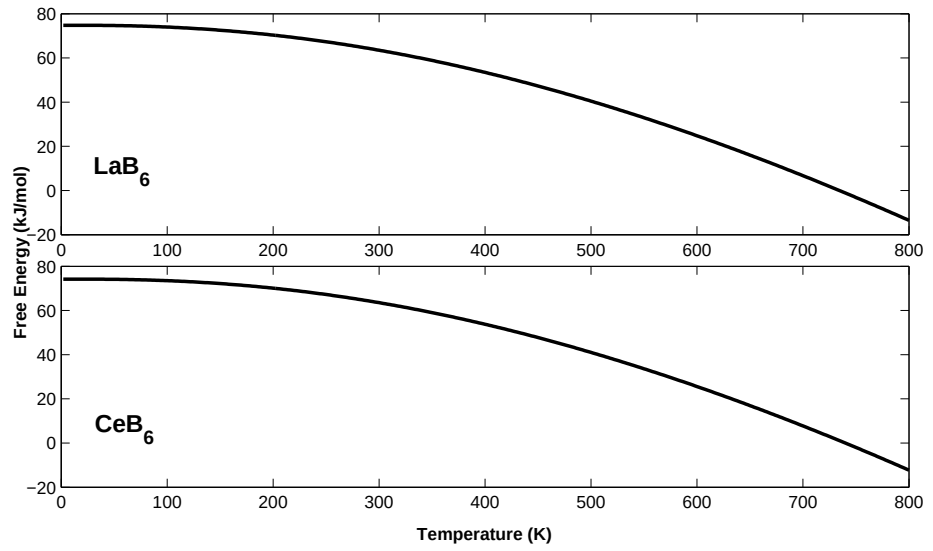


Figure 7.8: Vibrational contribution to Helmholtz free energy of LaB_6 and CeB_6 .

grid for phonon wave vectors $\mathbf{q}$ is found to be sufficient in order to get the mean relative error in each channel of phonon density of states.

Temperature dependent phonon contributions to Helmholtz free energy

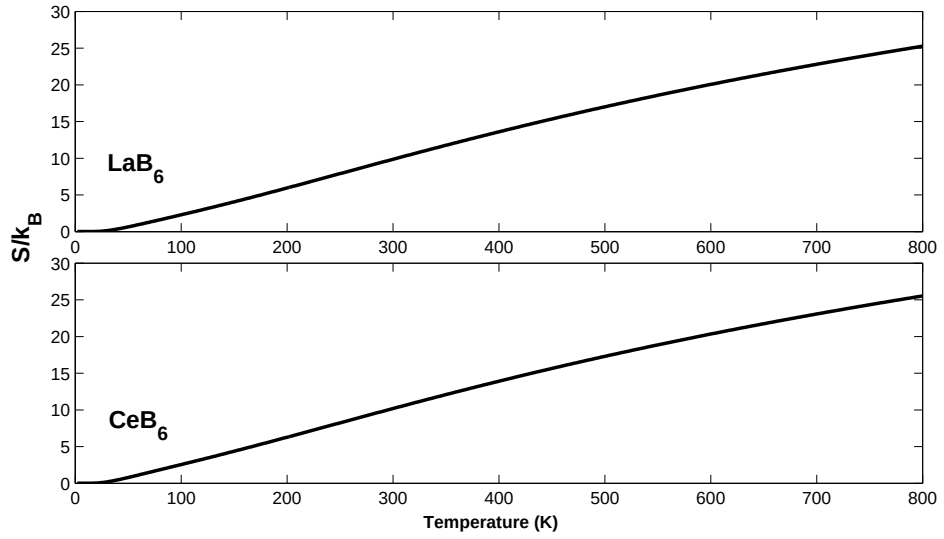


Figure 7.9: Vibrational contribution to entropy of LaB_6 and CeB_6 .

$\Delta F_{\text{vib}}(\omega_{\mathbf{q}j}(V), T)$ of LaB_6 and CeB_6 computed from Eq. 7.3, are displayed in Fig. 7.8. These calculations are done at the relevant static equilibrium lattice constant. Because of zero-point motion, the zero-temperature value of ΔF does not vanish. This quantity can be calculated from the asymptotic expression of Eq. 7.3 as;

$$\Delta F_0 = \int_0^{\omega_L} \frac{\hbar\omega}{2} g(\omega) d\omega \quad (7.13)$$

Calculated effect of zero-point energy upon the volume and bulk modulus for LaB_6 is $\Delta V_0/V_0 = 0.011$ and $\Delta B_0/B_0 = -0.026$. Similarly for CeB_6 we find, $\Delta V_0/V_0 = 0.011$ and $\Delta B_0/B_0 = -0.025$.

The vibrational entropies of LaB_6 and CeB_6 are calculated from Eq. 7.8 and displayed in Fig. 7.9. Unfortunately we could not be able to find any experimental information about the vibrational entropy in the literature. The values of the two materials are so similar and it should be noted that at high temperatures, electronic contribution to the entropy gets higher which is not included in the presented results.

To calculate the thermal properties, the free energy of LaB_6 and CeB_6 were

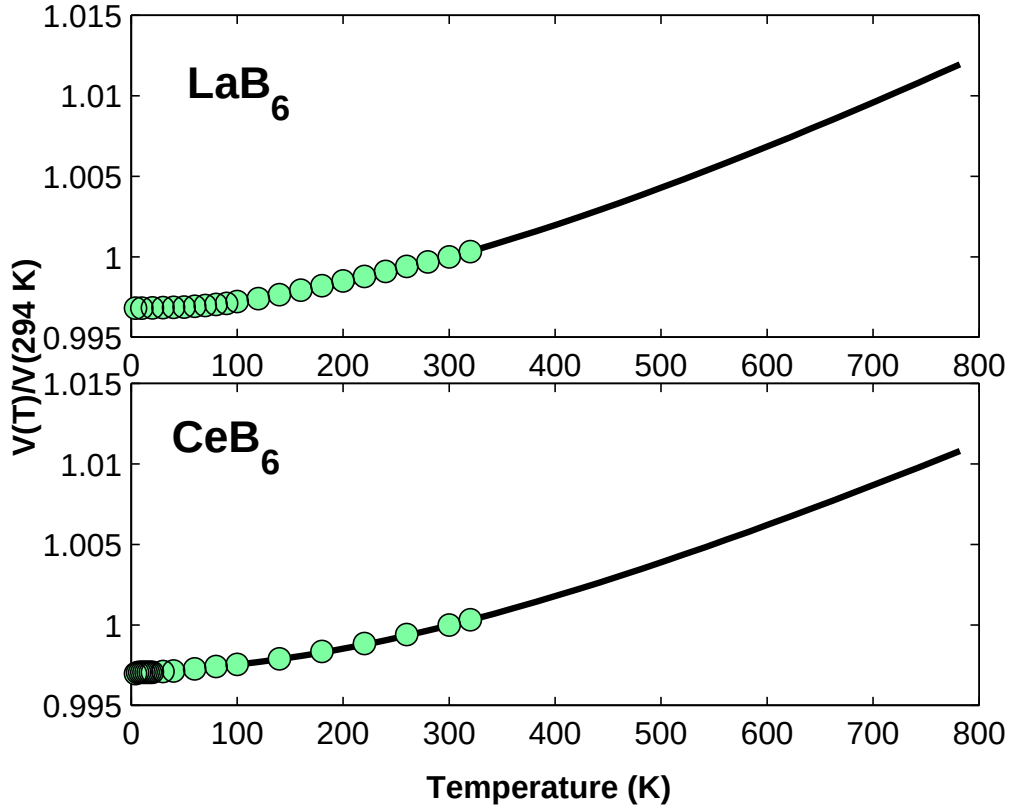


Figure 7.10: Thermal volume expansion of LaB_6 and CeB_6 (experimental data from Ref. [181]).

calculated as a function of volume and temperature. Calculations were performed on a primitive cubic cell at a series of lattice constants (4.058-4.195 Å) for LaB_6 , (4.084-4.222 Å) for CeB_6 . At each different temperature we calculated the *ab initio* free energy as a function of volume, and then performed a least squares fit of the results to a Vinet equation of state [60] (Eq. 7.9). The equilibrium volume at temperature T , $V_0(T)$ is obtained by minimizing free energy with respect to V . The volume thermal expansion is defined as

$$\eta(T) = \frac{V_0(T) - V_0(T_c)}{V_0(T_c)} \quad (7.14)$$

where T_c is the reference temperature of 294 K. Our results for volume thermal expansion of LaB_6 and CeB_6 are displayed in Fig. 7.10. The solid lines are our theoretical results and circles are experimental data from Ref. [181]. The

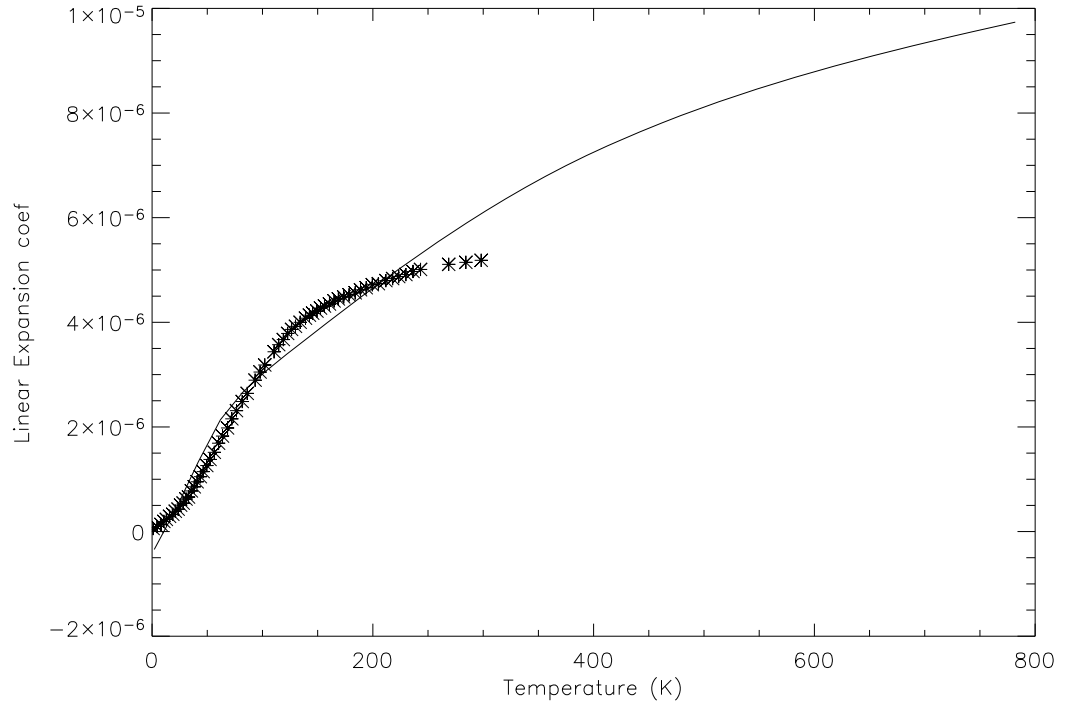


Figure 7.11: Temperature dependence of linear expansion coefficient of LaB_6 . The experimental values are from Ref. [181].

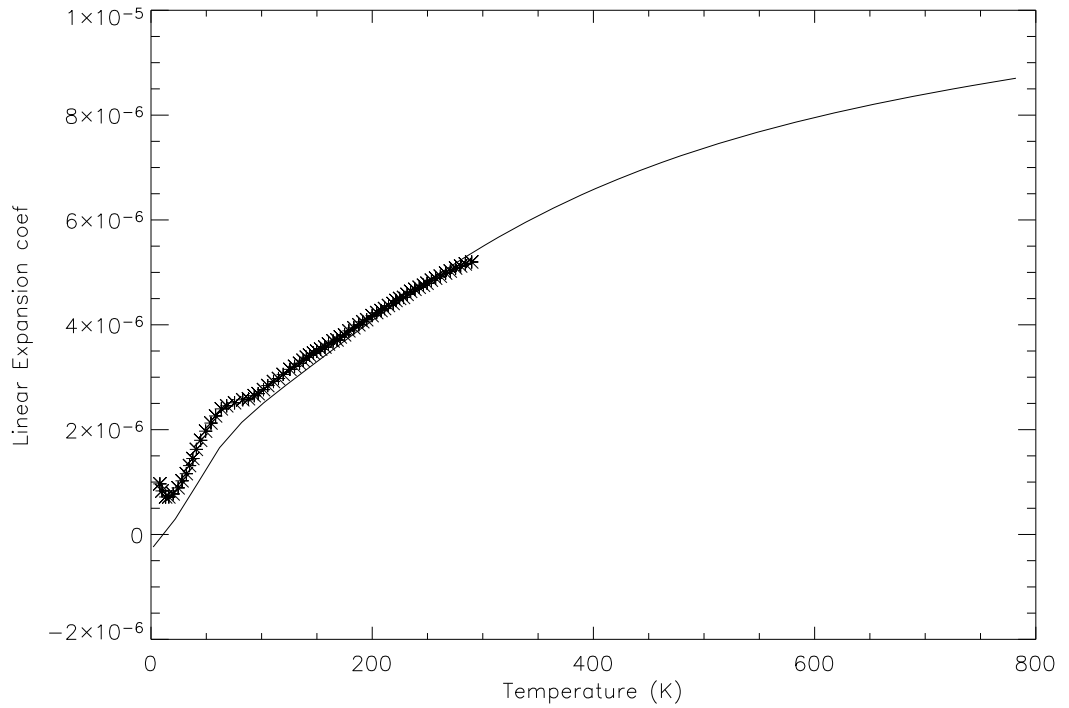


Figure 7.12: Temperature dependence of linear expansion coefficient of CeB_6 . The experimental values are from Ref. [181].

overall agreement for volume thermal expansion is perfect for both materials. The temperature dependences of the linear thermal expansion coefficients for

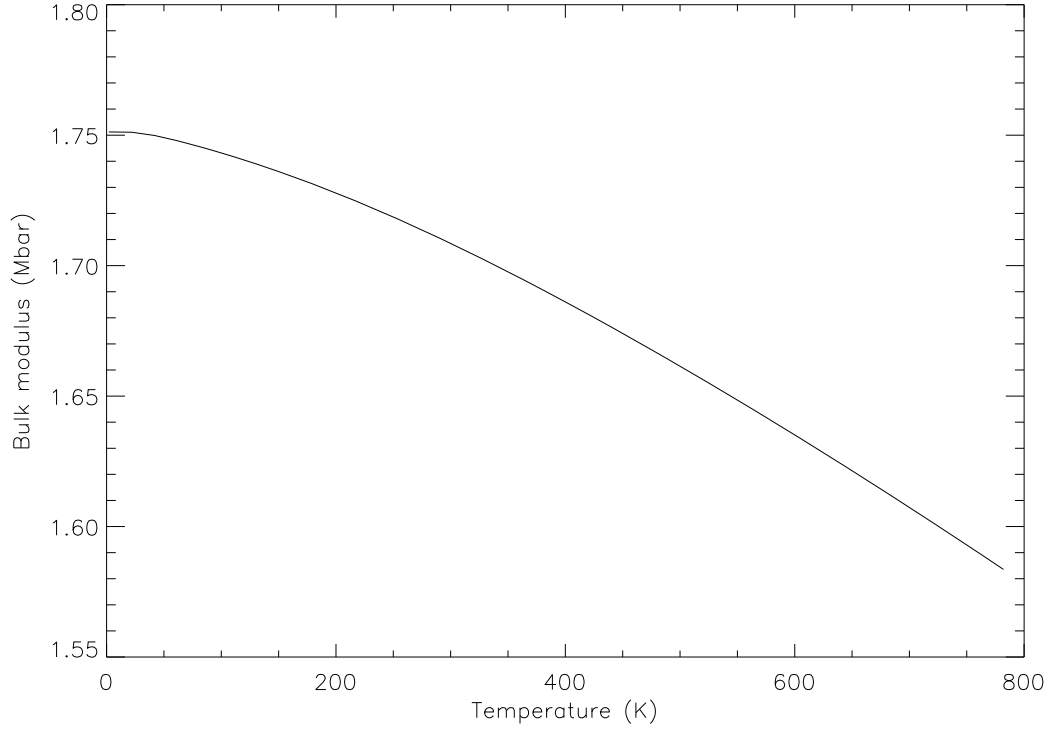


Figure 7.13: Temperature dependence of bulk modulus of LaB_6 .

Lanthanum and cerium hexaborides are given in Figs. 7.11 and 7.12, respectively. The agreement with respect to the experimental results of Ref. [181] is better for LaB_6 (CeB_6) when temperature decreases (increases).

The temperature dependence of the bulk modulus of LaB_6 and CeB_6 are displayed in Figs. 7.13 and 7.14, respectively. As an expected result, bulk modulus value decreases with increasing temperature for both materials. We have also calculated the temperature dependence of the pressure derivative of the bulk modulus and presented in Figs. 7.15 and 7.16 for LaB_6 and CeB_6 , respectively. Unlike bulk modulus, its pressure derivative increases with temperature and this increment is mostly linear.

In Figs. 7.17 and 7.18 we display the specific heat of LaB_6 and CeB_6 , respectively. The solid (dashed) line is our result for the specific heat at constant pressure (volume), while stars in Fig. 7.17 are experimental specific heat values of LaB_6 from Refs. [182]. In Fig. 7.18 stars and diamonds are experimental specific heat values of CeB_6 from Refs. [183] and [182], respectively. Our first principles results agree well with experiment for LaB_6 with a slight underestimation,

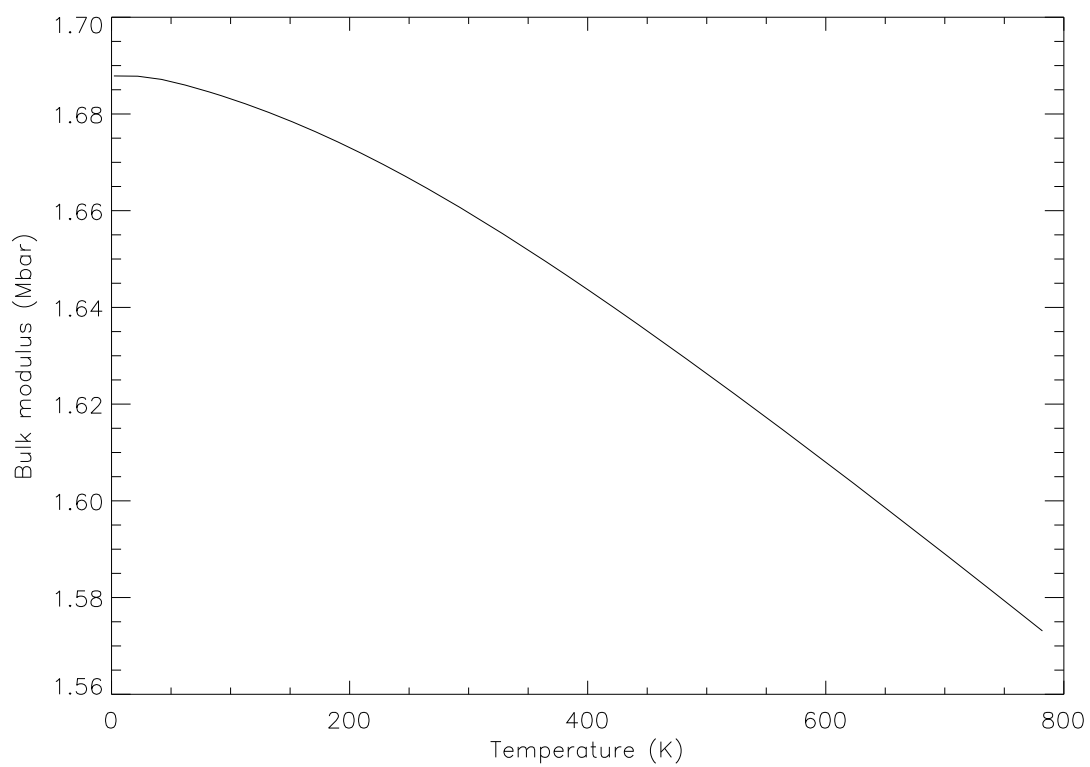


Figure 7.14: Temperature dependence of bulk modulus of CeB_6 .

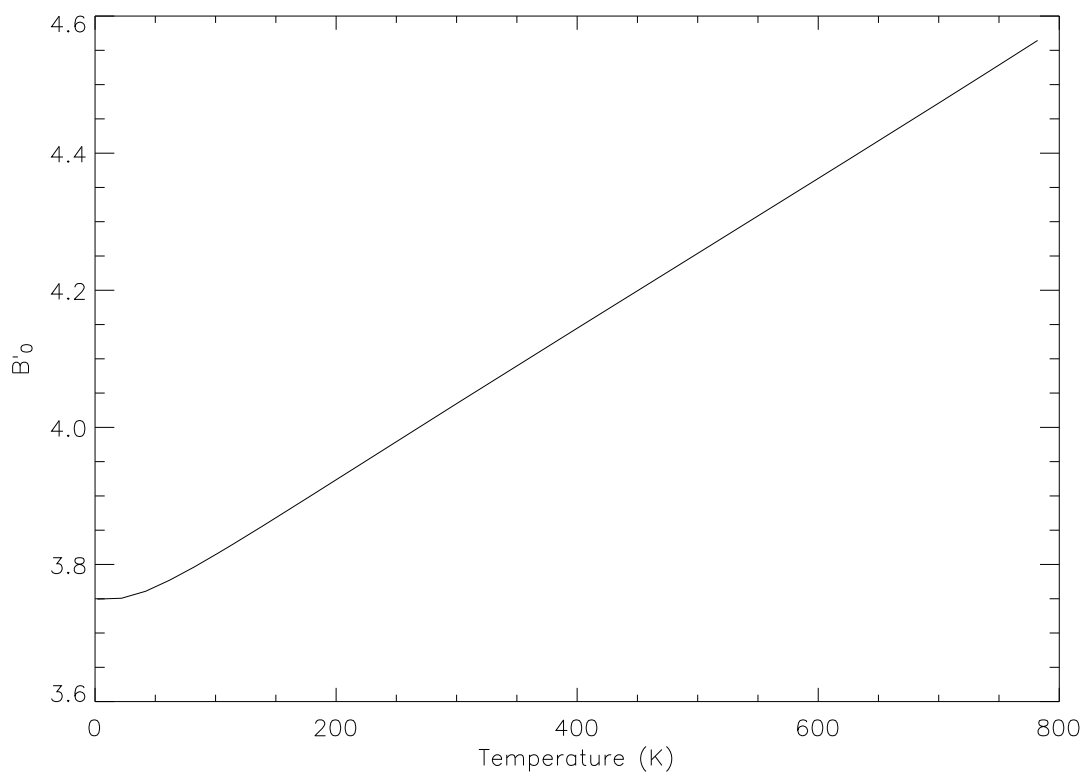


Figure 7.15: Temperature dependence of the pressure derivative of bulk modulus of LaB_6 .

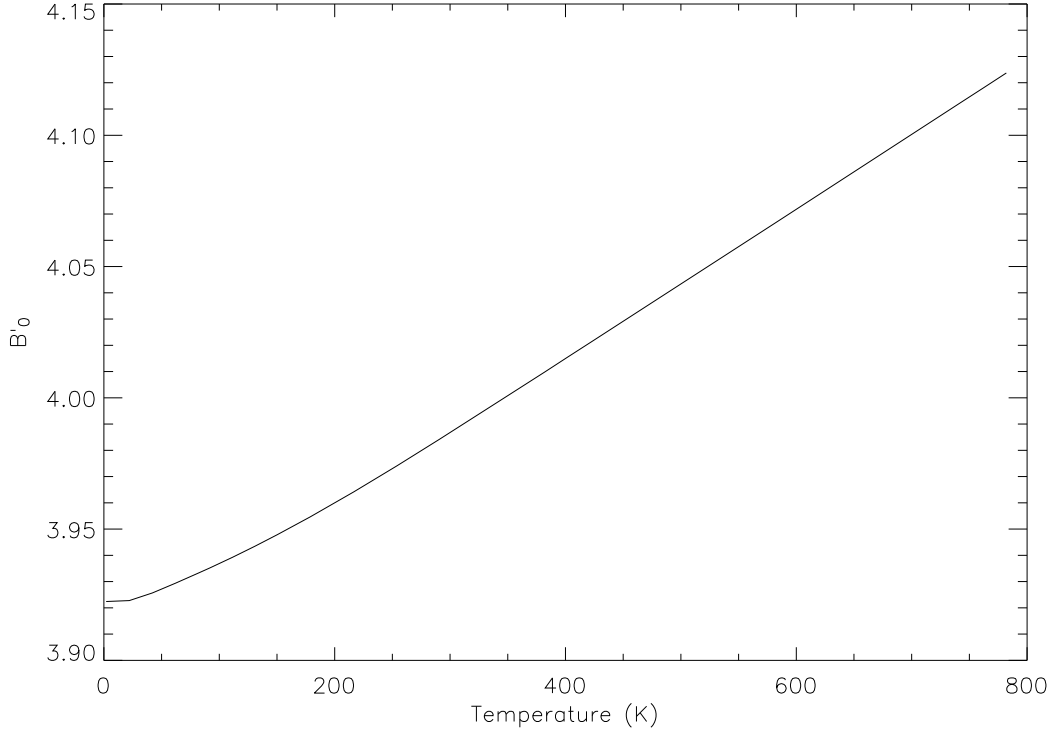


Figure 7.16: Temperature dependence of the pressure derivative of bulk modulus of CeB_6 .

while for CeB_6 the agreement is satisfactory with a slight overestimation. In CeB_6 , there exists two peaks in experimental specific heat values at temperature lower than 20 K because of the Kondo effect which is not discussed here in the quasi-harmonic approximation.

Pressure dependence of unit cell volume of LaB_6 and CeB_6 are displayed and compared to experimental data in Figs. 7.19 and 7.20, respectively. The solid lines in both figures are for $T=294\text{K}$ while dashed lines is for various temperatures from 2 K to 800 K separated by 100 K. For both materials, pressure dependence of the unit cell volume does not change too much with respect to temperature in the given range. In the experimental study of Teredesai *et al.* [177] it has been reported that for LaB_6 , at pressure around 10 GPa, there exists a phase transition from cubic phase to orthorhombic phase which is not observed for CeB_6 up to pressure at 20 GPa [178]. In our calculations we did not investigated this situation. For the cubic phase of two materials, the agreement between the calculated and experimental values is good with a slight underestimation. For

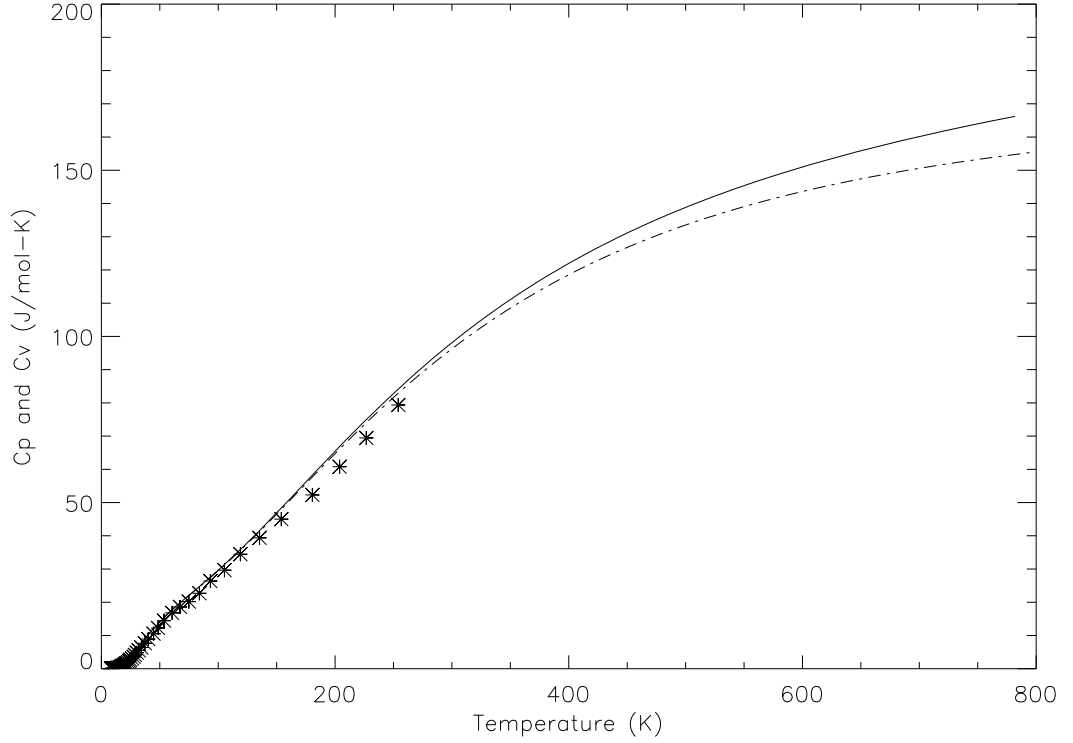


Figure 7.17: Temperature dependence of constant volume (dotted line) and constant pressure (solid line) specific heat of LaB_6 . The experimental values are from Ref. [182]

CeB_6 , if one takes into account the spread in the experimental values of Ref. [178], the agreement is better.

From the results presented so far, one question concerning the *ab initio* calculation of thermodynamical quantities is the relation between the error in calculating the static equilibrium lattice properties, such as lattice constant and bulk modulus, and ensuing error in the calculated thermodynamical quantities. While investigating the thermal properties of Cu, Narasimhan and de Gironcoli [169] suggested that a better value for the static value of a_0 and B_0 would be a good indicator of a better description of finite-temperature properties. Since the lattice constant and bulk modulus values for the materials considered in this chapter are in a good agreement with experimental measurements, our calculated thermodynamical quantities give compatible results with the experimental values.

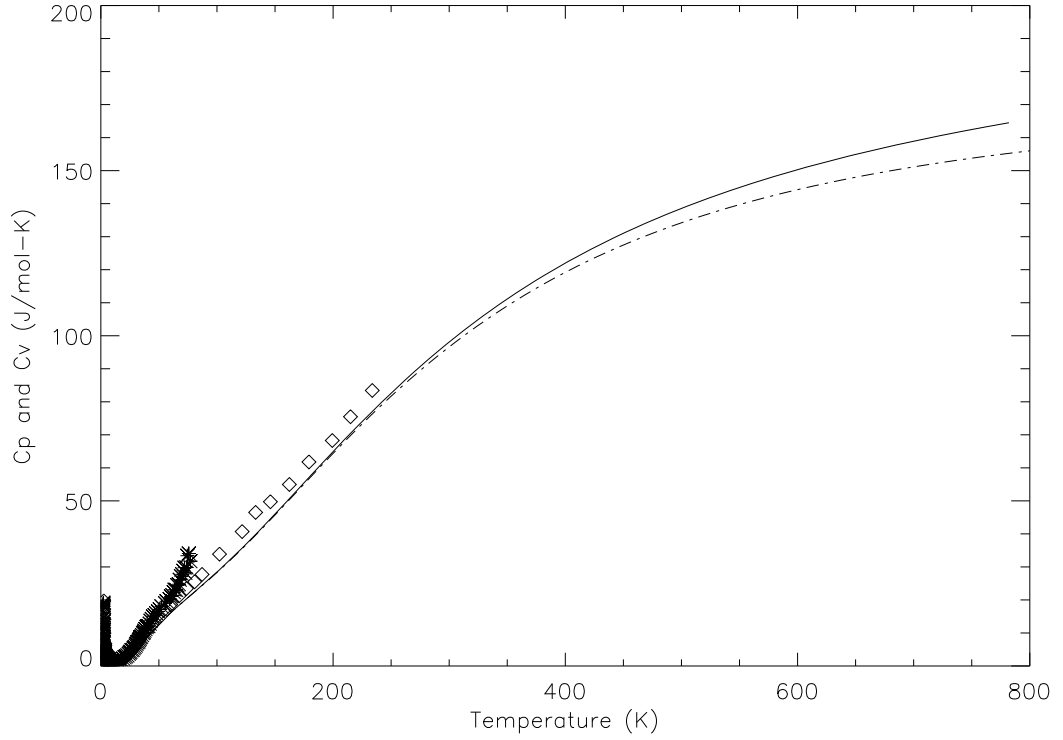


Figure 7.18: Temperature dependence of constant volume (dotted line) and constant pressure (solid line) specific heat of CeB_6 . The experimental values are from Ref. [183] (starred) and Ref. [182] (diamond)

7.4 Conclusion

In this chapter we have reported the results of first principles calculations of thermodynamical properties, such as vibrational free energy, entropy, temperature dependence of constant volume and constant volume and pressure specific heat, and mode Grüneisen parameters of LaB_6 and CeB_6 , in quasiharmonic approximation. Also, dependence of the error in calculated thermal quantities on the static values of bulk properties is investigated and it is suggested that a better static bulk modulus is a sign of better thermodynamical results.

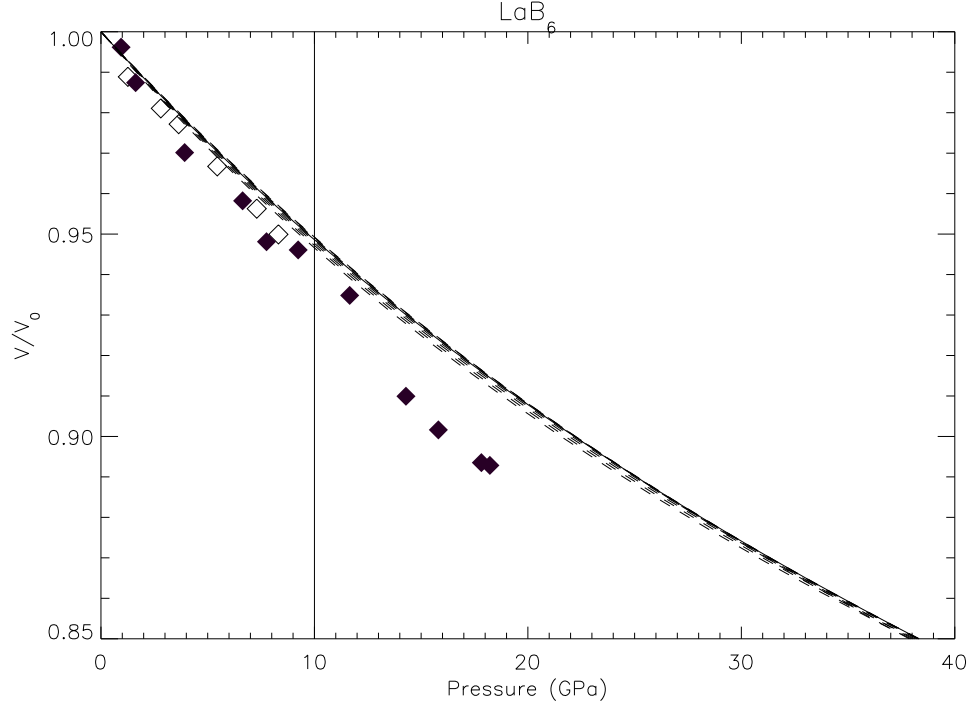


Figure 7.19: Pressure dependence of unit-cell volume of LaB_6 at several temperatures. Solid line in figure is for $T = 294\text{ K}$. Dot-dashed lines are separated by 100 K. The experimental values are from Ref. [175](empty diamonds) and Ref. [177](filled diamonds).

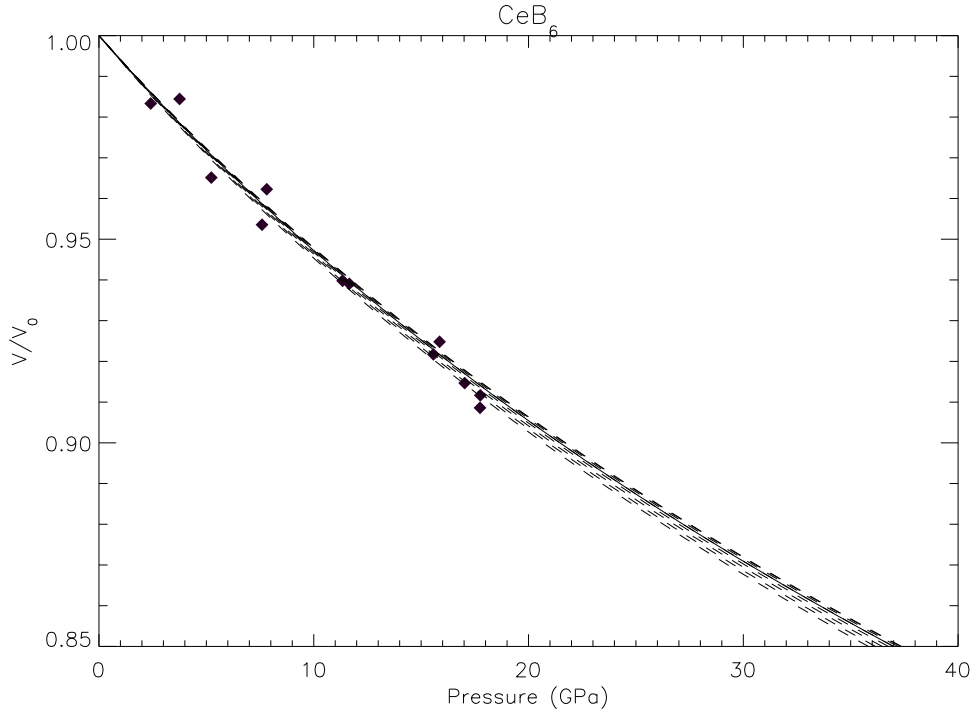


Figure 7.20: Pressure dependence of unit-cell volume of CeB_6 at several temperatures. Solid line in figure is for $T = 294\text{ K}$. Dot-dashed lines are separated by 100 K. The experimental values are from Ref. [178].

CHAPTER 8

CONCLUSIONS

The present thesis has been devoted to the study of the volume-dependent structural, elastic, dielectric, lattice dynamical and thermodynamical properties of some periodic materials within a fully *ab initio* approach. Our calculations have been performed with density functional and density functional perturbation theories in the framework of local density approximation using plane-wave pseudopotential method. These theories, with their approximations and implementations, are very powerful to calculate numerous physical properties without any need of empirical data. So it is possible to have accurate predictions when the experimental measurements are not available.

DFT allows us to determine the ground-state properties of the physical system while DFPT is a powerful tool to calculate various responses of the system to the application of small external perturbations. Calculation of the responses of the system is computationally very expensive compared to calculate the ground-state of the system. Nowadays computing time meaningfully decreases thanks to the recent development of numerical techniques, increasing power of processors, large capacity memories and of course parallel computing tools.

For the completeness of the thesis, Chapter 2 briefly reviews the DFT, LDA, plane-waves and pseudopotential theory and in Chapter 3, a basic description of the DFPT has been given without any proof.

Chapter 4 is an application of DFT and DFPT to a ternary chalcopyrite semiconductor CuAlSe_2 . This type of materials have wide applications in technology. Many ground-state and second-order physical properties and their behavior under a volume compression up to 10% have been investigated. Among these physical properties, elastic constants are not available experimentally and so we compared

our results with another similar compound CuInSe_2 . Experimental results for the Brillouin zone-center phonon frequencies of the CuAlSe_2 are often contradictory. We have reported the ab initio results for these frequencies including the experimental undetermined two Γ_2 modes.

CeO_2 is an insulator which is extensively used in modern catalytic industry. In the work of Chapter 5, phonon dispersion relations throughout the high-symmetry points of the Brillouin zone have been obtained from first-principles for the first time. Both phonon dispersions and other calculated structural, elastic, dielectric and lattice dynamical quantities are in a very good agreement with the available experimental measurements.

The subject of the Chapter 6 has been devoted to cerium hydrides CeH_2 and CeH_3 . These type of hydrogen systems are interesting because of their reversible effects due to the hydrogen concentration. Phonon dispersion relations of these materials have been measured only for their non-stoichiometric forms. We have calculated the phonon dispersion relations and mode Grüneisen parameters of stoichiometric CeH_2 and CeH_3 .

Quasi-harmonic approximation is a nice tool to obtain thermodynamical properties if there exists a complete knowledge of the vibrational spectrum. Thanks to the DFPT, in chapter 7, we present the thermodynamical results of two hexaborides LaB_6 and CeB_6 calculated from phonon dispersion relations and phonon density of states using quasi-harmonic approximation. The structural and elastic properties of these materials have also been calculated and compared with experimental available data.

One of the main goal of this thesis is the generation of useful pseudopotentials for the elements cerium, lanthanum and boron. These pseudopotentials are generated using the OPIUM code and used in the calculations of Chapters 6 and 7. For the entire materials included in thesis, we have used local density approximation to describe the exchange-correlation part of the total energy. Although LDA does not correctly describe the band-gaps of the materials in the electronic

structure calculations, our calculations show that this is not the case for structural and linear-response calculations which we have obtained very good results for different types of materials such as metals, semiconductors and insulators.

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Talk: Electronic structure of chalcopyrite CuInSe₂: LDA and GW results (C. Parlak, **T. Gürel** and R. Eryiğit)
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