Theoretical Investigations of Compressed Materials

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Abstract

The use of high pressure as a tool to design new materials as well as to investigate materials properties has become increasingly important during last one decade. The main goal of the present thesis is to enhance the significance of the high pressure method as a quantitative tool in solid state investigations. Virtually all of the properties of solids are directly determined by their electronic structure. Similarly, the changes in the properties of solids under pressure are determined by the changes in the electronic structure under pressure. We have attempted to provide a comprehensive description of the resulting theory in a electronic structure and the properties of condensed matter.

The theoretical basis for these investigations is the density functional theory, in combination with ab initio method. The study of pressure induced phase transitions for the compounds of CaF$_2$, Cr$_2$GeC, Ti$_3$SiC$_2$, as well as V at 0 K are presented. The lattice parameters, the phase transition pressures, the equation of states, the electronic structures have been calculated and shown a good agreement with experimental results.

A lattices dynamic study of the body center cubic (bcc) Fe under high pressure and high temperature is presented. The bcc iron could dynamical stabilize in the Earth inner core conditions. The unusual phase transition of bcc V under high pressure is investigated and it is shown that the driving mechanism is electron-phonon interaction.

Finally, a method based on the LDA+U approach has been applied to study spin state transition in FeCO$_3$. Our results show that magnetic entropy play a significant role in spin state transition.
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List of Publications

I. Dynamical stability of body center cubic iron at the Earth’s core conditions
W. Luo, B. Johansson, O. Eriksson, S. Arapan, P. Souvatzis, M.I. Katsnelson, and R. Ahuja
Proceedings of the National Academy of Sciences (PNAS), 107, 9962-9964 (2010)

II. Distortions and stabilization of simple-cubic calcium at high pressure and low temperature
Proceedings of the National Academy of Sciences (PNAS), 107, 9965-9968 (2010)

III. Electronic and elastic properties of CaF$_2$ under high pressure from ab initio calculations
H. Shi, W. Luo, B. Johansson, and R. Ahuja

IV. Substitutional alloy of Ce and Al

V. Magnetic Fe$_{n+1}$AC$_n$ ($n=1,2,3,$ and A=Al,Si,Ge) phases: From ab initio theory
W. Luo and R. Ahuja

VI. Nanolayered MAX phases from ab initio calculations
W. Luo, C.M. Fang, and R. Ahuja

VII. First-principles calculations of the electronic structure and pressure-induced magnetic transition in siderite FeCO$_3$
H. Shi, W. Luo, B. Johansson, and R. Ahuja
VIII. Study of Ti$_2$SC under compression up to 47 GPa

IX. Synthesis and compressive behavior of Cr$_2$GeC up to 48 GPa

X. Unusual lattice dynamics of vanadium under high pressure
W. Luo, R. Ahuja, D. Yang, and H-K. Mao
Proceedings of the National Academy of Sciences (PNAS), 104, 16428 (2007)

XI. Phase transition of vanadium at 69 GPa
Y. Ding, R. Ahuja, J.F. Shu, P. Chow, W. Luo, and H-K. Mao

XII. Ab initio prediction of high-pressure structural phase transition in BaH$_2$
W. Luo and R. Ahuja
J. Alloys and Compounds, 446-447, 405-408 (2007)

The following papers are co-authors by me, but are not included in the thesis.

XIII. Electronic structure of a thermoelectric material: CsBi$_4$Te$_6$
W. Luo, J. Souza de Almeida, J.M. Osorio-Guillen, and R. Ahuja

XIV. Elemental engineering: Epitaxial uranium thin films

XV. High pressure structural phase transition in zircon (ZrSiO$_4$)
W. Luo, J. Souza de Almeida, J.M. Osorio-Guillen, and R. Ahuja

XVI. The unique high-pressure behavior of curium probed further using alloy
S. Heathman, R.G. Haire, T. Le Bihan, R. Ahuja, S. Li, W. Luo, and B. Johansson

XVII. Noblest of all metals is structurally unstable at high pressure

**XVIII.** *Ab initio* investigation on the phase stability of Ti$_3$SiC$_2$, Ti$_3$Si$_{0.5}$Ge$_{0.5}$C$_2$ and Ti$_3$GeC$_2$ at high pressures
R. Ahuja, Z. Sun, and W. Luo
High Pressure Research, 26, 127-130 (2006)

**XIX.** High-pressure structural transitions in Cm and Am$_{0.5}$Cm$_{0.5}$ binary alloy
R. Ahuja, S. Li, W. Luo, and B. Johansson
High Pressure Research, 26, 1-5 (2006)

**XX.** Structural phase transitions in brookite-type TiO$_2$ under high pressure
W. Luo, S.F. Yang, Z.C. Wang, Y. Wang, R. Ahuja, B. Johansson, J. Liu, and G.T. Zou

**XXI.** Mean-field potential calculations of shock-compressed porous carbon

**XXII.** High-pressure synchrotron studies on TiO$_2$-II nanocrystalline doped with SnO$_2$

**XXIII.** Bcc titanium under negative pressure from *ab initio* calculations
W. Luo, B. Johansson, and R. Ahuja
in manuscript

**XXIV.** The temperature and magnetism driven phase transition in iron from *ab initio* calculations
W. Luo, B. Johansson, and R. Ahuja
in manuscript

**Contributions to the appended papers**
In articles where I am first author, I did all the calculations, the theoretical analysis and writing was done jointly. In others article where I am not first author, I did part of the theoretical study, performing calculations and theoretical analysis.
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Chapter 1

Introduction

Virtually all of the properties of solids can directly be determined by their electronic structure. Similarly, the changes in the properties of solids under pressure are determined by the changes in the electronic structures under pressure. The study of the electronic properties on compressed materials induced by pressure is of great importance. The questions that concern people in condensed materials are, what sort of phenomena to anticipate when the pressure range is indefinitely increased? Why do atoms combine into different structures in the way the do? How we should make stronger materials, better high temperature superconductors?

This thesis presents a theoretical investigation of structural and electronic properties of solid state materials using density functional theory. Our study involved two parts, one is designing new materials and the other one is the structural stability and phase transition, which are particularly emphasized on the reference to understand the experimental data and to make prediction. In Chapter 2, we present a brief introduction to some of the density functional based first-principles calculations, including the frozen phonon theory, the orbital-dependent functionals, and the linear response method. In Chapter 3, the electronic structures approach under high pressure is summarized. Chapter 4 illustrates the application of the \textit{ab initio} theory. Furthermore, it is a summary of the scientific work performed during the last four years which lead to the papers described in the list of publications.

This thesis based on five main examples namely, properties of metal, alloy, intermetallic ternary carbide and nitride named MAX-phase materials, metal hydride so called hydrogen storage materials, as well as the metal oxides are investigated. The first two examples are about metals, where I discussed mainly the dynamic stabilities investigation for vanadium under high pressure, as well as for Iron under high pressure and high temperature. The phonon frequencies of the bcc iron at ambient pressure as a function of temperature and magnetism are simulated and compared with the experimental data. These studies show that some of the phonon branches of bcc iron can be strongly temperature dependent, the others can be strongly magnetism dependent. The phase transition driven by electronic structural transition related to the phonon softening known as kohn anomaly is discussed.
for vanadium. The anharmonic vibrational phonon contribution to the bcc structure of iron is investigated under extreme pressure and temperature conditions. In addition, we have also studied the dynamic stability of titanium as a function of volume and temperature. The ferromagnetic phase in titanium is found to be stable under lattice expansion.

The material design, structure prediction and the electronic properties of the materials are one of the main work in present thesis. We have calculated the electronic structures and mechanical properties of intermetallic MAX phases. The MAX phases are ternary carbides and nitride with the general formula $M_{n+1}AX_n$ (MAX) with $n = 1-3$, where $M$ is an early transition metal, $A$ is an A-group (mostly IIIA and IVA) element and $X$ is either carbon or nitrogen. High pressure studies on the magnetic properties of MAX phase compounds are reported, and these compounds behaves like antiferromagnetic materials. The magnetism and its origin in MAX phases are investigated while replacing carbon by nitrogen.

One example on FeCO$_3$, with "LDA+U" calculation is given in this thesis. The transition pressure of spin states for FeCO$_3$ is obtained in experiment, but the calculated transition pressure is much too small. In order to be able to treat strong electron-electron correlations among the Fe-d electrons, we go beyond GGA, through the incorporation of additional strong electron-electron correlations on the central Fe atom. This is corrected by a "U" term that increases the transition pressure closed to experiment.

The metal hydrides, BaH$_2$ and KBH$_4$, can be considered as the hydrogen materials. Ba and K can put chemical pressure on hydrogen lattice and this can lead also to understand metallization of hydrogen. It is also important to know about hydrogen desorption in these metal hydride for their possible application for hydrogen storage.

The superhard material, titanium dioxides TiO$_2$ and calcium fluoride CaF$_2$ have been studied by using density functional theory (DFT) with generalized gradient approximation (GGA). Our results show the sequence of pressure-induced structural transition CaF$_2$, the elastic properties versus pressure are also discussed. The stress-strain coefficient calculations show that shear transformations in the non-cubic phase are more difficult than in the cubic phase.
Chapter 2

Electronic structure calculations

For theoreticians in condensed matter physics the ultimate goal is to predict the physical behavior of matter with any input form experiments. The purpose of the theoretical work that is summarized in the present thesis is to give a contribution towards the knowledge and the understanding of the physics of elemental metals. The *ab initio* is the Latin term for "from first principles" or "from scratch". In *ab initio* methods, 100% of the model is done mathematically, based primarily on Schrödinger equation in the present thesis.

The solution of the equations of motion for a system consisting of two particles is trivial. This is analogous to the problem of solving the equations of motion for a gravitationally bound system with more than two bodies. As we will show in this chapter the computational requirements for an attack by brute force are beyond our reach for all but the smallest systems. The discrete translational symmetry of the lattice influences the behavior of the electrons will be discussed below.

2.1 The Schrödinger equation

In the framework of quantum mechanics we could, in principal, obtain $\Psi$ by solving the Schrödinger equation proposed in 1926 [1],

$$\hat{H}\Psi = i\hbar \frac{\partial}{\partial t} \Psi$$  \hspace{1cm} (2.1)

where $\Psi$ is the Hamilton operator that defines the energy contributions to the system. The Hamiltonian can be divided in two parts, one describing the kinetics of the electrons and nuclei and the second part describing the Coulomb interactions between particles: electron-electron, electron-nucleus and nucleus-nucleus. There are a lot of different methods for
solving Eq. 2.1 [2]. If only the ground state properties of a system are of interest the more simple time independent Schrödinger equation can be used,

\[ \hat{H} \Psi = E \Psi \]  

(2.2)

Further, from the ground-state wave function, \( \Psi \), all ground-state properties are obtainable. The simplifications can be done if the motion of the ions can be disregarded, the Born-Oppenheimer approximation. This is can be justified by looking at the time scales involved in the electronic and the ionic interactions and the velocities of the electronic and ion [3]. The average time between two scattering events involving electrons is the order of \( 10^{-14} \) seconds. In the same way, the average velocity of electrons is several order of magnitude higher than for ions. This difference in time and speed scales is caused by the difference in mass between the nucleons and the electrons, the proton being almost 2000 times heavier than the electron. This approximation is not valid at higher temperatures where the ionic motion is so strong that the crystal melts.

Under this assumption Eq. 2.1 simplifies to a Hamiltonian describing only the behavior of the electrons,

\[ \hat{H}_e = \sum_i \nabla^2 r_i + \sum_{i \neq j} \frac{1}{|r_i - r_j|} + V_{ext} \]  

(2.3)

where \( V_{ext} \) includes all electron-ion interaction and any external potential e.g. the potential arising from an external magnetic field. So this Hamiltonian involves three parts, the first part is the kinetic energy term, the second part is the electron-electron Coulomb interaction and the third part is the interaction between the electron and the nuclei (called external interaction).

As the solution to the Schrödinger equation must describe the whole quantum system with all interaction included we can not use the single particles wave function but the many-body wave function has to be used,

\[ \Psi = \Psi(r_1 s_1, r_2 s_2, ..., r_N s_N) \]  

(2.4)

where \( s_i \) is the spin coordinate for electron \( i \) and \( N \) is the total number of electrons in the system. Solving Eq. 2.2 using the Hamiltonian from Eq. 2.3 and the many-body wave function turns out to be a Herculean task for anything but the simplest system, so some modifications are needed. The first approximation we have to adopt is the Born-Oppenheimer approximation, which isolates the electronic motion from be stationary, the kinetic energy will be zero and we can drop the first term in Eq. 2.3.
2.2. THE HARTREE-FOCK APPROXIMATION

2.2 The Hartree-Fock approximation

The exact many-body Schrödinger equation could be cast into the equivalent variational form which says that a solution to Eq. 2.2 is given a single wave function that, if we are looking for ground state properties, minimizes

\[ \hat{H} \Psi = \frac{\langle \Psi | \hat{H} | \Psi \rangle}{\langle \Psi | \Psi \rangle} \]  

(2.5)

where \( H \) is defined in Eq. 2.3 and \( \langle \Psi, \Psi \rangle \) is a shorthand notation for integrating over all space coordinates and summation over all spins. Using the many-body wave function Eq.2.4 it is still unsolvable. One way to reduce Eq. 2.3 further to a problem that we can solve is to use the Hartree approximation. Here the potential that a certain electron feels depends upon the other positions. Then this potential is approximated by an average single-particle potential. The one particle wave functions is used.

\[ \Psi(r_1s_1, r_2s_2, ..., r_Ns_N) = \Psi_1(r_1s_1) \Psi_2(r_2s_2) ... \Psi_N(r_Ns_N) \]  

(2.6)

Minimizing Eq. 2.5 and Eq. 2.6 yields as a result the so called Hartree equations,

\[ (-\nabla^2 + V_{\text{ext}}(r) + \sum_{j \neq i} \int d\mathbf{r}' |\Psi_j(\mathbf{r}')|^2 \frac{1}{|\mathbf{r} - \mathbf{r}'|}) \Psi_i(\mathbf{r}) = \epsilon_i(\mathbf{r}) \]  

(2.7)

the set of equations is now separable. However, the equations are a set of \( N \) coupled nonlinear equations. A possible simplification would be to let the sum run over all \( j \), including \( j = i \). In the independent electron picture the charge density at site \( r \) can then be identified as

\[ \rho(\mathbf{r}) = -e \sum_j |\Psi_j(\mathbf{r})|^2 \]  

(2.8)

and can be calculated once and for all and be used for calculating all \( \Psi_i \). The new equation is often also referred to as a Hartree equation.

\[ (-\nabla^2 + V_{\text{ext}}(\mathbf{r}) + \int d\mathbf{r}' \rho(\mathbf{r}') \frac{1}{|\mathbf{r} - \mathbf{r}'|} P_{si}(\mathbf{r}) = \epsilon_i \Psi_i(\mathbf{r}) \]  

(2.9)

The total wave function is the quantity described the state of the system. The problem that concerns us is to calculate the ground state energy for \( N \) electrons interacting with each other via a repulsive Coulomb potential and moving in some fixed external potential \( \Phi_{\text{ext}} \).

The weakness of the Hartree-Fock approximation is that the ground state wave functions belong to a very restricted set and that the electron correlation is neglected, or we could say that the Hartree-Fock approximation excludes the dynamics of the system. However, due to its complexity, this quantum mechanical problem has to be simplified considerably before it can be treated. The density functional theory provides an approach to the description of an atom, molecule or a solid, which has the advantage of being computationally efficient and at the same time also treats the correlation effect.
2.3 Density functional theory

Density Functional Theory (DFT) [4] is one of the most successful modern theories for calculating the properties of matter, the founder being given the Nobel prize in 1998. In DFT the basic variable is the charge (electron) density. The density functional theory relies upon two theorems due to Hohenberg and Kohn, which is given in the review [5]. First, the ground state energy, \( E[n(r)] \), of a many electron system in the presence of an external potential, \( V_{\text{ext}}(r) \), is showed to be a unique functional of the electron density \( n(r) \),

\[
E[n(r)] = \int d^3r V_{\text{ext}}(r)n(r) + F[n(r)].
\]  

(2.10)

where \( F[n(r)] \) is universal in the sense that it does not depend on \( V_{\text{ext}}(r) \). The second theorem states that \( E[n] \) is minimized for the ground-state electron density. For such system the variational equation \( \delta E_s n(r) = 0 \) yields the exact ground state density \( n_s(r) \) of the non-interacting system.

The main statement used to establish the Kohn-Sham equations [6] is that for any interacting system, there exist a local single-particle potential such that the exact ground state density of the interacting system equals the ground state density of the non-interacting system. Kohn and Sham subsequently proposed a local approximation to the exchange-correlation energy of the electrons, the local density approximation [6]. From these results they were able to drive an effective one-electron Schrödinger equation. In the variational principle the normalized expectation value of the energy is minimized, i.e., the Rayleigh-Ritz ratio. By applying the variational principle, in analogy with the derivation of the Hartree equation, we arrive to a set of couple effective one-electron equations,

\[
\left[ -\frac{1}{2} \nabla^2 + V_{\text{eff}}(r) \right] \psi_{\mu}(r) = \epsilon_{\mu} \psi_{\mu}(r).
\]

(2.11)

where

\[
V_{\text{eff}}(r) = V(r) + \int d(r') \frac{n(r')}{|r - r'|} + V_{\text{xc}}(r).
\]

(2.12)

The exchange-correlation potential is defined as

\[
V_{\text{xc}}(r) = \frac{\partial E_{\text{xc}} n(r)}{\partial n(r)}
\]

(2.13)

From \( \psi_{\mu} \) the density can be determined as a sum over occupied states,

\[
n(r) = \sum |\psi_{\mu}(r)|^2.
\]

(2.14)

The density, \( n(r) \), can then be inserted into Eq. 2.11 and a new set of \( \psi_{\mu}(r) \) can be calculated. In this manner \( n(r) \) can be solved by a self-consistent procedure. This set of equations, Eq. 2.11 - Eq. 2.14, are called the Kohn-Sham equations. The orbitals \( \psi_{\mu}(r) \) obtained from the Kohn-Sham equations can not be used to construct a total ground-state
wave function. The functions are only constructions and they have no physical correspondence. In the same way the eigenvalues, $\epsilon_\mu$, can not be related to the total ground-state energy. To be able to perform a calculation for a real system, an approximation of the exchange correlation functional $E_{xc}$ has to be made.

Local density approximation

The LDA is derived from the homogeneous electron-gas, and is strictly only valid for systems with slowly varying densities. The application of LDA is the fact that $E_{xc}$ is relatively small in comparison to the other contributions to the total energy of a system [7]. The other contributions, Coulomb interaction between nuclei-electron electrostatic energy form interaction between valence electrons, and the valence kinetic energy are treated exactly while the smaller exchange-correlation energy is approximated by the LDA.

The exchange-correlation functional, $E_{xc}$, is inspired by the local approximation introduced by Slater [8]. The approximation is local in the sense that only information of the density, $n(\mathbf{r})$, is needed locally at position $\mathbf{r}$. The approximation consists of the replacement of the exact energy by the LDA functional

$$E_{xc}^{LDA} = \int d\mathbf{r} n(\mathbf{r}) \epsilon_{xc}(n(\mathbf{r}))$$

(2.15)

where $\epsilon_{xc}$ is the exchange and correlation energy of a homogeneous electron gas with density $n(\mathbf{r})$. The exchange-correlation energy in Kohn-Sham equation is separated into exchange and correlation parts. These two quantities are then calculated a zero and unit polarisations. With this approximation to the density functional theory, the kohn-Sham equations become local in contrast to the non-local behavior found in the Hatree-Fock equation, and one-electron equation, Eq2.11, is therefore much easier to solve.

The LDA can easily be extended to spin polarized systems (magnetic systems), and this approximation if usually called the local spin density approximation (LSDA). In the functional form of the spin dependent external potential suggested by von Barth and Hedin [9], one assumes the spin dependence of the correlation energy to have the same form as the exchange energy.

For atoms and simple molecules, the LDA gives good results for geometrical quantities, such as bond lengths, and for electron densities, vibrational frequencies, and energy differences such as ionisation potentials. It is generally known that for metals LSDA tends to overestimate the bonding [10]. This in turn will affect the bulk modulus which will have a tendency to be too large in the LSDA calculations. To improve the LSDA, non-local information about the charge density could be provided from the gradient terms. Kohn and Sham [6] proposed an expansion of exchange-correlation functional in higher order gradients of the electron density.

Generalized gradient approximation

The general approach, where $E_{xc}$ does not necessarily have to be approximated by an expansion in higher order terms of the density gradient, is called generalized gradient
approximation (GGA). In the following we describe a general function of the GGA leading to the GGA-PW91 approximation \[11\].

First divide the exchange-correlation energy into its separate parts, \( E_{xc} = E_x + E_c \). These two contributions can in general be written as

\[
E_x = \int d\mathbf{r} n(\mathbf{r}) \epsilon_x F(s), \tag{2.16}
\]

\[
E_c = \int d\mathbf{r} n(\mathbf{r}) [\epsilon_x + H(t)]. \tag{2.17}
\]

Here \( E_x, E_c, \epsilon_x, \epsilon_c, \) and also \( H \) depends on the spin up \( (n^\uparrow) \) and spin down \( (n^\downarrow) \) densities, while \( s \) and \( t \) are two different scaled densities.

\[
s = \frac{|\nabla n|}{2k_F n}, \tag{2.18}
\]

\[
t = \frac{|\nabla n|}{2g k_s n}, \tag{2.19}
\]

where \( k_F \) is the Fermi wave vector and \( k_s \) is the local screening wave vector,

\[
k_s = (4k_F / \pi)^{1/2}. \tag{2.20}
\]

\( F(s) \) is a function of the scaled density gradients. For convenience the definition of the local Seitz radius is written down as \( r_s \).

\[
r_s = \left( \frac{3}{4\pi n} \right)^{1/3}. \tag{2.21}
\]

In the details of GGA-PW91, the exchange energy can be written

\[
E_x [n^\uparrow, n^\downarrow] = \frac{1}{2} (E_x [2n^\uparrow] + E_x [2n^\downarrow]). \tag{2.22}
\]

\[
E_x [n] = \int d\mathbf{r} n(\mathbf{r}) \epsilon_x (r_s, 0) F(s). \tag{2.23}
\]

For small gradients \( (s \to 0) \) \( F \) approaches one. Thus for vanishing \( |\nabla n| \) the exchange energy in the GGA formulation becomes equal to the LDA exchange energy. From the expression of the exchange energy, the exchange potential can be obtained as

\[
V_x = -\frac{3}{4} \left( \frac{3}{\pi} \right)^{1/3} n^{1/3} \left[ \frac{4}{3} F - \frac{r}{s} \frac{dF}{ds} - \left( u - \frac{4}{3} s^3 \right) \frac{d}{ds} \left( s^{-1} \frac{dF}{ds} \right) \right]. \tag{2.24}
\]

The correlation energy functional \( E_c [n, m] \) is a function of the total electron density \( n(\mathbf{r}) = n^\uparrow(\mathbf{r}) + n^\downarrow(\mathbf{r}) \), and magnetization \( m(\mathbf{r}) = n^\uparrow(\mathbf{r}) - n^\downarrow(\mathbf{r}) \).
2.3. DENSITY FUNCTIONAL THEORY

Orbital-dependent functionals: LSDA+U

The most enduring problem with the Kohn-Sham approach is that no systematic way has been developed to improve the functionals for exchange and correlation. The problems in LDA approach are most severe in materials in which the d-electronic tend to be localized and strongly interacting, such as transition metals. Various methods have been developed to extend the functional approach to incorporate effects that are expected to be important on physical ground. One of these is called LDA+U.

The LDA+U stands for methods that involve LDA- or GGA-type calculations coupled with an additional orbital-dependent interaction \([12]\). This approach has an intuitive appeal in that it leads to atomic-like states in systems like transition metal oxides system, where the electrons are strongly interacting \([13]\). The additional interaction is usually considered only for highly localized atomic-like orbitals on the same site, i.e. of the same from as the "U" interaction in Hubbard models. Hubbard \(U\) for localized \(d\) orbital is

\[
U = E(d^{n+1}) + E(d^{n-1}) - 2E(d^n). \tag{2.25}
\]

The effect of the added term is to shift the localized orbitals relative to the other orbitals, which attempts to correct errors known to be large in the usual LDA or GGA calculations. In the DFT+U method, the expression for the total energy reads as

\[
E_{\text{tot}} = (\rho^\sigma) + E_U(\hat{n}^\sigma) - E_{dc}(\hat{n}^\sigma). \tag{2.26}
\]

where \(\rho^\sigma\) is the charge density and \(\hat{n}^\sigma\) is the orbital dependent density matrix for spin \(\sigma\).

Density functional perturbation theory

Density functional perturbation theory (DFPT) \([14]\) has considerably widened the scope of DFT. It is based essentially on the computation of the derivatives of the total energy with respect to perturbations. The basic concepts of DFPT have been introduced through the Green’s function-based formalism, where the central issue is to solve a linear problem defined by the Stemheimer equation. The \(2n + 1\) theorem in DFT is used to lead a variational formalism of DFPT in which one may minimise a second order energy functional. Equivalence to the Green’s function-based method has been demonstrated by showing that minimisation of the second order energy functional is equivalent to solving the Stemherimer equation.

The density can be described as a sum over occupied states

\[
n'(r) = 2R_e \sum |\psi^\mu_\nu(r)\psi^\nu_\mu(r^\prime)|. \tag{2.27}
\]

The so obtained density, \(n(r)\), can then be inserted into Eq. 2.11 and a new set of \(\psi_\mu(r)\) can be calculated. In this manner \(n(r)\) can be solved by a self-consistent procedure. This set
of equations, Eq. 2.11 - Eq. 2.14, are called the Kohn-Sham equations. The orbitals $\psi_\mu(r)$ obtained from the Kohn-Sham equations can not be used to construct a total ground-state wave function. The functions are only constructions and they have no physical correspondence. In the same way the eigenvalues, $\epsilon_\mu$, can not be related to the total ground-state energy. To be able to perform a calculation for a real system, an approximation of the exchange = correlation functional $E_{xc}$ has to be made. The DFPT is a particularly powerful and flexible theoretical technique that allows calculation of such properties within the density functional framework, thereby facilitating an understanding of the microscopic quantum mechanical mechanisms behind such processes, as well as providing a rigorous testing ground for theoretical developments. The properties of static response functions, as well as of vibrational excitations in the harmonic approximation [15] are studied. DFPT relies on the '2n + 1 theorem' of perturbation theory to obtain the $(2n + 1)$ order derivatives of energy $E$ from $n$-order perturbed wave functions. This formalism is discussed in details in [14]. Applications to the calculation of phonon in transition metals are presented in [16].
Chapter 3

Computational methods

3.1 Introduction

Pressure drastically and categorically alters all elastic, electronic, magnetic, structural and chemical properties, and pushes materials across conventional barriers between insulators and superconductors, amorphous and crystalline solids, ionic and covalent compounds, vigorously reactive and insert chemicals, etc. In the process, these discoveries reveal surprising high-pressure physics and chemistry and create novel materials. In nature, high pressure are generated inside the Earth and celestial bodies, high-pressure studies are therefore also the key to understand their interior processes, dynamics and formation.

The theory involves a Hamiltonian which differs from the free ion Hamiltonian considered earlier only in the inclusion of an electrostatic potential perturbation term. Besides of the electrostatic crystal field potential, there are two perturbing quantities considered, the electrostatic repulsion and spin-orbital terms. With pressure the general tendency is for energy bands to broaden.

Equation of state

As same as the temperature and chemical content, the pressure also provides a way to study the materials properties and develops the materials structural dimensions by driving the phase transition. Under high pressure, the solid state materials change more condensed state. It is well and the density functional theory still works well to describe the interactional energy. Over the past decades, density-functional theory [6] has successfully provided a framework within which ground-state properties of many physical systems can be calculated [13].

However, while a high accuracy can very often be obtained in the 0-K \( ab \text{ initio} \) calculations, the \( ab \text{ initio} \) lattice dynamic calculation still remains a great challenge to us. The basic difficulty in the systematic theoretical calculation of the lattice dynamic properties of a substance by means of perturbation theories is how to incorporate correctly the structurally complicated phonon-electron and phonon-phonon interaction of the many-body problem.
Normally, by means of pressure, most of the materials tend to change their phases observed in nature to a new high pressure phase. The development of theories to describe the experimental properties and behavior of matter inevitably involves approximations which may be mathematical and/or physical in nature. The success of a theoretical calculation of an equation of state will give information about the various approximations which must be made. Such EOS provides a mathematical relationship between two or more thermodynamic potentials associated with matter through its pressure $P$, temperature $T$, volume $V$ and total energy $E$. Their relation is described by

$$P = -\left(\frac{dE}{dV}\right)_T.$$  (3.1)

The basic quantities involved are the Helmholtz free energy $F(V,T) = U(V,T) - TS(V,T)$, where $U$ is internal energy and $S$ is entropy, the volume and temperature are the independent variables, or the Gibbs free energy $G(P,T) = H(P,T) - TS(P,T)$. Where the pressure and temperature are the independent variables. The enthalpy $H$ is given by

$$H = E + PV.$$  (3.2)

One can use different forms of EOS. The most widely used is Murnaghan EOS, which is given by Murnaghan [17]

$$E(V) = U + \frac{B_0 V}{B'_0} \left( \frac{V_0}{V} \right)^{B'_0} - 1\right) - \frac{B_0 V_0}{B'_0} - 1).$$  (3.3)

The bulk modulus $B$ is defined by

$$B = -V\left(\frac{dP}{dV}\right)_T.$$  (3.4)

Assuming that the bulk modulus pressure derivative does not change much with pressure and taking it as a constant, we find that the pressure as a function of volume $P(V)$ is written as

$$P(V) = \left(\frac{B_0}{B'_0}\right)^\left(\frac{V_0}{V}\right)^{B'_0} - 1).$$  (3.5)

At temperature $T = 0$, the condition for the stable structure are constant pressure $P$ is that enthalpy should be minimum. One can also determine transition pressure by calculating internal energy $E(V)$ and using the Gibbs construction of tangent lines between the $E(V)$ curves for two phases, the slope of which is the pressure for the transition between the phases. At zero temperature, we can write

$$H(P) = E(V) + PV.$$  (3.6)

The equation of state as a function of pressure is perhaps one of the most important property of condensed matter. The total energy $E$ at $T = 0$ as a function of volume $V$ is the most easily accessible quantity for theoretical analysis because it is more straightforward to
carry out electronic structure calculations at fixed volume. The functional of equations are energy $E$, pressure $P$, bulk modulus $B$.

The way to determine the phase transition is by calculating the total energy for several volumes and taking the common tangent of the total energy versus volume curve for the investigated structures. Another way to determine the phase transition is by calculating the total energy for several volume and taking the common tangent of the total energy versus volume curve for the investigated structures

$$B = -V \frac{dP}{dV} = V \frac{d^2 E}{dV^2}, \quad (3.7)$$

with $E$ being the cohesive energy of the crystal. One can calculate the total energy for several values of the volume and fit to an analytic form, e.g. the Murnaghan equation of state. The minimum gives the equilibrium volume $V_0$ and total energy, and the second derivative is the bulk modulus $B$. The venerable subject of stress and strain in materials has also been brought into the fold of electronic structure. The basic definition of the stress tensor $\sigma_{\alpha\beta}$ is the generalization of 3.8 to anisotropic strain

$$\sigma_{\alpha\beta} = -\frac{1}{\Omega} \frac{\partial E_{\text{total}}}{\partial u_{\alpha\beta}}, \quad (3.8)$$

where $u_{\alpha\beta}$ is the symmetric strain tensor defined. The Murnaghan equation of state is used to calculate the energy minimum of the total energy as a function of volume curve having two free parameters, namely the bulk modulus and its derivative.

## 3.2 Lattice dynamics

We review in this section some fundamental aspects of lattice dynamics, as described in the model established by Born and von Kármán. This model has been a cornerstone of solid-state physics since its introduction almost a century ago. It is presented extensively in the seminal book of Born and Huang [18]. The interatomic force constants used to determine phonon frequencies in the system. The interatomic force constant matrix (IFC) consists of separate electronic and ionic contributions. For a periodic lattice of atoms, the only portions of the crystal Hamiltonian that depend on the ion positions are the ion-electron interaction terms, $V_{\text{el}}(r)$, and the ion-ion interaction term, $E_{\text{ion}}(R)$. The force on a given atom consists of a component that is responding to the surrounding electron charge density, $n(r)$, and another term that accounts for ion-ion interactions.

### Frozen phonon

The "frozen phonon" method is a direct calculation of the total energy as a function of the positions of the atoms. In this section, we give a brief overview of current approaches for calculating phonons from first-principles simulations. This approach is based on the adiabatic approximation to calculate the energy of displacement of the nuclei in the potential provided by the electrons. The displacements correspond to the polarization vector
for the phonon considered, multiplied by the periodic oscillation, and a displacement amplitude. By calculating the total energy for a set of displacement configurations (varying the values of displacement), one obtains the "deformation potential" for this phonon. This potential curve is typically parabolic around the equilibrium configuration.

An important information about materials is provided by the vibrational spectra that are measured by inelastic neutron scattering. Modern theoretical calculations provide robust information on eigenvectors, electron-phonon interactions, and other properties.

Electron-phonon coupling is described by the matrix elements that relate the electron transition from an initial electronic state \( |i\rangle \) to a final state \( |f\rangle \) through the absorption (emission) of a phonon. These matrix elements are given by (in atomic units)

\[
g_{q\nu}(k, i, f) = \sqrt{\frac{\hbar^2}{2M\omega_{q\nu}}{{|\psi_0^f, k+q|\varepsilon_{q, \nu} \cdot \delta V_{q\nu}^{ef}|\psi_0^i, k}}}.
\]

Here, \( k \) and \( q \) are momenta of electrons and phonon, respectively. The Fermi golden rule allows us to define phonon lifetimes due to the e-ph interaction. On quasi-elastic approximation, one can obtain the electron-phonon interaction energy (in wave length)

\[
\lambda = k_s = \left(\frac{4k_F}{\pi}\right)^{1/2}.
\]

Finally, we emphasize that both the formalism of density functional theory and the Born-von Kármán model of lattice dynamics rest on the Born-Oppenheimer approximation. The electron-phonon interaction can be reintroduced in the theory with a perturbation treatment. From the general Hamiltonian for the crystal

\[
\hat{H} = \hat{T}_e + \hat{V}_{e-n} + \hat{T}_n + \hat{V}_{n-n} + \hat{V}_{e-n},
\]

where \( \hat{T}_n \) is the kinetic energy of the nuclei, \( \hat{T}_e \) is the kinetic energy of the electrons, \( \hat{V}_{n-n} \) if the Coulombic repulsion energy of the nuclei, \( \hat{V}_{e-n} \) if the Coulombic attraction between electrons and nuclei and, finally, \( \hat{V}_{e-e} \) if the electron-electron interaction. The Born-Oppenheimer approximation is then equivalent to neglecting the off-diagonal terms, which is uncoupled between electron and phonon.

In perturbative treatment, the Shrödinger equation for the nuclei and electron can be written

\[
\hat{H}_{ad} = \sum_{k, s} \langle k, s|\hat{H}|k, s\rangle|k, s\rangle\langle k, s|,
\]

where \( k \) denotes the electron state and \( s \) is the phonon state

\[
\hat{H}\Phi - E\Phi = \sum_k (E_k(R) - E)\chi_k(R)\psi_k(r, R) + \sum_k (\hat{T}_n + \hat{V}_{n-n})\chi_k(R)\psi_k(r, R).
\]

\[
\left(E_{k'}(R) - E + \hat{V}_{n-n} + \hat{T}_n\right)\chi_{k'}(R) = 0.
\]

One can then extract the frequency for this phonon mode from the potential energy curve. For example in the case of a parabola, the frequency is \( K/M \), with \( K \) the second-derivative of the potential and \( M \) the nuclear mass. The advantage of this method is that
it provides the potential for the atomic displacements and it is not limited to the harmonic approximation. Studies of anharmonicity for selected phonon modes in transition metals have been performed with this method. The obvious disadvantage of the frozen-phonon method is its computational cost. For calculating long-wavelength modes, one needs to setup a supercell that can be quite large. Also, the method is rather cumbersome, since the phonon modes are calculated one at a time, and a special supercell is needed for each one. Obviously, the method is limited to phonon modes whose displacement pattern are commensurate to the supercell used. The calculation of the entire phonon dispersions along several directions, or even worse the phonon DOS, would be very tedious and probably too demanding computationally for a true ab initio approach.

**Linear response method**

Many physical properties are derivatives of the total energy, or of a suitable thermodynamic potential, with respect to perturbations. For example, perturbations might be atomic displacements, dilations or contractions of the unit cell, or an external electric field. The corresponding first order derivatives of the energy would then be the forces on the nuclei, the stresses and the dipole moment. Second order derivatives would include the dynamical matrix, elastic constants, the dielectric susceptibility, the Born effective charge tensors and internal strains, while third order derivatives would include the nonlinear dielectric susceptibility, phonon phonon interactions and Grüneisen parameters [19].

The linear response approach to the calculation of perturbations allows one to compute the dynamical matrix \( D(q) \) and phonon frequencies \( \omega_j(q) \) at a selected set of \( q \)-points. Implementations of DFPT are found in several computer programs. ESPRESSO (http://www.quantum-espresso.org/) used in this work is the program for electronic structure calculations within DFT and DFPT, using plane wave basis sets and pseudopotentials.

Electron-phonon interaction (EPI) in metals is a subject of intensive theoretical and experimental investigations. The interest in this problem arises from a variety of physical phenomena such as electrical and thermal resistivity, renormalization of the electronic specific heat, superconductivity, and for a quantitative understanding of those a proper description of the EPI is required [20].

**Anharmonic lattice dynamics**

Within the harmonic approximation, phonons are non-interacting and live forever. There are a number of phenomenon that cannot explained within the harmonic approximation, for example the temperature dependence of equilibrium properties. In this section, we describe a self consistent phonon calculations as a natural extension of the theory of the harmonic lattice. The self-consistent phonon (SCP) formalism has proved valuable in calculating the anharmonic contribution to lattice-dynamic properties.

There are two ways to calculate the properties of temperature-dependent phonon, quasi-harmonic (QH) and SCP. The quasi-harmonic approximation (QHA) plays an important role in predicting the lattice instability to occur at too low a temperature but it
is a poor approximation in the high-temperature low-density regime. For the strong anharmonic materials the QH DFT method is not enough to capture the anharmonistic associated to the thermal expansion. The SCP calculations are a natural extension of the theory of the harmonic lattice, which formalism has proved valuable in calculating the anharmonic contribution to lattice-dynamic properties at higher temperature. For example, ferromagnetic bcc iron, and most of translation metals crystalized in bcc structure, show unstable phonon modes regarding to the harmonic as well as QHA calculations, which could not be stabilized by the thermal expansion because the strong anharmonicity. Anharmonic effects manifest themselves as phonon-phonon interaction, which must be included in order to correctly describe the lattice dynamics of the systems, especially at higher temperature environment. In this section, we are going to present a self-consistent \textit{ab initio} lattice dynamic (SCAILD) method to study the anharmonic dynamics, in which the interaction between phonons will been taken into account [21]. In the SCAILD procedure for monoatomic solids the average squared frequency is a function of thermally averaged force constants and the average displacement is a thermodynamic function of the average frequency, both calculated self-consistently. The pressure is calculated from the derivative of the free energy with respect to volume in which anharmonic terms are explicitly included.

The Hamiltonian of lattice dynamical system can be expressed as

\[
H = H_h + H_{anh} \tag{3.15}
\]

are the harmonic and anharmonic parts of the Hamiltonian, respectively. In the first Brillouin zone, for each wave vector \( k \) one finds the eigenvalues \( \omega_{ks} \) and eigen- vectors \( e_{ks} \) of different phonon modes (longitudinal or transverse) labeled by the symbol \( s \), the displacements \( U_R \) and the kinetic energy operators \( P_R \) can be expressed as

\[
U_R = \frac{1}{\sqrt{MN}} \sum_{k,s} Q_{ks} e_{ks} e^{i k R} \tag{3.16}
\]

\[
P_R = \frac{1}{\sqrt{MN}} \sum_{k,s} P_{ks} e_{ks} e^{i k R} \tag{3.17}
\]

The harmonic Hamiltonian \( H_h \) of the crystal could be separated into the Hamiltonians of 3N independent harmonic oscillators.

\[
H_h = \frac{1}{2} \sum_{ks} (p_{ks}^2 + \omega^2_{ks} Q_{ks}^2) \tag{3.18}
\]

\( Q_{ks} \) and \( P_{ks} \) are the canonical phonon coordinates. The phonon-phonon interactions are missed in the harmonic Hamiltonian. The thermodynamic average of the operators \( Q_{ks}^\dagger Q_{ks} \) determines the mean square atomic displacements and is given by:

\[
\langle Q_{ks}^\dagger Q_{ks} \rangle = \frac{\hbar}{\omega_{ks}} \left[ \frac{1}{2} + n \left( \frac{\hbar \omega_{ks}}{k_B T} \right) \right] \tag{3.19}
\]
where $n(x) = 1/(e^x - 1)$ is the Planck function. In the classical limit, i.e. for sufficiently high temperatures, the operators $(1/\sqrt{M})Q_{ks}$ are replaced by real numbers,

$$R_{ks} \equiv \pm \sqrt{\frac{\langle Q_{ks}^+Q_{ks} \rangle}{M}}$$

(3.20)

From the atomic displacements to calculate the force $F_k$ of the lattice with Fourier transforming. The eigenvalues, phonon frequencies $\omega_{ks}$ can be obtained

$$\omega_{ks} = [-\frac{1}{M} \frac{\epsilon_{ks}F_k}{R_{ks}}]^{1/2}.$$  (3.21)

For the dynamic unstable materials there exist imaginary phonon frequencies, one can drive the total energy of the lattice going downward. Once the atomic planes or atomic positions shift, a new crystal structure would lower the total energy.

By considering the interaction between phonons in SCAILD method, the full Hamiltonian do not be separated into N independent Hamiltonians. The anharmonic Hamiltonian could be expressed as

$$H = \sum_{ks} \frac{1}{2} [p_{ks}^2 + \omega^2_{ks} (1 + \frac{1}{3} \sum_{k_1,k_2} s_1, s_2 A(k, k_1, k_2, s, s_1 s_2) \frac{Q_{k_1 s_1} Q_{k_2 s_2}}{Q_{ks} \omega^2_{ks}} + \ldots)] Q_{2ks}^2$$

(3.22)

The following mean-field Hamiltonian can be constructed

$$H^{MF} = \sum_{ks} \frac{1}{2} (p_{ks}^2 + \overline{\omega^2}_{ks} Q_{ks}^2),$$

(3.23)

where

$$\overline{\omega^2}_{ks} = \omega^2_{ks} (1 + \sqrt{M} \sum_{k_1,k_2} s_1, s_2 A(k, k_1, k_2, s, s_1 s_2) \frac{R_{k_1 s_1} R_{k_2 s_2}}{R_{ks} \omega^2_{ks}} + \ldots)$$

(3.24)

The eigenvalues $\overline{\omega^2}_{ks}$ are related to the forces, which induced by the displacements $U(R)$ can be calculated by any standard \textit{ab initio} method. In the SCAILD scheme equations 3.19-3.20 and 3.23-3.24 are solved by first calculating a starting guess for the phonon dispersions by means of a standard supercell calculation [22]. The phonon frequencies corresponding to k-vectors commensurate with the supercell are then used to calculate the atomic displacements.

**Kohn anomaly**

Fermi surface topological transition is related to the dominant anomaly of the static electron density response function. The anomaly is found to be made of analytically different terms: the first term, related to the appearance (or disappearance) of Kohn anomaly surfaces at the transition, is logarithmic when wave vector $q$ is on the surface. Kohn
anomalies appear at small but finite wave vectors in $q = 2k_F$, [23] which may induce a long-wavelength acoustic instability. Kohn anomaly involves transitions between two states which are both near the Fermi surface. Pressure affects the phonon frequencies, giving rise to Kohn Anomalies. The phonon wavevector, $q$, spans different Fermi sheets and links different electronic states, $k_2 = k_1 + q$, the electrons are no longer able to effectively shield the induced positive charge and the acoustic properties undergo a marked change, the Kohn anomaly[24].

The superconductivity is led by electron-electron attraction, which is from the strength of the electron-phonon interaction and the phonon frequencies. In the transition method series, the $d$ electrons near the Fermi surface undergo virtual-phonon-exchange scattering, and participate in the BCS condensation, although too immobile for significance in normal-sate conductivity. Most theories of $T_c$ in transition metals have concentrated on understanding electron phonon interaction.

### 3.3 Spin state transition

It should be noted that in DFT calculations, the electronic structure of a system with strong electron correlation, such as TM compounds, is not well described. The LDA or GGA often fails to describe systems with strongly correlated $d$ and $f$ electrons. In some cases this can be remedied by introducing a strong intra-atomic (on-site) Coulomb interaction in a Hartree-Fock-like manner, as a replacement of the LDA on-site energy. This approach is commonly known as the LDA+$U$ method [12]. There is a simple formulation of the DFT+$U$ method by Liechtenstein [25] and Dudarev [26], where a single parameter, $U_{\text{eff}}$, determines an orbital-dependent correction to the DFT energy. $U_{\text{eff}}$ is generally expressed as the difference between two parameters, the Hubbard $U$, which is the Coulomb-energetic cost to place two electrons at the same site, and a parameter $J$ representing the screened exchange energy. While $U$ depends on the spatial extension of the wave functions and on screening, $J$ is an approximation of the Stoner exchange parameter and almost constant $J \approx 1$ eV [27]. The $U_{\text{eff}} = 0$ case represents the DFT limit, and a larger $U_{\text{eff}}$ forces a stricter observance of the on-site idempotency, achieved by lowering the one-electron potential locally for the specified orbitals of the metal atoms (e.g. Fe $d$ orbitals) and in turn reducing the hybridization with, e.g., O atoms. The parameter $U_{\text{eff}} = 4$ eV was used by Ricardo et al. [28] for FeSbO$_4$ and Fang et al. [29] for FeO calculations. Rollmann et al. [30] investigated the structure and magnetic phases of hematite using the GGA+$U$ method with different $U$ (ranging from 1 to 9 eV) and demonstrated that the value of 4 eV is the best one for overall agreement with experiment. In this work, to obtain a more accurate theoretical understanding of the electronic and magnetic properties of FeCO$_3$, we performed the GGA+$U$ calculations with $U = 4, 5, 6$ eV and $J = 1$ eV, to simulate FeCO$_3$, under pressures, and compared with the GGA.
Chapter 4

Summary

4.1 Introduction

The properties of compressed materials could be modified by high pressure. The field of high-pressure physics encompasses virtually all branches of physics. In present, even the pressure of 1000 GPa could be produced by shock waves of high explosives or by projectile impact. But the more easy and simple way is to simulate the pressure and temperature in the computer. One can easily calculate many properties of the materials including volume, phase transitions, electrical, optical, magnetic, and chemical properties. For the applications, many phases of the materials that form at high pressure could be quenched to a low-pressure phase at ambient pressure. Frequently, dramatic changes in physical properties result from phase changes. Ferromagnetic iron transforms to a paramagnetic state at pressures above 10 GPa. Vanadium in bcc phase undergoes two successive phase transitions driven by high pressure, and the superconductivity enhanced in the high pressure phases. Vanadium changed back to bcc phase again at around pressure of 200 GPa. When considered the temperature effect under high pressure, many solids exhibit polymorphic phase changes. These changes are a rearrangement of the atoms or molecules in the solid.

4.2 Lattice dynamic at high pressure

The lattice dynamic contributes to the thermodynamic functions. The equations for the thermodynamic functions can in principle be evaluated directly using frequency values taken from the dispersion curves calculated over a fine grid of wave vectors within the first Brillouin zone. In general, the phonon spectrum depend on temperature. When quasiharmonic approximation is valid, the temperature dependence of the phonon spectrum may be calculated by including the temperature dependence of the lattice parameters. In magnetic crystal, besides the anharmonicity, the strong exchange interaction may also contributes to the temperature-dependent phonon spectrum.

It has been recognized that a small shift in the phonon frequencies in magnetic materials may be caused by the quadratic expansion of the exchange interaction. The lattice
vibration will change the exchange energy which then contributes to the temperature dependent phonon dispersion. The phonon frequency softening in nickel at high temperatures is observed due to this effect [31].

High pressure experiments on transition metals have proved to be of interest in establishing the type of ferromagnetic order in these materials. In general, small and negative pressure effects on the spontaneous magnetization near zero temperature and on the Curie temperature are reported for weak itinerant electron ferromagnets. In this thesis we present information on the magnetic properties of titanium and iron. The \textit{ab initio} lattice dynamic calculations on iron are in good agreement with the pioneering work of [32] on experiment at ambient conditions. The volume dependence and magnetism dependence of phonon frequencies is found to be relevant in our study.

Vanadium

Phonon frequency softening and phonon scattering play a crucial role in superconductivity in metallic systems. Recent advances in DFPT have made it possible to examine acoustic properties of materials at a level of accuracy previously made for only for electronic properties only [14]. This work predicted the presence of a weaker Kohn anomaly at \( q = \frac{2\pi}{a} [0.30.30.3] \) in the TA branch along the [100] direction from a first principles perspective. The anomaly extends over a broad range of wave vector space and also increases rapidly with pressure.

In figure 4.1a, we have shown phonon dispersion curve for vanadium. The solid lines are obtained by calculation and the open symbols are the experimental data taken from the experimental work, which were observed with x-ray thermal scattering [33]. There is a clear steep slope observed at \( \frac{1}{3}(\Gamma - H) \), because of Kohn anomaly, on computed transverse acoustic mode (TA) along [\( \xi 00 \)] direction. Our calculations are in good overall agreement with experiment including anomalous frequency distribution near high symmetry point N along \( \Gamma - N \). There are two branches of one LA mode and other degenerated TA1 (< \( \xi 00 \) >) and TA2 (<001>) modes along [\( \xi 0 \)] direction. There exists a crossover of LA mode with TA2 mode at zone boundary point N. The transverse dispersion curve for [\( \xi 0 \)] TA2 is higher than those of the longitudinal dispersion curve near the BZ of [\( \xi 0 \)] symmetry direction.

The vanadium is formed in bcc structure at ambient conditions and the phonon dispersion curve is shown in Fig.4.1. There is a clear steep slope observed at \( \frac{1}{3}(\Gamma - H) \), because of Kohn anomaly, on computed transverse acoustic mode (TA) along [100] direction. Our calculations are in good overall agreement with experiment including anomalous frequency distribution near high symmetry point N along \( \Gamma - N \). There are two branches of one LA mode and other degenerated TA1 (<100> and TA2 <001> modes along [110] direction. There exists a crossover of LA mode with TA2 mode at zone boundary point N. The transverse dispersion curve for [110] TA2 is higher than those of the longitudinal dispersion curve near the BZ of [110] symmetry direction.

The Fig.4.1b shows phonon density of state for bcc-vanadium varied as a function of pressure. The lower frequency phonon mode due to Kohn anomaly is found to be grown and soften, but all of other phonon frequency moves to higher value with pressure in-
4.2. LATTICE DYNAMIC AT HIGH PRESSURE

creased. Around $V/V_0 = 0.78$ (62 GPa) the negative frequency appeared in the PDOS spectrum, but the PDOS still shows the typical bcc structural spectrum. After $V/V_0 = 0.70$ (112 GPa) the PDOS shows a different profile of frequency distribution. It means that there is an evidence of the dynamic instability of bcc-V around $V/V_0 = 0.78$.

In order to understand high-pressure structural phase transition of vanadium by dynamical stability, we plot in Fig.4.2 the frequencies at $\Gamma$ center along high symmetry $\Gamma$-H and $\Gamma$-N direction of bcc BZ, and these are shown with solid lines. The frequencies of softening mode at H ($1/300$) are shown by dashed line as a function of pressure. As mentioned above, the soft modes due to Kohn anomalies are in the lower frequency part along $\Gamma$-H direction. Under the compression, the frequencies at ($1/300$) soften, the phonon modes smoothly and slowly go to negative value up to $V/V_0 = 0.79$. It is reasonable to suggest that the phonon mode softening related to Kohn anomaly drives the structural phase transition from bcc to hR1. Above this pressure up to $V/V_0 = 0.59$, the phonon dispersion of bcc phase shows a complete dynamical instability. At $\Gamma$ point, all the phonon branches along high symmetry directions are negative suggesting that no active phonon modes are present in bcc phase. This also indicates that bcc symmetry is broken under high pressure. It is worth to note that the angle of rhombohedral hR1 phase changes from 110.5° to 108.2° at around $V/V_0 = 0.67$. Further compression this angle changes back 109.47° at $V/V_0 = 0.58$. The origin of these two times change in rhombohedral angle can not be just explained by lattice dynamic calculation. Different from the phase transition of bcc to hR1 at $V/V_0 = 0.79$, the transition of hR1 with angle 108.2° to bcc at $V/V_0 = 0.58$ shows an abrupt change in phonon frequency.

Figure 4.1: The phonon dispersion (a) and density of states (b) for vanadium as a function of pressure
Figure 4.2: The angle of rhombohedral hR1 phase changes from 110.5° to 108.2° at around $V/V_0 = 0.67$. Further compression this angle changes back 109.47° at $V/V_0 = 0.58$. The origin of these two times change in rhombohedral angle can not be just explained by lattice dynamic calculation. Different from the phase transition of bcc to hR1 at $V/V_0 = 0.79$, the transition of hR1 with angle 108.2° to bcc at $V/V_0 = 0.58$ shows an abrupt change in phonon frequency.

Iron

Iron is one of the important material in the history of mankind. In this section we focused our attention to the dynamical stability of Fe at extreme conditions. Variation of phonon frequencies with temperature and volume are shown in Fig.4.3 and Fig.4.4. The analysis of the T1(N) mode shows in fact a slight decrease of its frequency in the 0-1750 K range. The critical ingredient for this behavior is the presence of ferromagnetism which renders the bcc phase thermodynamically unstable long before it becomes dynamically unstable. At ambient pressure, the dominant role of magnetism for the stability of a iron at ambient pressure is readily visible by an unusual feature of its phase diagram, the existence of a second, nonmagnetic, bcc phase ($\delta$-iron) between 1660 K and the melting point at 1811 K.
4.2. LATTICE DYNAMIC AT HIGH PRESSURE

Figure 4.3: Variation of the frequencies with volume expansion in the ferromagnetic bcc phases of iron. The solid color straight lines indicate the experimental frequencies at the same temperatures.

There are well-known temperature dependent acoustic phonon branches in bcc structure of Iron, which are the Longitude acoustic (LA) mode at $[2/32/32/3]$ along the high symmetry $[111]$ direction and the transverse acoustic (TA) mode at Bullirium boundary along the high symmetry $[110]$ direction. It is identified that these modes are only sensitive to the temperature. We note that the most softening mode is along the easy axis for all the temperatures. Our phonon frequency calculations in Fig.4.4 yield that the magnetic moment in the ferromagnetic bcc Iron is varied from 2.3 $\mu$B to 1.85 $\mu$B, there are some other modes responded. The most sensitive modes occur at boundary of $[100]$, which acoustic frequencies are softening quickly as spin moment decreased.

Whether the bcc iron is lattice dynamically stable in the Earth’s inner core, it is still an open question. Calculations by Vočadlo yielded an imaginary frequency which indicates that within the harmonic approximation this mode for bcc iron is unstable in the earth’s
inner core pressure and 0 K temperature[34]. We use the self-consistent \textit{ab initio} lattice dynamics, so called SCAILD method to study the stability of the high temperature bcc phase of iron and in particular the frequency of the $T_1$ N-point phonon, which is of vital importance to include anharmonic interactions. The hcp-bcc transition of iron in the Earth’s inner core could be martensite in nature, which means the atomic positions of the parent and the resultant crystal structure are highly correlated, thus limiting the configuration coordinates which must be varied. Burgers proposed that the transition from bcc to hcp occurs through the displacements of the zone-boundary $T_1$ N-point phonon together with a long-wavelength shear.

The temperature-dependent phonon DOS of bcc-Fe are simulated at ambient pressure and a pressure of 235 GPa (corresponding to the relative volume $V/V$=0.62), respectively. It is shown in figure 4.5. The green line represents ferromagnetic $\alpha$ Fe at ambient pressure and a temperature of 1150 K. This gives a good agreement with experimental data on phonon DOS measured for $\alpha$ Fe at pressure of 6 GPa and temperature of 920 K. The orange line shows the $\delta$ Fe at a temperature of 1750 K. The red solid is obtained for a non-magnetic bcc-Fe phase at a temperature of 4500 K. According to the well known Burger mechanism, the bcc to hcp structural transformation can be achieved by two simultaneous distortions: (1) opposite displacements of the bcc (110) planes in the [110] directions, which corresponds to the $TA_1(N)$ phonon mode at the bcc BZ boundary, [35] and [36]

Figure 4.4: Variation of the frequencies with volume expansion in the ferromagnetic bcc phases of iron. The solid color straight lines indicate the experimental frequencies at the temperatures 0 K.

![Frequency - Magnetic moments at 0 K](image-url)
4.2. LATTICE DYNAMIC AT HIGH PRESSURE

Figure 4.5: The phonon dispersion (a) and the phonon density of states (b) of bcc-Fe as a function of temperature are shown, respectively. The green and yellow color lines give the simulation for low temperature phase of $\alpha$-Fe and high temperature phase of $\delta$-Fe, respectively, at ambient pressure. The red color lines show the simulation at high pressure with relative volume of $V/V_0 = 0.62$, where solid line indicates the results at temperature of 4500 K, and the dotted line presents the one at temperature of 5000 K.

(2) shear deformation in the [001] direction while keeping the volume and the bcc (110) planes unchanged. At high temperature, the dispersion curve of Fe shows two anomalies. 1) The transverse $T$, [110] phonon with (110) polarization is soft. 2) At $q = 3/2[111]$, the so-called $\omega$ point, phonon intensity reaches down to zero energy transfer. Both modes are temperature dependent. For example the bcc-hep transition of Ba, first-principles calculations clearly indicate a substantial softening of this $T_1$ N-point phonon mode when approaching the transition pressure [37]. Such dynamical precursor effects of the lattice instability have also been found in group-IV transition metals such as Ti, Zr, and Hf [38].

The Fig. 4.6 shows the lattice dynamical stability range of bcc-phase of pure iron at the Earth’s core conditions. The orange error bar ([2]) shows the melting data of Brown [39]. The red colored error bars ([3]) are melting points from shock wave experiments of Yoo et al. [40]. The green error bar ([6]) shows the bcc phase of Fe-10%Ni alloy from Dubrovinsky et al. static high-pressure experimental work using diamond anvil cell [41]. The lattice dynamical stability of bcc-Fe is calculated below the experimental melting temperature for Earth’s core pressure of 250 to 380 GPa. The green stars and the blue solid squares show the lattice dynamical stable and unstable points from this work, respectively. Red area indicates the inner core conditions.
4.3 High pressure phase transition

Metal hydrides

The alkali-earth dihydrides have attracted attention due to their potential application as hydrogen storage materials as well as optical applications. CaH$_2$, SrH$_2$, and BaH$_2$ crystallize in the orthorhombic phase (Co$_2$Si-type, space group $D_{2h}^{16}$ (Pnma)) and having the same lattice parameter ratios ($c/a; (a+c)/b$) at ambient conditions. All of these compounds have the similar dynamical properties at ambient conditions [42]. But under high pressure, the electric and elastic properties exhibit a different behavior. Up to now, only YbH$_2$ has known to show a high-pressure first-order structural phase transition from orthorhombic (Co$_2$Si-type) structure to the hexagonal (Ni$_2$In-type) structure which has space group $D_{6h}^1$ ($P6_3/mmc$) with the metal atoms in 2 (c) positions and the hydrogen atoms in 2(a) and 2(d) positions [43] and [44]. BaH$_2$ is one of the compounds which is least studied. Resistivity study under pressure up to 12.5 GPa does not show any significant indication of phase transition in BaH$_2$ [45]. On the other hand, it has shown that the elastic properties of BaH$_2$ compare to CaH$_2$ are different [46]. High pressure studies on alkali-earth dihydrides will be also helpful to understand metallization of hydrogen.

For understanding the energy band structure under high pressure, the local density of state for orthorhombic and hexagonal phase are calculated as shown in 4.9. Our electronic structure calculations show a band gap of 2.9 eV for orthorhombic phase where as the hexagonal phase shows a band gap of 1.8 eV. The local densities of state show that the valence band of orthorhombic phase is mainly constituted by Barium d electrons. The

![Figure 4.6: The high-pressure and high-temperature ($P - T$) phase diagram](image)
4.3. HIGH PRESSURE PHASE TRANSITION

Figure 4.7: Orthorhombic phase of BaH$_2$. Barium binds to four H1 atoms in blue color and five H2 atoms in red color b(1); hydrogen H1 binds to 4 Barium atoms and forms tetrahedral b(2); hydrogen H2 binds to 5 Barium atoms and forms octahedral b(3).

Figure 4.8: Hexagonal phase of BaH$_2$. Barium binds to five hydrogen atoms at site 2d in blue color and six hydrogen atoms at site 2a in red color (1); hydrogen at site 2d binds to 5 Barium atoms and forms hexahedral (2); hydrogen at site 2a binds to 6 Barium atoms and forms octahedral (3).

The conduction band is mainly formed by hydrogen s electrons, Barium d and p electrons. The hydrogen atoms in hexagonal lattice are much delocalized compared to the ambient pressure phase.

For understanding the effect of hydrogen vacancy on structural stabilities for ambient phase and high-pressure phase, the total energy of defect lattice with hydrogen vacancy are calculated. The chemical formula is chose as Ba$_{32}$H$_{64}$ for ambient phase and Ba$_{36}$H$_{72}$ for high-pressure phase. The total energy difference comparing to the perfect lattice is obtained by the following chemical equation as

$$ Ba_{32}H_{64} - \frac{1}{2} H_{mol} + Ba_{32}H_{63} \] \] (4.1) 

at ambient phase; and

$$ Ba_{36}H_{72} - \frac{1}{2} H_{mol} + Ba_{36}H_{71} \] \] (4.2) 

for high-pressure phase. After doing the full of structure relaxation for hydrogen and metal atoms site, unit cell shape and size, the results show a higher total energy of defect system.
The calculations predict that KBH$_4$ undergoes two phase transitions under high pressure. The lattice transforms first from the NaBH$_4$-type disordered cubic phase into the tetragonal NaBH$_4$ structure with space group $P4_2/mnc$ at 6.7 GPa, implying a disorder-order type second order phase transition caused by reorientation of tetrahedra. At higher pressure, 9.7 GPa, a further transformation occurs into a high-pressure orthorhombic KGaH$_4$-type phase. The coordination number for hydrogen bonding to potassium increases from 12 in the cubic and tetragonal phases to 14 in the high-pressure Pnma phase. Experimental data obtained by Raman spectroscopy up to 17.6 GPa verified the existence of a reversible phase transition with a rather wide transition region, 6 - 8.7 GPa on compression and 8 - 5 GPa on decompression. X-ray diffraction data for the high pressure phase were compatible with the predicted Pnma structure and with the predicted volume change at the transition, but the tetragonal phase could not be unambiguously identified.

**High spin to low spin transformation in FeCO$_3$**

As an example of the high spin to low spin (HS-LS) transition we discuss the FeCO$_3$, a rhombohedral crystal, siderite. Fe$^{2+}$ in FeCO$_3$ is high spin at ambient pressure with $S = 2$ and as pressure in increased, a LS ground state configuration with $S = 0$ is reached. As further pressure was applied there was no significant change up to about 30 GPa.

The bonding and the volume associated with the two spin states are different. By fitting the variation of total energy with volume to Birch-Murnaghan equation of state, we obtained the bulk modulus ($B_0 = 114$ GPa) and the pressure derivative of the bulk modulus ($B_0' = 3.99$), which are in good agreement with the experimental values of 117 GPa and 4 [47] within the GGA+$U$ ($U = 5$ eV), respectively.

By fitting the calculated energies versus unit cell volumes in the GGA +$U$ ($U =$
4.3. **HIGH PRESSURE PHASE TRANSITION**

Figure 4.10: Primitive unit cell of FeCO$_3$. Blue, brown and red spheres represent Fe, C and O atoms, respectively. Total energies as a function of the unit volume for the GGA and GGA + $U$ (5 eV) calculations. The least-squares-fitted curves to Birch-Murnaghan equation of state are shown.

Figure 4.11: Total and partial DOS for the HS phase of FeCO$_3$ at 0.6 GPa, calculated within the GGA+$U$ (5 eV). The positive and negative curves indicate the spin-up and spin-down states, respectively.
Figure 4.12: Projections of the charge density in the (100) plane crossing at Fe atom site for the HS and LS phases in the GGA +U (5 eV) case. The upper map: HS phase at 0.6 GPa (low pressure); The lower map: LS phase at 32 GPa (high pressure). The red regions denote Fe atoms.

When we consider lower volumes, we observe a collapse of the magnetic moments, from the HS to LS state, for which the magnetic moment is decreased from 2.2 uB/atom to 0. By placing a common tangent to the HS and LS curves, we obtain a value for the pressure of around 28 GPa. The corresponding volume collapse is 9.7%. This volume collapse can be explained by the fact, that the delocalized Fe-3d electrons form electron pairs, leading an increase of attraction between neighbor Fe atoms.

The corresponding phase-transition pressure in the $U = 4$ eV case is around 25 GPa. Finally, the geometry calculations for the LS states near the transition point show that there is a distortion mutation at the transition point. For the GGA +U (5 eV) calculations, angle is reduced from 52.5° to 52° during the HS to LS transition. However, the internal structural parameter of the C-O distance is nearly not changed.

From Fig.4.11, we can conclude that for the spin-up case, the Fe 3d and O 2p orbital form the top of valence bands, indicating a strong Fe-O 3d-2p hybridization characteristic near Fermi-energy, and O 2p and C 2p orbitals do the most contributions to the bottom of conduction bands, whereas for the spin-down case, the top of valence bands mainly consists of O 2p orbitals and the Fe 3d orbitals form the bottom of the conduction bands. When comparing the spin-up DOS of the lower-pressure (0.6 GPa) case to that of the higher-pressure (32 GPa) case near Fermi level, we can see that the Fe 3d-orbital contribution to the top of valence bands in the high-pressure case is more pronounced than in the lower-
pressure case. This can be explained by the fact of more delocalized d electrons under higher pressure.

In the Fig.4.12, it is noted that the Fe atoms are not in one plane crossing the center Fe atom, being due to the projections. For the HS phase at 0.6 GPa (low pressure), there is few 3d electron overlap between two neighbor Fe atoms. For the LS phase at 32 GPa (high pressure), the projections of the charge density reveal obvious 3d bonding between neighbor Fe atoms. According to the Pauli Exclusion Principle, the high-spin state is vanished by paired 3d electrons with decreasing Fe-Fe distance. On the other hand, as mentioned before, there is a mutation of angle occurring at the phase transition point. In the HS phase, there are net unpaired electrons localized around Fe atoms, presenting magnetic order, which leads a repulsion between neighbor Fe atoms with respect to the For the HS phase at lower paired-electron case. Therefore, these abrupt changes for pressure of 0.6 GPa, the bthe shape of the unit cell and the volume collapse also and gap are 1.3 eV. The corresponding value for the HS phase at 32 GPa is 0.9 eV.

The total and partial DOS calculations show that the electronic structures of the HS and LS phases. In the GGA + U calculations, with increasing pressure, the top of valence bands changes from strongly hybridized Fe 3d and O 2p orbitals to almost pure Fe 3d character. Whereas in the GGA method, the occupied states close to the Fermi energy are almost Fe 3d electrons dominated. The analyze of the DOS and electronic charge density calculations reveals that the delocalization of 3d electrons with increasing pressure leads to the HS-LS transition, accompanying a formation of a new d-bond between two neighbor Fe atoms.

4.4 MAX phase materials

The advancement in new materials processing and fabrication techniques has made it possible to better control the atomistic level of structures in a way, which was not feasible only a decade ago. If one can couple this atomic control with a good understanding of the relationship between structure and properties, this will in the future lead to a significant contribution to the synthesizing of tailor-made materials.

In this part of summary we have focused on, the structurally related nanolayered ternary compounds MAX phases. These compounds possess an unusual set of properties: On the one hand they behave like metals regarding to their machinability and their thermal and electrical conductivities. On the other hand they behave like ceramics in terms of their stiffnesses, oxidation resistances, thermal stabilities and high melting points. These combinations of properties may be interesting for industrial applications, searching e.g. for high performance materials. The general relations between the electronic structure and materials properties of MAX phases have been elaborated based on ab initio calculations.
Magnetic MAX phase materials design

In recent years, the structurally related layered ternary compounds $M_{N+1}AX_N$, where $N = 1, 2$ or $3$, $M$ is an early transition metal, $A$ is an A-group (mostly IIIA and IVA) element, and $X$ is either $C$ and/or $N$, attract increasing interest owing to their unique properties. These ternary carbides and nitrides combine unusual properties of both metals and ceramics. Like metals, they are good thermal and electrical conductors with electrical and thermal conductivities ranging from $0.5$ to $14 \times 10^6 \Omega^{-1}m^{-1}$, and from $10$ to $40$ $W/m\cdot K$, respectively. They are relatively soft with Vickers hardness of about $2-5$ GPa. Like ceramics, they are elastically stiff, some of them like $Ti_3SiC_2$, $Ti_3AlC_2$ and $Ti_4AlN_3$ also exhibit excellent high temperature mechanical properties. They are resistant to thermal shock and unusually damage tolerant, and exhibit excellent corrosion resistance. Above all, unlike conventional carbides or nitrides, they can be machined by conventional tools without lubricant, which is of great technological importance for the application of the $M_{N+1}AX_N$ phases. These excellent properties mentioned above make the $M_{N+1}AX_N$ phases another family of technically important materials.

The search for new combinations of MAX ceramics is still going on in order to be able to tune the properties of the MAX-phase to obtain the optimum coating. An attempt is yet to be made to synthesize magnetic MAX-phase. If one can make magnetic MAX phases compound, it will be a good functional materials. For example, it could be a one of the candidate for the spintronics application. Due to the abundance of Iron on earth, a MAX phase with Iron will be a promising candidate for magnetic MAX phase compound.

We have investigated the structural stability and magnetism for a set of compounds $Fe_{n+1}AC_n$ ($n=1,2,3$, and $A=Al,Si,Ge$) using $ab$ $initio$ theory. The crystal structure of
4.4. MAX PHASE MATERIALS

MAX phases are shown in Fig. 4.13. From our calculation, we have shown that some of Fe\(_{n+1}\)AC\(_n\) phases (n=2) with the general MAX phase formula and a layered hexagonal structure that belongs to space group can have a combination of properties of MAX phase at the same time having magnetism. Fe\(_3\)AlC\(_2\) phase indicate the most stable ferromagnetic properties among these MAX phases and magnetic moment is 0.73 \(\mu\)B/Fe-atom. In addition, the phase stability is predicted by comparing the total energy of the Fe\(_2\)AlC and Fe\(_2\)SiC phases with the total energy of the competing equilibrium phases at corresponding composition.

Our results indicate that only Fe\(_3\)AlC\(_2\) shows stable ferromagnetic behavior and an average moment up to 0.73 \(\mu\)B/Fe-atom. The iron in different symmetry position shows different magnetic moment because of connecting with different atoms in stacking sequence. The iron atoms in Fe\(_2\)AC compounds possess only one equivalent position, 4f site, so they show an unique magnetic moments. Our calculations show that the Fe\(_2\)AC phase exhibits much stronger magnetic moment, 1.18 \(\mu\)B/Fe-atom than those of Fe\(_2\)GeC and Fe\(_2\)SiC. The structure of Fe\(_3\)AC\(_2\) can be described as hexagonal layers stacked in the

Figure 4.14: Total DOS and PDOS (a) for the Fe\(_2\)AlC and (b) for Fe\(_3\)AlC\(_2\) ferromagnetic phases. The green line, red line, and blue line are displayed corresponding to the density of s states, of p states, and d states, respectively.
repeated sequence A-Fe-C-Fe-C-Fe slabs [48, 49, 50]. There are two inequivalent Fe layers: Fe (I) atom at $2a$ position layers with a C layer on one side and a A layer on the other, that shows a large magnetic moment; but Fe (2) layers at $4f$ site which are sandwiched between two C layers, that presents a low magnetic moment. These typical characteristics are observed in Fe$_4$AC$_3$ as well. The stacking sequence refers to the Fe (II), $4e$ positions are between two C layers. The magnetic moment of iron at $4e$ site displays much weaker moment than that Fe (I) at $4f$ site, indicating the different electrons coupling of electrons at different sites as shown in the paper V.
Bibliography


