Pressure Induced Phase Transformation of SnO2: An ab initio constant pressure study

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PRESSURE INDUCED PHASE TRANSFORMATION OF SNO$_2$

AN AB INITIO CONSTANT PRESSURE STUDY

BY

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ABSTRACT

The behavior of SnO₂ under rapid hydrostatic pressures is studied using constant-pressure ab initio simulations. The rutile-type SnO₂ gradually transforms into the CaCl₂-type structure at 15 GPa. At a pressure of about 20 GPa, a phase transformation into a cubic fluorite-type structure is observed. The orthorhombic Pnma cotunnite-structured phase is observed above 150 GPa. The mechanisms of these phase transformations at the atomistic level are discussed.

Key words High Pressure. Phase Transformation. Tin dioxide
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CHAPTER ONE

-1- Background

-1.1- Introduction (What is Phase Transformation)

The physical properties of all technologically interesting materials are strongly dependent upon their chemical composition as well as their microstructure. The most efficient way of obtaining the desirable microstructure is via accurate control of phase transformations in solids. Changes in the positions and arrangements of atoms and molecules can be measured as a function of the pressure. From these changes, researchers can understand the properties of existing materials and make new materials with new highly desirable properties. Examples of the benefits of these studies include gaining a better understanding of the magnetic fields of the Earth and other planets; developing better cutting tools, car engines, and armor plating; helping the food industry improve sterilization processes; reaching a deeper understanding of earthquakes; gaining new information on ultra-dense hydrogen and helium to aid the development of tomorrow's clean energy sources; and exploring potential applications for the biochemical community involving studies of the dynamics of structural changes in viruses and proteins[1].

The physical properties of all the materials that make up our world dictate the functions of those materials. These properties (electrical, magnetic, elastic, etc.) are dictated by how atoms and molecules are arranged and attached together. For example, water is a liquid because its molecules are weakly held together; diamond is so strong because its atoms are very strongly bonded together.
When pressure is applied to materials, the atoms in the materials are brought closer together, which changes dramatically the physical properties of the materials.

For example, squeezing hydrogen gas makes it into a liquid, a soft solid, a hard electrically insulating solid, and when its atoms are brought into extreme proximity to each other, an electrically conducting metal. It is also necessary to note that a phase transition is induced by acting from the outside to modify an intensive thermodynamic variable characterizing the system: temperature, pressure, magnetic or electric field, etc. This variable is coupled with an extensive variable (for example, pressure and volume are coupled) in the sense of classic thermodynamics.

This science constitutes the basis for chemical synthesis and thermal treatment or sintering in the processing of almost all crystalline solids. The structure resulting from a solid state phase transformation depends intimately on the crystallographic relationship between the Bravais lattices of the initial and product phases, on the elastic moduli of the separate phases, and on the kinetics (or rate) of the transformation[2].

**-1.2- Stability and Transition – Gibbs-Duhem Criterion**

A phase transition occurs when a phase becomes unstable in the given thermodynamic conditions with intensive variables (pressure, temperature, enthalpy, energy etc.). Its necessary to study the thermodynamic conditions to understand the phase transitions involved in the process.
We can describe the thermodynamic state of a system or material with the thermodynamic potentials classically obtained with a Legendre transformation. Thermodynamic potentials are parameters associated with a thermodynamic system and have the dimensions of energy. They are called "potentials" because in a sense, they describe the amount of potential energy in a thermodynamic system when it is subjected to certain constraints. The different potentials correspond to different constraints to which the system may be subjected. These thermodynamic potentials can also be calculated with quantum statistics if the partition function of the system is known. The choice of variables for studying and acting on it determines the potential. We note that in working with variable (Temperature, T and Volume, V), it is necessary to use the free energy F; the system will be investigated with the free enthalpy G (also called the Gibbs function) if the system is described with variables (Pressure, P and Temperature, T).

In thermodynamics, it is possible to show that a stable phase corresponds to the minimum of potentials F and G. More generally, by imagining virtual transformations of the thermodynamic quantities X from equilibrium, we have the stability criterion for this equilibrium situation, written as:

$$\Delta U + P \Delta V - T \Delta S \geq 0.$$  (1.1)

Where $\Delta U$, $\Delta V$, and $\Delta S$ are virtual variations of internal energy U, volume V and entropy S from equilibrium respectively. This is the Gibbs – Duhem stability criterion. We can easily deduce from equation (1.1) that a stable phase is characterized by a minimum of F (with constant T and V), G (with constant T and P), H (with constant S and P), U (with constant S and V), and by a maximum of the entropy (with constant U and V) [3-4].
-1.3- **Thermodynamic classification of Phase Transitions**

Two types of phase transitions can exist: transitions with latent heat on one hand, and transitions with out latent heat on the other hand. This is a thermodynamic classification. More generally, the Physicist P. Ehrenfest proposed a classification of phase transitions based on the thermodynamic potentials in 1933.

Ehrenfest proposed distinguishing:

* First-order transitions which are accompanied by discontinuities of thermodynamic quantities such as the entropy and density, are themselves associated with the first derivatives of thermodynamic potentials. For example,

\[
S = -(\frac{2G}{2T})_p, \quad V = (\frac{2G}{2P})_T, \quad H = (\frac{2G}{2I/T})_T
\]  

(1.2)

Where S, G, T, P, V and H are Entropy, Gibbs free energy, Temperature, Pressure, volume and Enthalpy, respectively. In the phase transition, these quantities corresponding to the first-order derivatives of potential G are discontinues (the latent heat is associated with discontinuity of the entropy).

* Second-order transitions for which the thermodynamic potential and their first-order derivatives are continuous, while some second derivatives with respect to state variable are reduced to zero or approach infinite asymptotically at the transition point. In this way, we can write:

\[
\frac{C_p}{T} = (\frac{2^2G}{2T^2})_p = (\frac{2S}{2T})_p
\]  

(1.3)

\[
K_vV = (\frac{2^2G}{2P^2})_T = (\frac{2V}{2P})_T
\]  

(1.4)

Where \(C_p\) and \(K_v\) are the specific heat at constant pressure and the compressibility at constant temperature, respectively. For these transitions, we continually pass from one
phase to another without being able to really speak of the coexistence of the two phases [3-4].

1.4. The Broad Categories of Phase Transition

The thermodynamic characteristics of a phase transition can be used to lay the foundations for a classification of phase transformation. Beyond this thermodynamic classification, it is almost impossible to give a satisfactory typology of phase changes because they involve extremely different properties of the substance. Moreover, they are encountered in all systems, whether physical, chemical or biological. Schematically, phase transformation can be classified in two broad categories: reconstructive and displacive phase transformations.

In a reconstructive transformation a "rebuilding" (crystallographic and/ or chemical) is required to convert the initial phase, into the product phase. Such reconstruction can be accomplished through the motion of atoms. During the transformation, the arrangement of the atoms is modified and is associated with a change in the symmetry of the crystal. This change, or break, in symmetry is characterized by going from a phase with high symmetry to another phase with lower symmetry induced by displacement of atoms in the solid or vise versa. These structural transitions are often accompanied by a modification of a physical quantity (density, elastic constants, thermal conductivity, etc.) and are mostly with the appearance of a new property.

When a structural change occurs by the coordinated movement of atoms (or groups of atoms) relative to their neighbors then the change is termed displacive transformation. The displacive transformations are also called diffusionless transformations and a class
of phase changes that do not occur by the long-range diffusion of atoms but rather by some form of cooperative, homogeneous movement of many atoms that results in a change in crystal structure. These movements are small, usually less than the interatomic distances, and the atoms maintain their relative relationships. The most commonly encountered transformation of this type is the martensitic transformation which, while being the best known, is actually only one subset of non-diffusional transformations.

-1.5- The Broad Categories of Applications of Phase Transitions

A very large number of phase transition phenomena have important technological applications: in metallurgy, electronics, process engineering, in the food industry, etc. Transitions are also utilized in technical systems and materials. Phase transitions are also utilized in the agriculture and food industry and pharmacy (alimentary gels and capsules for encapsulation of drugs, for example).

-1.6- Tin-Dioxide

Tin dioxide is the inorganic compound with the formula SnO₂. It crystallizes in the rutile structure, wherein the tin atoms are six coordinated and the oxygen atoms three coordinated. SnO₂ is usually regarded as an oxygen-deficient n-type semiconductor. Hydrous forms of SnO₂ have been described in the past as stannic acids, although such materials appear to be hydrated particles of SnO₂ where the composition reflects the particle size [7].
Cassiterite is a tin oxide mineral, SnO$_2$. It is generally opaque but is translucent in thin crystals. Its luster and multiple crystal faces produce a desirable gem. Cassiterite is the chief ore of tin today. Most sources of Cassiterite today are found in alluvial or placer deposits containing the resistant weathered grains. The best source of primary Cassiterite is the tin mines of Bolivia, where it is found in hydrothermal veins.

Cassiterite is a widespread minor constituent of igneous rocks. The Bolivia veins and the old exhausted workings of Cornwall, England, are concentrated in high temperature quartz veins and pegmatites associated with granitic intrusive. The veins commonly contain tourmaline, topaz, fluorite, apatite, wolframite, molybdenite, and arsenopyrite. The current major tin production comes from placer or alluvial deposits in Malaysia, Thailand, Indonesia, and Russia. Hydraulic mining methods are used to concentrate the fine particles of ore.[8]

Fig 1. Cassiterite crystals and crystal structure of Cassiterite.

Recent advance developments in computer algorithms in producing solid-to-solid phase transitions through simulations are expected to pave the way for tracking the transformation mechanism(s) for pressure-induced phase transitions in Tin-dioxide.
-1.6- Pressure Response for Crystalline Oxides

There have been sustained interests in investigations of pressure-induced phase transitions and in the associated structural changes because they are of both fundamental and technological importance. Most studies in materials chemistry and in high-pressure research have been focused on oxides, which have provided the largest group of inorganic compounds leading to technologically important materials. In particular, oxides materials exhibit extensive polymorphism at high pressure, and different phase transitions that yield highly coordinated structures have been uncovered and have attracted much attention because of their potential as super hard materials. In particular, the dioxides MO\textsubscript{2}, where M can be cations from group 4 and 14, present a similar sequence of phase transitions from rutile (P4\textsubscript{2}/mnm), to CaCl\textsubscript{2}-type (Pnmm), to α\textsuperscript{-}PbO\textsubscript{2}-type (Pbcn), and to Pyrite-type (Pa\textsuperscript{3}))[1,9].

SnO\textsubscript{2} together with PbO\textsubscript{2} and SiO\textsubscript{2} are the most representative materials of the homogeneous group 14 dioxides for potential applications in numerous fields. After previous knowledge on the SnO\textsubscript{2} system has been surveyed, its phase transformations will be explored by the density functional theory (DFT) approach, within the theoretical frame outlined below.

The ionicity of materials is believed to be responsible for the formation of different high-pressure phases in binary compounds, but generally accepted a clear picture has not been emerged yet. Also, the transformation mechanism of these phase changes at the microscopic level is still unsolved.
-1.7- Total Energy Calculations

By employing *ab initio* calculations based on the density functional theory, it is possible to study or predict the pressure-induced phase transitions. These methods deal with energy volume calculations and the thermodynamic criterion of Gibbs free energies and are very precise and accurate. However, these methods can be only employed for the known structures.

Recent developments in computer algorithms have removed this major limitation and made it possible to observe the dynamical aspect of solid-solid phase transitions with an increase of pressure. The equations of motion for molecular dynamics simulations under isobaric conditions were first developed by Andersen and by Parrinello and Rahman [12]. In the Andersen constant pressure MD method, the volume of simulation cells are treated as a dynamical variable; hence the simulation cell is allowed to change its volume, but not its shape. A constant shape also makes the dynamics analysis easier. The generalization of Andersen’s method taking this anisotropy into account is due to Parrinello and Rahman. In the Parrinello and Rahman method, the volume of a simulation cell and its shape are dynamical variables.

-1.8- Birch–Murnaghan Equation of State

In physics and thermodynamics, an equation of state is a relation between state variables. More specifically, an equation of state is a thermodynamic equation describing the state of matter under a given set of physical conditions. It is a constitutive equation which provides a mathematical relationship between two or more state functions associated with the matter, such as its temperature, pressure, volume, or
internal energy. Equations of state are useful in describing the properties of fluids, mixtures of fluids, solids, and even the interior of stars.

In continuum mechanics, an equation of state suitable for modeling solids is naturally rather different from the ideal gas law. A solid has a certain equilibrium volume $V_0$, and the energy increases quadratically as volume is increased or decreased a small amount from that value. In high-pressure studies, the most widely used equation of state is the *third-order Birch-Murnaghan equation of state* based on finite-strain theory, and is given as a function of volume as follows:

$$P(V) = \frac{3B_0}{2} \left[ \left( \frac{V_0}{V} \right)^{7/3} - \left( \frac{V_0}{V} \right)^{5/3} \right] \left\{ 1 + \frac{3}{4} (B'_0 - 4) \left[ \left( \frac{V_0}{V} \right)^{2/3} - 1 \right] \right\}$$  \hspace{1cm} (1.5)

Where $V_0$ is the equilibrium volume and $B_0$ and $B'_0$ are the bulk modules and its pressure derivative at zero temperature and pressure, respectively. Using the quantity $P = dV/dE$, the equation can be rewritten as:

$$E(V) = E_o + \frac{9V_o B_o}{16} \left\{ \left[ \left( \frac{V_o}{V} \right)^{2/3} - 1 \right]^3 B'_0 + \left[ \left( \frac{V_o}{V} \right)^{2/3} - 1 \right]^2 \left[ 6 - 4 \left( \frac{V_o}{V} \right)^{2/3} \right] \right\}$$  \hspace{1cm} (1.6)

This equation is used primarily in total energy calculations, in which the internal energy of the system can be determined as a function of volume. Fitting energy-volume data to the equation of state provides Gibbs free energy (or enthalpy at zero-temperature) and bulk modules, and its pressure derivative at the equilibrium [10-11].
1.9- Objectives

Extensive theoretical and experimental studies have been performed to study the phase transitions of oxides materials and much progress have been made. Most of the high pressure phases of oxides have been determined successfully but there are still unknowns and controversies. For example, the knowledge of the transformation mechanism(s) and intermediate states during phase transitions remains one of the most challenging problems because of some limitations in theoretical and experimental procedures. In this study, we perform a constant pressure \textit{ab initio} technique based on the density functional theory to develop atomistic level understanding of the pressure-induced phase transition in SnO$_2$. Particularly, we focus on the transformation mechanism and intermediate states. The simulations results will provide substantial information to experimentalists to control possibly the transition properties and will be able to eliminate the existence doubts in the literature.
CHAPTER TWO
THEORETICAL FOUNDATION OF PHASE TRANSFORMATION

-2.1- Introduction

Computational methods are becoming more and more important in the fields of solid state physics and material sciences. Often properties of solid are not directly accessible from experiments for various reasons. A material might oxidize easily, which changes the electronic properties at the surface and makes the interpretation of surface-sensitive experiments such as photo emission difficult. Furthermore, the sample size or mass might not be sufficient for certain experiments. The beam diameter of a synchrotron for example is typically in the range of several micrometers; hence a single nanotube cannot be easily studied with this powerful light source. Finally one might be interested in studying fictitious systems e.g. in order to predict the stability or the properties of a composition which has not (yet) been produced. All three cases do actually occur for phase change materials. For these tasks numerical simulations provide a valuable tool. In order to be able to predict as well as reproduce experimental results, these simulations should be based simply on first principles of quantum mechanics, i.e. independent of any empirical (experimental) parameters. These methods are called ab initio, which is Latin expression for “from the beginning”. An exact mathematical ab initio treatment of the Schrodinger equation of a many-atom-system composed of electrons and nuclei is highly complex and virtually impossible. Nevertheless suitable methods to derive a wide range of physical properties of condensed matter systems are available in fields such as material science, mechanical engineering, chemistry and physics. With in this section Density Functional Theory (DFT) is introduced, a computational method which has been highly successful in calculating the electronic
ground state properties of many-atom systems and is becoming a valuable tool in the field of phase change materials.

In order to study such systems with moderate computational effort a range of approximation is introduced. As the change in the electronic states occurs rapidly compared to the nuclear motion the electrons can be considered to be in their ground state for every ionic configuration. This approximation which is called Born-Oppenheimer (or adiabatic) approximation, allows one to completely separate the calculation of the electronic structure from the ionic motion. Usually the many-body-problem of interacting electrons is then reduced to a single-particle problem. A typical example of such a single-particle method is the Hartee-Fock approximation. This method provides an approximate solution to the many-body problem and uses a single Slater determinant to express the many electron wave functions. The so-called Hartee-Fock equation which has to be solved includes a Coulomb term (Hartee term) and an exchange term (Fock term), which stems from the anti-symmetry of the wave function with respect to two-particle permutation, due to Pauli’s exclusion principle. The effects of electron correlation beyond that of exchange energy are completely neglected in this method. A more appropriate approach – though still based on the single particle approximation – to correctly describe the electronic system is provided by Density Functional Theory. In contrast to Hartee-Fock, DFT provides in principle an exact solution of the-body problem in the electronic ground state. However for practical calculations a series of approximation is employed.
2.2- The Theorem of Hohenberg and Kohn

In DFT all ground state properties such as the total energy are expressed as a functional of the charge density distribution. The fundamentals of this concept were derived by Hohenberg and Kohn [3, 13]. They proved that the following theorem holds exactly:

a) There is a universal functional $F[\rho(r)]$ of the spatial electron density distribution $\rho(r)$, which defines the total energy of the electronic system by

$$E = 8v(r)t(r)dr + F[t(r)]$$

(2.1)

b) The total energy $E$ has a minimum $E_o$ when the charge density $\rho(r)$ coincides with the true charge density $\rho_o(r)$ in the external potential. This theorem is exact if the ground state has no degeneracy.

Thus the Hohenberg and Kohn theorem states that the ground state energy $E$ is a universal functional of the charge density and that the ground state charge density can be obtained by applying the variation principle to the energy. Levy found an alternative formulation of the Hohenberg and Kohn theorem where the functional of the ground state energy is given by

$$E[t(r)] = \min_{\{H\}}$$

(2.2)

Under the constraint, that the wave functions $\psi$ used for variation reproduce the charge density distribution $\rho(r)$.

$$t(r) = \langle i | \psi(r) d(r - r_i) \rangle$$

(2.3)

Here $H$ is the Hamiltonian and $i$ the index of the spatial coordinate. This leads to the relation
At this point the exact form of the total energy functional remains still undermined, however the scheme used to derive electronic round state properties can already be outlined here. First of all one has to find a suitable approximation of $E[\rho(r)]$ and then apply the variation principle to the total energy functional

$$dE[t(r)] = 0$$  \hspace{1cm} (2.5)$$

Under the constraint, the number of particles $N$ is conserved

$$\int t(r) dr = N$$  \hspace{1cm} (2.6)$$

This constraint is expressed via the Lagrange parameter $\mu$

$$d\{E[t(r)] - N[\int t(r) - N]\} = 0$$  \hspace{1cm} (2.7)$$

In this case the Lagrange parameter $\mu$, is equivalent to the chemical potential since Eq.(2.7) can be written as $\delta E[\rho(r)] / \delta \rho(r) = \mu$ [3].

A strategy how to calculate the electronic states of complex systems in the ground state according to DFT has been first presented by Kohn and Sham and will be introduced in the following two sections.

-2.3- The Kohn-Sham Equation

The main idea of Kohn and Sham was to map the system of $N$ interacting electrons onto an auxiliary system of $N$ non-interacting electrons with the same density as the interacting system [14]. In this case the charge density can be expressed in terms of single particle orbital $\psi^i$.

$$t(r) = \sum_{i=1}^{N} \sqrt{\rho^i(r)} / 2$$  \hspace{1cm} (2.8)$$
With the kinetic energy $T$ of the non-interacting particle given by

$$T[t(r)] = -\int_{i=1}^{N} \delta dr \{ \left. \frac{\partial}{\partial r} \right| i(r) \frac{1}{2} d^2 \} i(r)$$  \hspace{1cm} (2.9)$$

Kohn and Sham rewrote the total energy functional in Eq. (2.1) in the following way:

$$E[t(r)] = T[t(r)] + E_{\text{tot}}[t(r)]$$  \hspace{1cm} (2.10)$$

$$= T[t(r)] + e^2 \delta dr dr' \frac{t(r) t(r')}{r-r'} + \delta dr v(r) t(r) + E_{xc}[t(r)]$$  \hspace{1cm} (2.11)$$

Besides $T$ given by the first term, Eq. 2.10 contains a second term $E_{\text{tot}}$ consisting of the Hartree energy, which describes the electrostatic energy of the electronic system (second term in Eq. 2.11) and the exchange-correlation energy $E_{xc}$, which accounts for the exchange and correlation effects of the electrons. This term is unknown and –in contrast to all other terms on the right side of the equation – cannot be determined exactly for a complex, inhomogeneous system. Therefore finding a suitable description for $E_{xc}$ poses the basic challenge in DFT calculations.

Within this scheme, the system of interacting particles in an external potential $V$ is now replaced by a system of non-interacting particles in an effective potential $V_{\text{tot}}$. The single particle wave functions in Eq. (2.8) are orthogonal to each other and fulfill the norm

$$\mathcal{G}_i(r)/ \mathcal{H} \subseteq 1$$  \hspace{1cm} (2.12)$$

If the variational principle for the total energy $E$ is applied with respect to $\psi(r)$, the norm becomes the constraint instead of the particle conservation and one obtains

$$d\{E[i] \} = \int_{i=1}^{N} f_i(\mathcal{G}_i(r)/ \mathcal{H}) = 0$$  \hspace{1cm} (2.13)$$
The solution of Eq. 2.13 can be obtained by solving the effective single-particle Schrödinger equation for $\psi$ for $N$ particles.

$$\text{d}\{ - \frac{1}{2} \text{d}^2 + V_{\text{ext}}(r) + \frac{1}{2} g \text{d}r' \frac{t (r')}{|r - r'|} + \frac{dE_{\text{xc}}(r)}{dt (r)} \} \psi(r) = f \psi(r) \quad (2.14)$$

Where $V_{\text{xc}}(r) = dE_{\text{xc}}[t (r)]/dt (r)$ and $V_H = \frac{1}{2} g \text{d}r' \frac{t (r')}{|r - r'|}$. In the above equations, the following atomic units were used: $\hbar = 1, e = 1, m_e = 1$.

This equation is called the Kohn-Sham (KS) equation and the effective one-electron Hamiltonian associated with Eq. 2.14 is called the KS Hamiltonian. It is worth mentioning that – although providing a suitable description e.g. for the electronic band structure or the charge distribution within a solid – its eigenvalues $\varepsilon_i$ and the single particle wave functions $\psi_i$ have no physical meaning. In fact the single particle wave function $\psi_i$ is simply an abject which is related to the true charge density $\rho$ and will be called KS wave function in the following. Thus the Slater determinant constructed from $\psi_i$ is not the true many-electron wave function either. Equation 2.14 rather represents a single-electron approximation which contains the many-body interactions in an effective potential $V_{\text{tot}}$

$$V_{\text{eff}}(r) = V_{\text{ext}}(r) + V_H (r) + V_{\text{xc}} (r) \quad (2.15)$$

Where $V_{\text{ext}}$ represents the external potential, $V_H$ the Hartree potential and $V_{\text{xc}}$ the exchange-correlation potential. As the effective potential is constrained from the charge density and in turn the charge density is constructed from the wave functions, one obtains a set of equations which has to be solved self-consistently [15].
2.4 - The Local Density Approximation

Approximation enters density functional theory due to the fact that the exchange correlation energy is unknown for inhomogeneous systems. The simplest approximation proposed by Kohn and Sham is the Local Density Approximation (LDA). Their idea is to use the exchange-correlation energy of the homogeneous electron gas, which can be calculated using Quantum Monte Carlo simulation [4, 16]. Here one puts $\rho = \rho(r)$ and neglects the special dependence of $\rho$. Then the exchange-correlation energy at $r$ is replaced by the corresponding energy of the homogeneous electron gas with density $\rho$. Mathematically this is described in the following way: the exchange-correlation energy of the free, homogeneous electron gas is given by

$$E_{xc}^{hom} = t \int f_{xc}^{hom}$$

(2.16)

Where $\varepsilon_{xc}^{hom}$ is the spatial constant exchange-correlation density of the homogeneous gas. For the inhomogeneous system one obtains

$$f_{xc}^{LDA}(r) = f_{xc}^{hom}[t(r)]$$

(2.17)

thus

$$E_{xc}^{LDA}[t(r)] = \delta dr \cdot f_{xc}^{LDA}(r)$$

(2.18)

and

$$V_{xc}^{LDA}[t(r)] = dE_{xc}^{LDA}[t(r)]/dr$$

(2.19)
The simplest form of the LDA to the exchange-correlation potential has been proposed by Slater et al., where $V_{xc}$ becomes

$$V_{xc}([t \ r]) = -\left(\frac{3a}{2}\right)\left(\frac{3t}{r}\right)^{1/3}$$

(2.20)

This choice for the exchange-correlation functional is usually called $a$ method. The coefficient $a$ can be determined from the known results for the electron gas. For example it is known that the electron gas gives the same form for the exchange term. Thus if only the exchange term evaluated in the electron gas is considered one obtains $a=2/3$. Slater et al. originally obtained $a=1$ by averaging the exchange term of the Hartree-Fock equation.

An extension of the LDA is the General Gradient Approximation (GGA) which describes the exchange-correlation energy not only as a function of the local density but also of its variation

$$E_{xc}^{GGA}[t(r)] = \int d\mathbf{r} (r) f_{xc}^{GGA}(t(r), d\mathbf{r}(r))$$

(2.21)

In common parameterizations $\varepsilon_{xc}$ is an analytical function designed to satisfy certain condition, e.g. that the exchange hole is negative everywhere and represents a deficit of one electron.

**2.5 Beyond Density Functional Theory**

Density Functional Theory and the various methods to solve the KS equations presented here is nowadays widely and very successfully used to calculate electronic ground state properties of solids, atoms and molecules, clusters, surfaces, nanotube or even biological systems. In solids structural properties such as the lattice constants are
reproduced with an error of ± 2%; the bulk modules are reproduced with an error of about ± 10% [16]. Calculations of the total energy serve to determine the ground state structure, which is given by the structure with the lowest energy. In liquids DFT calculations combined with molecular dynamics are used to determine the structure factor and the pair correlations function, which is usually also determined within an error of a few percent. Molecular binding energies and band structures (for the occupied states) are obtained with good agreement to experimental data. DFT is even applied to calculate magnetic properties or phonon frequencies. However, as it is strictly a theory describing the electronic ground state of an independent-particle system it fails in the calculation of excited state properties such as the determination of the electronic band gap, the calculation of optical response or of the transport properties. Therefore we have to go beyond ground state DFT to describe these properties accurately with computational methods.

-2.6- Molecular Dynamics Simulation

We carry out computer simulations in the hope of understanding the properties of assemblies of molecules in terms of their structure and the microscopic interactions between them. This serves as a complement to conventional experiments, enabling us to learn something new, something that cannot be found out in other ways. The two main families of simulation technique are molecular dynamics (MD) and Monte Carlo (MC); additionally, there is a whole range of hybrid techniques which combine features from both. In this lecture we shall concentrate on MD. The obvious advantage of MD over MC is that it gives a route to dynamical properties of the system: transport coefficients, time-dependent responses to perturbations, rheological properties and spectra.
Computer simulations act as a bridge between microscopic length and time scales and the macroscopic world of the laboratory: we provide a guess at the interactions between molecules, and obtain `exact' predictions of bulk properties. The predictions are `exact' in the sense that they can be made as accurate as we like, subject to the limitations imposed by our computer budget. At the same time, the hidden detail behind bulk measurements can be revealed. An example is the link between the diffusion coefficient and velocity autocorrelation function (the former easy to measure experimentally, the latter much harder). Simulations act as a bridge in another sense: between theory and experiment [17-18].

We may test a theory by conducting a simulation using the same model. We may test the model by comparing with experimental results. We may also carry out simulations on the computer that are difficult or impossible in the laboratory (for example, working at extremes of temperature or pressure).

Ultimately we may want to make direct comparisons with experimental measurements made on specific materials, in which case a good model of molecular interactions is essential. The aim of so-called _ab initio_ molecular dynamics is to reduce the amount of fitting and guesswork in this process to a minimum. On the other hand, we may be interested in phenomena of a rather generic nature, or we may simply want to discriminate between good and bad theories. When it comes to aims of this kind, it is not necessary to have a perfectly realistic molecular model; one that contains the essential physics may be quite suitable.
-2.6.1- **Classical Molecular Dynamics**

Molecular dynamics is a powerful computational method to study dynamical and structural properties of materials at atomistic level. The equations of motion of atoms in a simulation box are solved using an interatomic potential. The potential contains a number of adjustable parameters that comes from fitting physical quantities like cohesive energy, lattice constants, structural parameters, etc. with experimental data or *ab initio* MD simulations data.

In simulations, using periodic boundary conditions is customary to simulate infinite systems. Thermodynamic variables such as pressure and temperature can be defined. This technique can be used to study a large number of phenomena including phase transitions, liquid structures, and defects in solids, amorphous materials, surfaces, and clusters. Classical MD simulations have been employed to investigate solid-solid and liquid-liquid phase transitions using various algorithms, which allow both volume and shape change of simulation cells, and are very useful for understanding of phase transitions at microscopic level, determining the transitions paths, and electronic properties at each applied pressure. Classical molecular dynamics approximates electronic distributions in a rather coarse-grained fashion by putting either fixed partial charges on interaction sites or by adding an approximate model for polarization effects.

-2.6.2- **Ab Initio Molecular Dynamics**

Classical molecular dynamics using “predefined potentials”, either based on empirical data or on independent electronic structure calculations, is well established as a powerful tool to investigate many -body condensed matter systems. At the very heart of
any molecular dynamics scheme is the question of how to describe - that is in practice how to approximate – the interatomic interactions. The traditional route followed in molecular dynamics is to determine these potentials in advance. Typically, the full interaction is broken up into two-body, three-body and many-body contributions, long-range and short-range terms etc., which have to be represented by suitable functional forms.

Despite overwhelming success, the need to devise a fixed model potential" implies serious drawbacks. Among the most delicate ones are systems where (i) many different atom or molecule types give rise to a myriad of different interatomic interactions that have to be parameterized and / or (ii) the electronic structure and thus the bonding pattern changes qualitatively in the course of the simulation. The reign of traditional molecular dynamics and electronic structure methods was greatly extended by the family of techniques that is called here “ab initio molecular dynamics”. The basic idea underlying every ab initio molecular dynamics method is to compute the forces acting on the nuclei from electronic structure calculations that are performed.

In this way, the electronic variables are not integrated out beforehand, but are considered as active degrees of freedom. This implies that, given a suitable approximate solution of the many-electron problem systems can be handled by molecular dynamics. But this also implies that the approximation is shifted from the level of selecting the model potential to the level of selecting a particular approximation for solving the Schrödinger equation. Applications of ab initio molecular dynamics are particularly
widespread in materials science and chemistry, where the aforementioned difficulties (i) and (ii) are particularly severe.

Despite its obvious advantages, it is evident that a price has to be played for putting molecular dynamics on ab initio grounds: the correlation lengths and relaxation times that are accessible are much smaller than what is affordable via standard molecular dynamics.

What is needed in ab initio molecular dynamics instead? Suppose that a useful trajectory consists of about $10^M$ molecular dynamics steps, i.e. $10^M$ electronic structure calculations are needed to generate one trajectory. Furthermore, it is assumed that $10^n$ independent trajectories are necessary in order to average over different initial conditions so that $10^{M+n}$ ab initio molecular dynamics steps are required in total. Finally, it is assumed that each single-point electronic structure calculation needed to devise the global potential energy surface and one ab initio molecular dynamics time step requires roughly the same amount of CPU time. Based on this truly simplistic order of magnitude estimate, the advantage of ab initio molecular dynamics vs calculations relying on the computation of global potential energy surface amounts to about $10^{3N-6-Mn}$.

The crucial point is that for a given statistical accuracy (that is for M and n fixed and independent on N) and for a given electronic structure method, the computational advantage of “on-the-fly” approaches grows like $\sim10^N$ with system size.

The two most popular extensions of classical molecular dynamics to include first–principles derived potential functions are discussed below. The focus is on the Kohn–
Sham method of density functional theory, as this is the method almost exclusively used in applications. However, most other electronic structure theories can be used as well and it is anticipated that thanks to more powerful computers and wider acceptance of dynamical methods within the quantum chemistry community in the future a larger variety of methods will be applied [19-20].

-2.7 Born–Oppenheimer Molecular Dynamics

The interaction energy \( U(R^N) \) in the molecular dynamics method has the same physical meaning as the Kohn–Sham energy within the Born–Oppenheimer (BO) approximation. The Kohn–Sham energy depends only on the nuclear positions and defines the hyper surface for the movement of the nuclei. The Lagrangian for Born–Oppenheimer dynamics is therefore

\[
L_{BO}(R^N, \dot{R}^N) = \frac{1}{2} \sum_{i=1}^{N} \frac{1}{M_i} (\dot{R}_i)^2 - \min_{\{\psi_i\}} E_{KS}[\psi_i, R^N] \tag{3.1}
\]

And the minimization constraint to orthogonal sets of \( \{\psi_i\} \). The equations of motion are

\[
M_i \ddot{R}_i = -\frac{\partial}{\partial R_i} \left[ \min_{\{\psi_i\}} E_{KS}[\psi_i, R^N] \right] \tag{3.2}
\]

Extensions to other ensembles along the ideas outlined in the last notice are straightforward. In fact, a classical molecular dynamics program can easily be turned in to a BOMD program by replacing the energy and force routines by the corresponding routines from a quantum chemistry program [21].
-2.8- Car-Parrinello Molecular Dynamics

The basic idea of the Car–Parrinello approach can be viewed to exploit the time–scale separation of fast electronic and slow nuclear motion by transforming that into classical–mechanical adiabatic energy–scale separation in the framework of dynamical systems theory. In order to achieve this goal the two–component quantum / classical problem is mapped onto a two–component purely classical problem with two separate energy scales at the expense of losing the explicit time–dependence of the quantum subsystem dynamics [22-23].

This is achieved by considering the extended Kohn–Sham energy functional $E^{KS}$ to be dependent on $\{\} _i$ and $R^N$. In classical mechanics the force on the nuclei is obtained from the derivative of a Lagrangian with respect to the nuclear positions. This suggests that a functional derivative with respect to the orbital’s, which are interpreted as classical fields, might yield the force on the orbital’s, given a suitable Lagrangian. Car and Parrinello postulated the following Lagrangian using $E^{KS}$.

$$L_{cp}[R^N, R^N, \{\} _i, \{\} _i] = \frac{1}{2} M_i R_{i}^2 + \frac{1}{2} \hbar \langle \{\} _i \rangle R_{N}^{\frac{2}{\hbar}} f^{KS}[\{\} _i, R^N]$$

(3.3)

The corresponding Newtonian equations of motion are obtained from the associated Euler–Lagrange equations

$$\frac{d}{dt} \frac{2L_{cp}}{2R_i} = \frac{2L_{cp}}{2R_i}$$

(3.4)
like in classical mechanics, but here for both the nuclear positions and the orbitals. Note that the constraints contained in $E^{KS}$ are holonomic. Following this route of ideas, Car–Parrinello equations of motion are found to be of the form

$$\ddot{M}_t \ddot{R}_I(t) = -\frac{\partial E^{KS}}{\partial R_I} + \sum_y \Lambda_y \frac{\partial}{\partial R_I} \langle \psi_i | \psi_j \rangle$$

(3.5)

$$\mu \ddot{\psi}_i(t) = -\frac{\partial E^{KS}}{\partial \langle \psi_i |} + \sum_j \Lambda_{ij} \frac{\partial}{\partial R_I} | \psi_j \rangle$$

(3.6)

where $\mu$ is the “fictitious mass” or inertia parameter assigned to the orbital degrees of freedom; the units of the mass parameter $\mu$ are energy times a squared time for reasons of dimensionality. Note that the constraints within $E^{KS}$ lead to “constraint forces” in the equations of motion. In general, these constraints will depend on both the Kohn–Sham orbitals and the nuclear positions through the overlap matrix of basis functions.

The constant of motion is

$$E_{cons} = \frac{1}{2} \sum_i M_i \dot{R}_i^2 + \frac{1}{2} \sum_j n_{ij} \langle \psi_i | \psi_j \rangle + E^{KS} \{ \{ \} \}, R^N$$

(3.7)

- 2.9- Pseudopotential

The norm–conserving Pseudopotential approach provides an effective and reliable means for performing calculations on complex molecular, liquid and solid state systems using plane wave basis sets. In this approach only the chemically active valence electrons are dealt with explicitly. The inert core electrons are eliminated within the frozen– core approximation, being considered together with the nuclei as rigid non–polarizable ion cores. In turn, all electrostatic and quantum–mechanical interactions of the valence electrons with the cores, as the nuclear Coulomb attraction screened by the
core electrons, Pauli repulsion and exchange and correlation between core and valence electrons, are accounted for by angular momentum dependent Pseudopotentials. These reproduce the true potential and valence orbital’s outside a chosen core region but remain much weaker and smoother inside. The valence electrons are described by smooth pseudo orbital’s which play the same role as the true orbital’s, but avoid the nodal structure near the nuclei that keeps the core and valence states orthogonal in an all–electron framework. The respective Pauli repulsion largely cancels the attractive parts of the true potential in the core region, and is built into the therefore rather weak Pseudopotentials. This pseudoization of the valence wave functions along with the removal of the core states eminently facilitates a numerically accurate solution of the Kohn–Sham equations and the Poisson equation, and enables the use of plane waves as an expedient basis set in electronic structure calculations. By virtue of the norm–conservation property and when constructed carefully Pseudopotentials present a rather marginal approximation, and indeed allow for an adequate description of the valence electrons over the entire chemically relevant range of systems [24].

-2.9.1- **Why Pseudopotentials?**

Pseudopotential should be additive and transferable. Additivity can most easily be achieved by building Pseudopotentials for atoms in reference states. Transferability means that one and the same Pseudopotentials should be adequate for an atom in all possible chemical environments. This is especially important when a change of the environment is expected during a simulation, like in chemical reactions or for phase transitions.
Pseudopotential replaces electronic degrees of freedom in the Hamiltonian by an effective potential. They lead to a reduction of the number of electrons in the system and thereby allow for faster calculation or the treatment of bigger systems.

Pseudopotential allow for a considerable reduction of the basis set size. Valence states are smoother than core states and need therefore less basis functions for an accurate description. The pseudized valence wave functions are nodeless (in the here considered type of Pseudopotentials) functions and allow for an additional reduction of the basis. This is especially important for plane waves. Consider the 1s function of an atom

\[ 1s(r) \sim e^{-Z^* r} \]  

(3.8) with \( Z^* \sim Z \), the nuclear charge. The Fourier transform of the orbital is

\[ 1s(G) \sim 16\% \frac{Z^{5/2}}{G^2 + Z^2} \]  

(3.9)

From this formula we can estimate the relative cutoffs needed for different elements in the periodic table (see table 4.1).

Table 1: Relative cutoffs (in energy units) and number of plane waves for several atoms.

<table>
<thead>
<tr>
<th>Atom</th>
<th>Z</th>
<th>Cutoff</th>
<th>Plane Waves</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Li</td>
<td>3</td>
<td>4</td>
<td>8</td>
</tr>
<tr>
<td>C</td>
<td>6</td>
<td>9</td>
<td>27</td>
</tr>
<tr>
<td>Si</td>
<td>14</td>
<td>27</td>
<td>140</td>
</tr>
<tr>
<td>Ge</td>
<td>32</td>
<td>76</td>
<td>663</td>
</tr>
<tr>
<td>Sn</td>
<td>50</td>
<td>133</td>
<td>1534</td>
</tr>
</tbody>
</table>

And the last but not least advantage of Pseudopotentials is, most relativistic effects are connected to core electrons. These effects can be incorporated in the Pseudopotentials
without complicating the calculations of the final system. We do have many norm-
conserving Pseudopotentials approach including: Hamann–Schluter–Chiang Conditions,
Bachelet-Hamann-Schlüter (BHS) form, Kerker Pseudopotentials, Trouiller–Martins
Pseudopotentials, and Kinetic Energy Optimized Pseudopotentials. For this paper I will
try to write something about the Trouiller–Martins Pseudopotential \[24\].

-2.9.2- **Trouiller–Martins Pseudopotential**

This method is a generalized form of the Kerker Pseudopotentials which is made to
include polynomials of higher order. The rational behind this was to use the additional
parameters (the coefficients of the higher terms in the polynomial) to construct
smoother Pseudopotentials. The Trouiller–Martins wave functions has the following
form \[25\]

\[
\Phi_l (r) = r^{l+1} e^{p(r)}
\]  

(3.10)

With

\[
p(r) = c_0 + c_2 r^2 + c_4 r^4 + c_6 r^6 + c_8 r^8 + c_{10} r^{10} + c_{12} r^{12}
\]  

(3.11)

and the coefficients $C_n$ are determined from

\[
\frac{d^n \Phi}{dr^n} \bigg|_{r=r_c} = \frac{d^n \Psi}{dr^n} \bigg|_{r=r_c}
\]  

(3.12)

\[
\frac{d\Phi}{dr} \bigg|_{r=0} = 0
\]  

(3.13)
-2.10- Pressure Control Techniques

Application of high pressures has been recognized as a powerful tool in materials synthesis since the first success in transforming graphite into diamond under a pressure of 7 GPa in 1953 [26]. Utilizing high pressures provides us with a means to overcome the ‘ordinary’ stability limits of materials set by the ‘ambient-condition’ thermodynamics. With high-pressure techniques it is possible to mimic the earth-core conditions in the laboratory and build up not only carbon diamonds but also a beautiful variety of metastable ‘gems’ of other elements and their combinations. In materials science, high-pressure techniques have been utilized mainly in: (i) search for new materials, (ii) stabilization of metastable/unstable compounds with e.g. extraordinarily high/intermediate/mixed oxidation states of the constituent elements, (iii) investigation of structural phase transformations and (iv) study of pressure-dependent physical properties of materials.

Constant pressure simulations with variable super-cell geometry are desirable to investigate a solid phase transition with a change of symmetry. The first one to introduce a constant pressure MD method was Andersen [27], in which isotopic fluctuations in volume of the simulation cell is allowed, and hence the size of the cells is considered as a dynamical variable. A powerful extension of this method it’s made later by Parrinello and Rahman [28]. This method considers changes of the shape of simulation super-cells due to external stress or pressure.

In the Parrinello-Rahman method, nucleation for solid-solid phase transition is not taking in account the finite size of the simulation, and hence the method overestimates
transition pressures. The large value of the most metastable transition pressure can be attributed to an intrinsic activation barrier.

In order to overcome difficulties due to the use of periodic boundary conditions, and to perform more realistic calculations, new simulation techniques have been developed. One popular technique consists in applying pressure via a liquid state to simulation clusters without using periodic boundary conditions. In this method, a large cluster is embedded in hydrostatic medium for which a liquid is chosen. The interaction between the atoms in the liquid and the atoms in the cluster is chosen to be repulsive in order to prevent the liquid atoms from entering the cluster, then a large number of atoms of liquid state and cluster are required and hence it is only applied in classical MD simulations.

-2.10.1- **Andersen Method**

In this method, the volume of simulation cell is a dynamical variable and the simulation cell is allowed to change its volume, but not its shape. A constant shape also makes the dynamics analysis easier. However, this method is not very useful for studying materials under phase transitions.

-2.10.2- **Parrinello Rahman Method**

In the Parrinello Rahman method, a simulation cell can change its shape and volume, and hence the internal stress of the system can match the externally applied stress. The lattice vectors $\mathbf{r}, \mathbf{a}, \mathbf{b}, \mathbf{c}$ of the simulation cell are treated as dynamical variables, a 3x3 matrix, can be defined such that the volume of simulation cell is given
by \( \Omega = \det h = a.b \times c \). The position of the particles \( i \) then can be written in terms of scaled coordinates, where \( S \) components have \( \{ \xi, \eta, \zeta \} \) each going from 0 to 1. The Lagrangian can be written by:

\[
L = \frac{1}{2} \sum_i \dot{R}_i \dot{S}_i \mathbf{G}_{ij} \{ (\dot{r}_{ij}) + \frac{1}{2} W T_r (\mathbf{\tilde{h}}^T \mathbf{\tilde{h}}) - P_{\text{ext}} X \} \quad (3.14)
\]

Where \( \mathbf{G} = \mathbf{\tilde{h}}^T \mathbf{\tilde{h}} \) is a metric tensor which function is to convert the distances measured in scaled coordinates to distances in original coordinates, \( \{ (r) \} \) is a pair potential, \( P_{\text{ext}} \) is the external hydrostatic pressure, \( \mathbf{\tilde{h}}^T \) is the transpose of the \( \mathbf{\tilde{h}} \) matrix and \( W \) is the fictitious mass or inertia parameters controlling the time scale of motion of the cell \( \mathbf{\tilde{h}} \).

The equation of motion is defined as:

\[
\dot{\mathbf{S}} = m^{-1} R | (\mathbf{\tilde{r}}_{ij})(\mathbf{\tilde{S}}_i - \mathbf{\tilde{S}}_j) - \mathbf{G}^{-1} \mathbf{\dot{G}} \mathbf{\dot{S}}_i \quad (3.15)
\]

\[
\mathbf{\dot{h}} = W^{-1}(P - P_{\text{ext}}) \mathbf{v} \quad (3.16)
\]

gives the relation between the variations of \( \mathbf{\dot{h}} \), the microscopic tensor \( \mathbf{P} \) and the external pressure. Where \( | (\mathbf{\tilde{r}}) \equiv \frac{-d \ell}{|dr|} \). The matrix \( \mathbf{v} \) has elements \( v_i = \frac{-d \ell}{d h_i} \), and the matrix \( \mathbf{P} \) is given in dyadic tensor notation by

\[
\mathbf{Xr} \equiv \sum_i m \mathbf{\dot{V}}_i. \mathbf{\dot{V}}_i + | (\mathbf{\tilde{r}})(\mathbf{\tilde{r}}_i - \mathbf{\tilde{r}}_j)(\mathbf{\tilde{r}}_i - \mathbf{\tilde{r}}_j) \quad (3.17)
\]

and

\[
\mathbf{\dot{V}}_i = \mathbf{h} \mathbf{\dot{S}}.
\]

The equations 3.16 and 3.17 control the dynamic simulation box with \( N \) particles under periodic boundary conditions.
The Kohn-Sham wave functions \( \{ i(\vec{r}) \} \) are normalized on cell \( \vec{h} \) and they are not independent fields. The wave function needs to be expressed in the scaled coordinates \( \vec{S} = \vec{h}^{-1} \vec{r} \).

We can write the orbital \( \{ i(\vec{r}) \} \) as

\[
\{ i(\vec{r}) \} = \frac{1}{\sqrt{X}} \{ (\vec{h}^{-1} \vec{r}) \} = \frac{1}{\sqrt{X}} \{ (\vec{S}) \}
\]

The resulting charge density in the unit cell is given by

\[
n(\vec{r}) = \frac{1}{X} n(\vec{S})
\]

The scaled fields \( \{ (\vec{S}) \} \) and charge density \( n(\vec{S}) \) do not depend on the dynamical variables associated with the cell degrees of freedom. However original \( \{ i(\vec{r}) \} \) depends on the cell variables \( \vec{h} \) by the normalization of the cell volume \( X = \text{deth} \).

The Lagrangian used in \textit{ab initio} molecular dynamics with pressure control, can be expressed as:

\[
L = n/ \#d\vec{s}_i \{ (\vec{S}) \}^2 + \frac{1}{2} \sum_j M_i (\dot{\vec{S}}_i G \dot{\vec{S}}_j) - E[\{ i \}, \{ \vec{h} \hat{S}_j \}] + \frac{1}{\#} \left( \#d\vec{s}_i \right)^* (\vec{S}) - d_{ii} + \frac{1}{2} W^T_r (\dot{\vec{h}}^* \dot{\vec{h}}) - P_{\text{ext}} X
\]

It contains nine dynamical degrees of freedom, which are associated to the lattice vectors of the simulations cell \( \vec{h} \), \( E[\{ i \}, \{ \vec{h} \hat{S}_j \}] \) is the DFT-LDA energy functional and \( \delta \) is the identity matrix.

The forth term is the orthonormality constraint on the \( \{ i(\vec{r}) \} \) and \( \wedge_{\nu} \), which are Lagrangian multipliers. \( W \) is the same as in the classical Parrinello Rahman and \( n \) is the inertia parameters that control the time scale of electronic motion. \( M_j \) is the mass of nuclei [30].
CHAPTER THREE
PRESSURE-INDUCED PHASE TRANSITION IN SNO₂

-3.1- Introduction

Tin dioxide (SnO₂) is a semiconductor crystallizing in the rutile structure with space group \( \text{D}_{4h}^{14} \) (P4₂/mmm). Its unit cell consists of two tin and four oxygen atoms (see Fig.1). SnO₂ is a material used in numerous technological applications such as transparent electrodes, gas detectors, far-infrared detectors, and high-efficiency solar cells [32].

![Fig. 2 Bulk unit cell of SnO₂. Open circles represents Sn atoms; dark circles, O atoms.](image)

The great interest in the high pressure phase transitions in SnO₂ comes from the possible geophysical outcome of SiO₂. SnO₂ is regarded as a low-pressure analogue of SiO₂, the most abundant component of the earth’s mantle [31]. The lack of an adequate understanding of the high pressure behavior of silica has motivated many experimental studies of phase transitions in SnO₂ by using various experimental techniques such as quenching experiment, in situ X-ray diffraction, Raman spectroscopy, and shock wave experiments [33]. In the Earlier studies [34], the transformation from the rutile structure type SnO₂ to the orthorhombic phase with the \( \alpha \)-PbO₂ structure was reported at about 12Gpa and the phase boundary between the rutile and the \( \alpha \)-PbO₂ phases was
determined, using a quench method [34]. At 25GPa, the $\alpha$-PbO$_2$-type SnO$_2$ transformed to a cubic phase, to which was assigned the fluorite (CaF$_2$)-type structure [35]. The later studies also confirmed that the $\alpha$-PbO$_2$-to- the fluorite-type phase transformation at 23.6 GPa by in situ observation using synchrotron radiation [36]. This phase transformation was later questioned in the x-ray diffraction studies in which it was argued that the $\alpha$-PbO$_2$ structured SnO$_2$ does not transform into the fluorite-type phase but a modified fluorite structure having space group Pa$\bar{3}$ [37]. The Pa$\bar{3}$ phase is unquenchable, converting to the $\alpha$-PbO$_2$ phase on release of pressure. Recent X-ray diffraction studies at high pressure revealed that the rutile type of SnO$_2$ undergoes a second-order transition to the CaCl$_2$ structure, just as do SiO$_2$ [38], GeO$_2$ [39], and PbO$_2$ [40], prior to the transformation to the $\alpha$-PbO$_2$ structure [41]. The sequence of phase transitions of SnO$_2$ appears to be similar to what has been observed in SiO$_2$: from stishovite (rutile) ($P4_2/mnm, Z=52$) to CaCl$_2$-type ($Pnmn, Z=52$) to $\alpha$-PbO$_2$-type ($Pbcn, Z=54$) and finally in to pyrite (modified fluorite) - type ($Pa\bar{3}, Z=54$) [42-46].

Analyzing experimental data for SnO$_2$ is indeed quite difficult because experiments yielded contradictory observations. The physical origin of contradictory observations is not clear but several factors in these studies might limit obtaining meaningful data or correct interpretations for the high pressure phases of SnO$_2$. The controversies might be associated with the misinterpretation of the diffraction patterns of SnO$_2$ due to the small scattering factor from oxygen atoms. It is also possible that the sample properties might favor the formation of specific crystalline states in SnO$_2$. The use of powdered samples does not provide direct information about the symmetry of the crystal studied. Furthermore, experimental conditions, in particular, loading conditions and the degree of
hydrostatic compressions, might result in some of these crystalline states. The influence of these factors on pressure-induced phase transitions in SnO$_2$ cannot be easily addressed experimentally and hence reliable simulations become very appealing to reveal its true high-pressure behavior. Computer simulations, in particular at the *ab initio* level, have the potential to supply information complementary to experiments by providing an accurate microscopic description of the evolution of the atomic structures under applied pressure. *Ab initio* techniques even allow us to go beyond the experimental limit and to determine definite and unambiguous structural parameters.

In this study, a constant pressure *ab initio* technique is applied to study the pressure-induced phase transformation in SnO$_2$. Three different phase transformations are observed in this material through the simulation and their transformation mechanism at the atomistic level are determined.

**-3.2- Methodology**

The calculations were performed with the SIESTA package [47]. The method is based on density functional theory (DFT) adopting a localized linear combination of atomic orbital basis sets for the description of valance electrons and norm-conserving nonlocal pseudopotential for atomic core. The pseudopotential was constructed using Trouiller and Martins scheme [48]. For the exchange correlation energy we used the generalized gradient approximation of Perdew-Burke and Ernzerhof [49]. The double-$\zeta$ plus polarized orbitals were employed. A real space grid was equivalent to a plane wave cutoff energy of 150 Ry. The simulation cell consists of 48 atoms with periodic boundary conditions. We used four special k-points sampling for the Brillouin zone
integration. The MD simulations were performed using the NPH (constant number of atoms, constant pressure, and constant enthalpy) ensemble. The reason for choosing this ensemble is to remove the thermal fluctuation, which facilitates easier examination of the structure during the phase transformation. Pressure was applied via the method of Parrinello and Rahman [50] and the structure is equilibrated with a period of 1000 time steps (each time step is one femto-second (fs)) at each applied pressure. We also used the power quenching technique during the MD simulations. In this technique, each velocity component is quenched individually. At each time step, if the force and velocity components have opposite sign, the velocity component is set equal to zero. All atoms or supercell velocities (for cell shape optimizations) are then allowed to accelerate at the next time step. 10 Ry.fs$^2$ fictitious Parrinello-Raman mass in the unit of real moment of inertia was found to be suitable for this system.

In order to determine the intermediate state during the phase transformation, we used the KPLOT program [51] that supplies detailed information about space group, cell parameters and atomic position of a given structure. For the symmetry analysis we used 0.2 Å, 4º, and 0.7 Å tolerances for bond lengths, bond angles and interplanar spacing, respectively.
3.3 Results and Analysis

The rutile structure of SnO$_2$ was first equilibrated at zero pressure. Pressure was gradually increased up to 60 GPa. The pressure-volume relation obtained through the constant pressure \textit{ab initio} simulation is given in Fig. 3. The volume presents an abrupt decline when the pressure is increased from 15 GPa to 20 GPa, indicating a first order pressure-induced phase transition in SnO$_2$. We analyze the structure at each applied pressure using the KPLOT program and find the formation of a CaCl$_2$ type structure at 15 GPa. The CaCl$_2$ type structure is orthorhombic, having the Pnmm space group. This distortion includes the existence of two internal parameters, shown in Table 2.
Table 2. Structural data of SnO$_2$ crystal under gradual compression. Cell parameters a, b, and c, are in Å$^0$; the volume per unit formula, V, is in Å$^3$, and the pressure transition values, PT, is in GPa. The Experimental values were taken from reference [55].

<table>
<thead>
<tr>
<th>Structure</th>
<th>Rutile-type</th>
<th>CaCl$_2$-type</th>
<th>Fluorite-type</th>
<th>Cotunnite-type</th>
</tr>
</thead>
<tbody>
<tr>
<td>Symmetry</td>
<td>Calc</td>
<td>Exp</td>
<td>Calc</td>
<td>Exp</td>
</tr>
<tr>
<td>a</td>
<td>4.807</td>
<td>4.73</td>
<td>3.745</td>
<td>4.67</td>
</tr>
<tr>
<td>b</td>
<td>5.033</td>
<td>4.53</td>
<td>6.129</td>
<td>5.904</td>
</tr>
<tr>
<td>V</td>
<td>39.05</td>
<td>35.7</td>
<td>33.0</td>
<td>34.0</td>
</tr>
<tr>
<td>P$_T$</td>
<td>0</td>
<td>0</td>
<td>15</td>
<td>13.6</td>
</tr>
</tbody>
</table>

Because the Pnnm symmetry is a subgroup of P4$_2$/mnm, this first transition has a displacive character [52]. The cation coordination number is 6 for the two structures.

The bulk structures of this system and of other SnO$_2$ polymorphs are depicted in Fig. 4.

Fig 4. Ball stick representation of SnO$_2$ polymorphs (black and red colors represent Sn and O atoms, respectively). (a) Rutile (P4$_2$/mnm), (b) CaCl$_2$-type (Pnnm), (c) fluorite-type (Fm3m). This Phase transformations were carried out under a gradual pressure increase.
This CaCl₂ structure is maintained until the first order phase transition occurs at 20 GPa. At this pressure, the CaCl₂ – type transforms into the cubic-fluorite type structure. The fluorite-type structure, space group Fm3m, is an 8-fold oxygen coordinated structure with Sn-O distances of 2.165Å at the equilibrium volume. The difference between a cubic pyrite-type structure (space group Pa3) and cubic-fluorite type structure (space group Fm3m) arises from a modification to the oxygen positions. In both structures the cations form an fcc sublattice, and the anions lie on 8c sites (u=0.25) in the Fm3m structure, whereas in the Pa3 SnO₂ optimized structure u=0.335. This difference yields a cation coordination number 6+2 and 8 for the pyrite and fluorite-type structures, respectively [53].

An ideal way to elucidate the mechanism of this phase change is to investigate directly the pressure-dependence of the simulation cell vectors. Fig. 5. and Fig 6. shows the cell lengths and angles as a function of MD time step at 20 GPa, respectively. The simulation cell vectors A, B, and C are along the [100], [010] and [001] directions, respectively. The magnitude of these vectors is plotted in the figure. As one can clearly see from the figure, the SnO₂ structure exhibits a strong anisotropic compression. During the phase transformation, the structure is compressed along B ([010]) direction while it is expanded along the other directions. During the phase transformation, the simulation cell angles change less than 0.2°, indicating that the phase transformation is not associated with the shear deformation.

Using the KPLOT program, we carefully analyze the structure each MD step. The CaCl₂ symmetry is preserved up to 440 MD step and then an ideal CaF₂ type phase is formed.
This observation demonstrates that the CaCl$_2$-to- CaF$_2$ phase transformation proceeds via the orthorhombic intermediate phases having Pnnm symmetry.

Fig 5. Change of the simulation cell lengths as a function of MD step at 20 GPa.

Fig 6. Change of the simulation cell angles as a function of MD step at 20 GPa.
Figure 7. The evolution of the CaCl$_2$–type structure at 15 GPa (a). The CaCl$_2$–type structure at 430 fs (b) the intermediate Orthorhombic phases at 435 fs.

In order to investigate the influence of loading condition, we also study the behavior of SnO$_2$ under fast compression (the Rutile-type SnO$_2$ is directly subjected to high pressures). As in the gradual loading conditions, SnO2 phase transforms to the CaCl$_2$–type (Pnnm space group) at 15 GPa, a cubic fluorite-type structure (space group Fm3m) at 20GPa, and an orthorhombic cotunnite-structure (space group Pnma) at 150 GPa. During the cubic fluorite-type structure to an orthorhombic cotunnite-structure phase transformation, the structure is compressed along C ([001]) direction while it is expanded along the B ([010]). During the phase transformation, the simulation cell angles change less then 0.2°, indicating that the phase transformation is not associated with the shear...
deformation. This phase, space group Pnma, has nine oxygen anions placed around the Sn$^{4+}$ cation.

![Diagram of bulk structures of SnO$_2$ polymorphs](image)

**Fig 8.** Bulk structures of SnO$_2$ polymorphs (black and red colors represent Sn and O atoms, respectively). (a) Rutile (P4$_2$/mnm), (b) CaCl$_2$-type (Pnnm), (c) fluorite-type (Fm3m), (d) Orthorhombic cotunnite-structure (Pnma). This Phase transformations were carried out under a fast compression (Quenching).

The increase of the Sn-O distances as compared to those of the Pnnm and the Fm3m phases is consistent with an increase of the cation coordination number of tin ions from 6 (Pnnm) and eight (Fm3m) to nine (Pnma). The cotunnite phase is suggested as a candidate for a useful superhard material. Therefore its formation is particularly important in this material.

Other investigations of analogous systems of metal dioxides exhibit the same transformations at high pressures. The PbO$_2$ system shows a similar sequence of phase
transformations as the computational predictions of SnO$_2$, but the transformations occur at lower pressures, as is expected due to the larger ionic radius of Pb with respect Sn. In addition to the rutile-type, CaCl$_2$-type, $\alpha$-PbO$_2$-type, and pyrite-type structures, a further transformation to a phase orthorhombic I (Pbca) was found in PbO$_2$ at 11Gpa, where as at 29Gpa a cotunnite-type structure with 9-fold coordination was observed [54].

Table 3. The atomic positions and the lattice parameters of the intermediate states determined for the Rutile-type SnO$_2$ to Orthorhombic cotunnite- -type phase transition of SnO$_2$.

<table>
<thead>
<tr>
<th>Phase</th>
<th>Lattice Parameters($\text{Å}^6$)</th>
<th>Atomic positions (x, y, z)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Orthorhombic</td>
<td>a=3.7450 b=5.0333 c=3.5012</td>
<td>Sn: 0.0 0.5 0.5</td>
</tr>
<tr>
<td></td>
<td></td>
<td>O: 0.96606 0.24914 0.0</td>
</tr>
<tr>
<td>Cubic</td>
<td>a=5.0656 b=5.0656 c=5.0656</td>
<td>Sn: 0.0 0.0 0.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>O: 0.25 0.25 0.25</td>
</tr>
<tr>
<td>Orthorhombic cotunnite-structure</td>
<td>a=5.000 b=6.1292 c=3.0311</td>
<td>Sn: 0.0 0.5 0.5</td>
</tr>
<tr>
<td></td>
<td></td>
<td>O: 0.25 0.25 0.0</td>
</tr>
</tbody>
</table>
CHAPTER FOUR: CONCLUSION AND DISCUSSION

-4.1- Conclusion and Discussion

Solid-to-solid phase transformation driven by pressure shows a very extensive trend that requires a deep theoretical understanding. Here, an application to the case of SnO$_2$ is presented, whose high-pressure polymorphisms were investigated experimentally. The performance of the first-principles calculations based on DFT has been illustrated by an application to the complex high-pressure polymorphism of SnO$_2$ phases.

A displacive rutile to CaCl$_2$ type structural transformation under high-pressure was observed at 15 GPa through the simulations. Further increase in pressure results in a first order phase transformation into the cubic-fluorite type structure at 20 GPa. The transformation mechanism of the CaCl$_2$-to- the cubic-fluorite type phase transformation is also successfully characterized. It should be noted that the transformation pathway for a reconstructive phase transition is not simple and the path involves large atomic displacements and/or strains. Therefore, the system can transform from one phase to another by passing through various closely related paths during the transition. In other words, the transformation mechanism might follow various transition pathways or involve several intermediate states, which can be different from what has been proposed in the present simulations.

Our simulations indicate the rutile-type $\rightarrow$ CaCl$_2$ type $\rightarrow$ Cubic fluorite-type structure (Fm$\bar{3}$m) $\rightarrow$ orthorhombic cotunnite-structure (Pnma) phase transformations. Our predictions however are slightly different from the experimental proposed sequence of phases for SnO$_2$: rutile-type $\rightarrow$ CaCl$_2$ type $\rightarrow$ $\alpha$-PbO$_2$ $\rightarrow$ pyrite type Pa$\bar{3}$ $\rightarrow$ ZrO$_2$. 
orthorhombic phase I ($Pbca$) $\rightarrow$ cotunnite-type ($Pnam$). No $\alpha$-PbO$_2$-type phase was observed in the present simulation. This is not surprising because the transformation is very sluggish during pressure increase without heating. At room temperature, some experimental studies also found no indication of $\alpha$-PbO$_2$-type phase or small amounts of the $\alpha$-PbO$_2$-type phase were observed under room-temperature compression of SnO$_2$ in the range of 12–21 GPa, while the sample recovered to ambient conditions from 49 GPa consisted of about half of this phase. In other studies, the $\alpha$-PbO$_2$-type phase was observed at 15–20 GPa after heating. Similar observations were reported during compression of plattnerite rutile-structured PbO$_2$, which indicates the formation of the $\alpha$-PbO$_2$ type phase requires thermal activation or high shear stresses. Additionally, the pyrite-type $\text{Pa}$$_3$ was not observed in the present study and instead the cubic fluorite-type structure was formed in the simulation. Note that these two phases, the pyrite-type $\text{Pa}$$_3$ and the cubic fluorite-type, are closely related. The other disagreement with experiments is that the orthorhombic I phase ($Pbca$) of ZrO$_2$ was not been obtained in the simulations. The origin of the contradictory observation in the present study and the experiments (in particular the pyrite-type $\text{Pa}$$_3$ and the cubic fluorite-type and the orthorhombic I phase ($Pbca$) of SnO$_2$) is not clear but might be due to some factors that might limit obtaining meaningful data or correct interpretations for the high pressure phase of SnO$_2$. The controversy might be associated with the misinterpretation of the diffraction patterns in the experiment. It is also possible that the sample properties might favor the formation of specific phases SnO$_2$. Samples used experiments have defects (impurities, vacancies etc) while simulated structures are defect free. The degree of hydrostatic pressure is another factor that might be responsible for the contradictory observations. The degree of the hydrostaticality in experiments is determined by the efficiency of the pressure-transmitting
medium. At high pressures, the pressure-transmitting medium solidifies resulting in strong nonhydrostatic effects. Even in the low pressure regime, pressure in the diamond anvil cell is not exactly hydrostatic. On the other hand, perfect hydrostatic pressure can be always preserved in simulations.
LIST OF REFERENCES


General References:


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