



UNIVERSITÀ DEGLI STUDI DI MILANO
FACOLTÀ DI SCIENZE E TECNOLOGIE

DIPARTIMENTO DI CHIMICA
Doctoral School in Chemistry - XXXIII Cycle

**High-pressure materials discovery with advanced
computational methods**

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If you wish to understand the
fragrance of the rose, or the
tenacity of the oak;
if you are not satisfied until you
know the secret paths by which
the sunshine and the air achieve
these wonders;
if you wish to see the pattern
which underlies one large field of
human experience and human
measurement,
then take up chemistry.

C. A. Coulson, 1973

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Thesis Overview

The focus of this thesis is the prediction of new materials that can be formed or synthesized under high pressure. It has been shown by several works in literature, that pressure can alter the chemistry [1] of an element by activating its (semi)core electrons, unoccupied orbitals and even the non-atom-centered quantum orbitals located on the interstitial sites [2], leading to many new surprising phenomena.

The main concept is the “ PV ” term that appears in the enthalpy. The enthalpy is a measure of the thermodynamics stability of a material at constant pressure. It can be shown by a back-of-the-envelope calculation that the “ PV ” term can be of the same order of magnitude of the free energy barriers that separate different polymorphs of a material. The primary role of pressure is to modify the free energy surface by creating and stabilizing new minima, which at ambient pressure may not even exist. Therefore pressure is a very effective way to explore polymorphism [3–5] and to synthesize new crystal structures [6, 7]. In particular pressure can be used to synthesize materials in high oxidation state ($\text{ACu}^{III}\text{O}_3$) or with uncommon formal valence (as in YN_2 , as shown in Chapter 3).

High pressure experiments are challenging! The size of the samples is limited and the analysis of X-Ray diffraction patterns is complicated by several issues. Very often it is not possible to refine accurately the atomic positions of light elements (i.e. 1st and 2nd row elements in the periodic table). Also the precise determination of the specific space group can be demanding. This is where theory and calculation come to a rescue. The main challenge for theory is to predict the crystal structure of compounds at high pressure.

In this work I applied different strategies to predict new compounds under pressure:

- explore known polymorphs (aka prototypes)
- global optimization via genetic algorithms

The first strategy can be easily applied to compounds with few components, fixed stoichiometry and at moderate pressure. The idea is that atoms with similar radius and valence tend to crystallize with the same structure. This is the case of ABO_3 oxides which constitute the largest family of oxides: the crystal structure at

ambient pressure is found to depend on the atomic radii of the elements. The most common is the perovskite structure where tilting of octahedra and off-centering of the B-cation is responsible for a large variety of physical properties. In addition to the perovskite structure few other structures are known to have similar molecular formula (i.e. ilmenite, wollastonite, calcite, aragonite, enstatite, corundum). The most important is the post-perovskite which is formed from the perovskite structure when the rotation of the octahedra exceeds a critical angle.

The second strategy is more computationally expensive than the first one and it is more effective when the pressure is very high and when the stoichiometry is not fixed because of pressure-induced chemical reactions. In this case, pressure induces such large changes in the valence configuration that no iso-structural compound exists at ambient pressure. Anyway there are cases (i.e. molecular crystals) in which CSP, even at low pressures, would be very difficult exploiting only on analogy with known prototypes. Crystal structure prediction is in principle a computationally intractable problem, but in recent years clever optimization methods, such as genetic algorithms (i.e. USPEX), have provided an effective and successful solution to this problem.

This PhD work was carried out in tight collaboration with the experimental high pressure group of Prof. Martin Bremholm at Aarhus University. The group main expertise is on high pressure (oxidative) synthesis and X-Ray powder diffraction at high pressure. Most experiments were carried out at the Advanced Photon Source in Chicago and a small part at ESRF, Grenoble. This was probably *the best* collaboration a scientist student can hope for, since it consisted in frequent exchange of ideas and proposals from experiments to theory and vice versa, not just exchange of data. Theoretical calculations were not just a support for experiments and vice versa. For instance the precise refinement of the atomic of SrRuO_3 positions from PXRD required several iterations between theory and experiments and my calculations helped to solve the magnetic-driven monoclinic distortion at intermediate pressure. Another example of strong collaboration is when Prof. Bremholm proposed to study lanthanide di-nitrides. Together with my supervisor we proposed to address first yttrium as a proxy for the lanthanides, for computational reasons. It turned out that high pressure synthesis of yttrium nitrides was quite fast and PXRD patterns show rather sharp diffraction peaks contrary to the lanthanide nitrides. This thesis focuses mainly on the structural properties of stoichiometric bulk materials. Because of the large number of systems studied, I do not address temperature effects, defects and surfaces/interfaces, and I will also not show many *spaghetti diagrams* (i.e. band structures). The reason is that my thesis focused mainly on the crystal structure rather than on the electronic structure. The effects of the pressure on the electronic properties are extremely interesting but require further experimental investigations (i.e. measurement of transport properties, photoemis-

sion spectroscopy). These aspects cannot be studied comprehensively in just one PhD thesis, experimental or theoretical!

Following, there is an overview of this thesis divided in chapters content.

- Chapter 1 is a theoretical introduction to the theoretical principles behind the methods applied in this thesis and the different approaches to the issues I encountered. It also explains the strengths and the weaknesses of each method and how they are relevant in their respective field of application.
- Chapter 2 focuses on the investigation of perovskite and perovskite-like structures, and their behavior under great pressure. In particular, I focused on the structural and mechanical properties of SrRuO_3 , SrGeO_3 and HgPbO_3 , looking for the structural transitions these compounds undergo under pressure and how their properties change.
- In Chapter 3 I focus the attention on the properties of transition metals nitrides, in particular compounds of yttrium. Stimulated from studies conducted on lanthanum dinitrides, I used yttrium as a proxy specie for lanthanides and discovered that many interesting features are associated with yttrium nitrides themselves. In particular, after searching for the most stable compositions for Y-N system by the means of USPEX, I investigated the structural transitions and mechanical properties of YN_2 and YN_3 , concentrating on fascinating features such as the formation of longer nitrogen chains as pressure increases or the nature of $\text{N}\cdots\text{N}$ bonding in the different moieties discovered in the structures.
- The final chapter is a summary of this work of thesis which lasted over three years and underlines the possible future applications and further investigation needed for the projects tackled.

Chapter 1

Theoretical Methods

In this first chapter I recall some of the theoretical principles and methods I applied during the last three years. The aim of this section is not to give a complete analysis of all the theoretical concepts, since many books and papers can provide a much more exhaustive deepening. Instead, the purpose is to give an idea of what tools were employed in this work of thesis and to give a fresh overview of the main concepts they are based on. In the first part I will briefly recall the notions governing Density Functional Theory, starting from Hohenberg–Kohn theorems to a short review of the most used functionals nowadays. Then I will go through the concept behind plane wave pseudopotentials, the Bloch theorem and the Quantum Espresso utility. Finally I will discuss the main issues concerning Crystal Structure Prediction and how the USPEX method aims to solve them. In the end there is also a brief overview of the experimental methods used to perform the high-pressure experiments that support the theoretical data behind the results illustrated in this thesis.

1.1 Density Functional Theory

Density Functional Theory (DFT) is a computational quantum mechanical modelling method used in many scientific fields to look for and therefore analyze the electronic structure of a many-body system, such as atoms, molecules and condensed phases. These properties are investigated by the means of different functionals which, in the specific case of DFT, are functions of the spatial electron density (ρ). This method, developed in the late 1960s, became very popular in the 1990s, when the approximations used in the theory were greatly refined to better model the exchange correlation interactions. Since in periodic systems computational costs are relatively low compared to Hartree-Fock theory, DFT is nowadays one of the most widely used methods for electron structure determination all over the world. On the basis of quantum-mechanical considerations, *ab-initio* DFT allows to predict and rationalize many properties of a given material without requiring high-order pa-

rameters. The electronic structure is determined by the use of an external potential (V_{ext}), which is obtained from the elemental composition and the structure of the material, and an effective potential (V_{eff}), which is a mathematical representation of the interelectronic interactions.

1.1.1 Hohenberg-Kohn Theorems

Density Functional Theory was first formulated by Walter Kohn and Pierre Hohenberg in the framework of two theorems, known as Hohenberg-Kohn theorems (H-K) [8].

A solid is a system made of nuclei and electrons interacting with each other by Coulomb interactions. Given the enormous difference in mass between nuclei and electrons, in the realm of the adiabatic Born-Oppenheimer approximation it is possible to uncouple electronic and nuclear degrees of freedom. Nuclei are therefore considered as fixed charges generating a static external potential V in which the electrons are moving as governed by the ground-state wave-function (ψ_0). The many-body Schrödinger equation (1.1) allows to determine the properties of a system of N electrons interaction with a fixed external potential.

$$\hat{H}\psi(r_1, \dots, r_N) = E\psi(r_1, \dots, r_N) \quad (1.1)$$

In the latter equation, $\hat{H}$ is the Hamiltonian operator, defined as:

$$\hat{H} = -\frac{1}{2m_e} \sum_{i=1}^N \nabla_i^2 + \sum_{i=1}^N V_{ext}(\mathbf{r}_i) + \frac{e^2}{2} \sum_{i \neq j} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} \quad (1.2)$$

while $\mathbf{r}_i$ is the position of the i -th electron and $V_{ext}(\mathbf{r}_i)$ is the external potential acting on the electrons, which is given by the position of the fixed nuclei. If the wave function ψ is known, the expectation value of the system can be calculated as:

$$E[\psi] = \frac{\langle \psi | \hat{H} | \psi \rangle}{\langle \psi | \psi \rangle} \quad (1.3)$$

Although it can look quite straightforward, this approach has a main problem: since the Coulomb term in the eq. 1.2 couples the degrees of freedom of all the electrons of the system, it is impossible to exactly solve eq. 1.1, and therefore obtain the exact wave-function of the system. For this reason, in 1964 Hohenberg and Kohn developed a theory that changes the focus from the energy of the system ($E[\psi]$) to the electron density of the ground state ($E[\rho]$), so that the energy becomes a functional of the electron density, which does not depend on the wave-function anymore [8].

This theory is based on two theorems:

- The first H-K theorem states that the external potential V_{ext} , and hence the

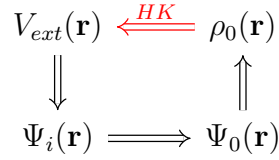


Figure 1.1: Schematic representation of the H-K theorem. The black arrows represent the usual solution of the Schrödinger equation, where the potential $V_{ext}(\mathbf{r})$ determines all the states of the system $\Psi_i(\mathbf{r})$, including the ground state $\Psi_0(\mathbf{r})$ and the ground state electron density $\rho_0(\mathbf{r})$. The Hohenberg-Kohn theorem, highlighted by the red arrow, closes the cycle.

total energy of the ground state, is a unique functional of the electron density $\rho(\mathbf{r})$. In other terms:

$$\rho(\mathbf{r}) \Rightarrow \exists! E_0 = E[\rho(\mathbf{r})] \quad (1.4)$$

- The second H-K theorem is a variational theorem, since it states that, given a trial electronic density $\rho_{trial}(\mathbf{r})$, the value of the functional $E[\rho_{trial}(\mathbf{r})]$ cannot be lower than the ground state energy of the system, and therefore the density that minimizes the total energy is the exact ground state density.

From the first H-K theorem it can be deduced why this theory has been applied over the years on such a large scale, even replacing some other wave-function-based methods: for every system with N electrons, in fact, the energy depends only from the 3 spatial coordinates, making the problem more manageable than $4N$ coordinates dependent (i.e. $\mathbf{r}_i, s_i$, with s_i being the spin of the i -th electron) wave-function problem.

The second H-K theorem, instead, implies that, knowing the total energy of the ground-state ($E[\rho(\mathbf{r})]$), in principle $\rho(\mathbf{r})$ itself could be easily calculated, because the density of the system would be the one that minimizes the energy functional.

The two theorems by themselves do not give an analytical formulation of the total energy functional $E[\rho(\mathbf{r})]$, but a good approximation was provided almost exactly a year after the publication of H-K theorems by Walter Kohn and Lu Jeu Sham.

1.1.2 Kohn-Sham Method

The Kohn-Sham method was developed in 1965 with the aim to reduce the intractable many-body problem of interacting electrons in a fixed external potential to a more manageable problem of non-interacting electrons moving in an effective potential, with the purpose to obtain from the latter problem the same density (ρ) of the former [9].

Central to the Kohn-Sham method is the introduction of a fictitious auxiliary system of N_e particles whose properties are the same as those of the electrons besides the non-interacting behavior. The *ansatz* is based on two assumptions:

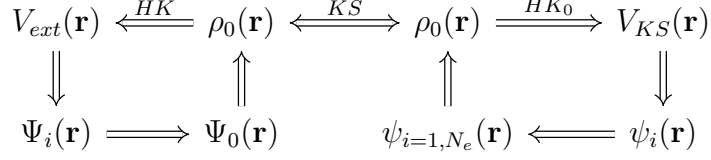


Figure 1.2: Schematic representation of Kohn-Sham theory, to compare to fig.1.1. The label " HK_0 " denotes the Hohenberg-Kohn theorem applied to the fictitious non-interacting system considered in the K-S *ansatz*. The double arrow labeled with "KS" highlights the assumption that the density of the many-body system is the same as the density of the non-interacting system. Therefore, in principle, solving the independent-particle Kohn-Sham problem determines *all properties* of the full many-body system.

- The exact ground state density can be fully represented by the ground state density of the auxiliary system of non-interacting particles. This is called "*non-interacting- V -representability*".
- The auxiliary Hamiltonian is chosen to have the usual kinetic operator and an effective *local* potential $V_{eff}^\sigma(\mathbf{r})$ acting on an electron of spin σ at point $\mathbf{r}$. It is assumed that the potential V_{ext} is spin-independent, nevertheless the auxiliary effective potential $V_{eff}^\sigma(\mathbf{r})$ must depend upon spin in order to give the correct density.

Since $\rho_{ref}(\mathbf{r}) = \rho(\mathbf{r})$, the energy functional of the system can be rewritten as a sum of three different contributions:

$$E[\rho(\mathbf{r})] = T[\rho(\mathbf{r})] + V_{Ne}[\rho(\mathbf{r})] + V_{ee}[\rho(\mathbf{r})] \quad (1.5)$$

in which $T[\rho(\mathbf{r})]$ represents the kinetic energy, $V_{Ne}[\rho(\mathbf{r})]$ is the interaction potential between nuclei and electrons, while V_{ee} is the interaction potential between electrons, which can be divided itself into two different contributions:

$$E[\rho(\mathbf{r})] = T_{ref}[\rho(\mathbf{r})] + V_{Ne}[\rho(\mathbf{r})] + J[\rho(\mathbf{r})] + E_{xc}[\rho(\mathbf{r})] \quad (1.6)$$

Supposing that the energy in eq.1.6 is the *exact* energy of the system, this equation can be as a definition of $E_{xc}[\rho(\mathbf{r})]$, as this quantum-mechanical contribution can be obtained by subtracting the kinetic energy of the non-interacting system (namely, $T_{ref}(\rho(\mathbf{r}))$). $V_{Ne}[\rho(\mathbf{r})]$ and $J[\rho(\mathbf{r})]$ ¹. The *exchange-correlation* term $E_{xc}[\rho(\mathbf{r})]$ will then be defined as:

$$E_{xc}[\rho(\mathbf{r})] = T[\rho(\mathbf{r})] + V_{ee}[\rho(\mathbf{r})] - (T_{ref}[\rho(\mathbf{r})] + J[\rho(\mathbf{r})]) \quad (1.7)$$

Since the right-hand side of eq. 1.7 only contains functionals, $E_{xc}[\rho(\mathbf{r})]$ must be a functional itself. If this universal functional could be known, then the exact ground

¹ $J[\rho(\mathbf{r})]$ is a universal function of $\rho(\mathbf{r})$ and thus it is the same in both systems.

state energy and density of the many-body problem could be found by solving the Kohn-Sham equation for independent-particles. To the extent that an approximate form of $E_{xc}[\rho(\mathbf{r})]$ describes the true exchange-correlation energy, the K-S method provides a feasible approach to calculate the ground state properties of a many body system.

The Kohn-Sham method follows a formalism similar to Hartree-Fock to obtain the electronic structure of a system. Let's consider a set of non-interacting electrons moving in an external potential $V_{eff}(\mathbf{r})$. The electrons behavior can be described by the monoelectronic eigenfunctions ψ_i^{KS} , so, for N_e^e electrons:

$$h_i^{KS}\psi_i^{KS} = \varepsilon_i^{KS}\psi_i^{KS} \quad (1.8)$$

in which the *Kohn-Sham hamiltonian* h_i^{KS} is defined as:

$$h_i^{KS} = -\frac{\hbar^2}{2m_3}\nabla_i^2 + V_{eff}(\mathbf{r}) \quad (1.9)$$

The monoelectronic eigenfunctions $\psi_i^{KS}(\mathbf{r})$ are directly connected to the electron density $\rho(\mathbf{r})$ since:

$$\rho(\mathbf{r}) = \sum_{i=1}^{N_e} |\psi_i^{KS}(\mathbf{r})|^2 \quad (1.10)$$

Recalling the second H-K theorem, it can be deduced that:

$$\int \rho(\mathbf{r})d\mathbf{r} - N_e = 0 \quad (1.11)$$

At this point, the problem is reduced to solving the constrained optimization with the Lagrange multiplier method:

$$\delta \left(E[\rho(\mathbf{r})] - \lambda \int \rho(\mathbf{r})d\mathbf{r} \right) = 0 \quad (1.12)$$

In the latter equation, λ is the Lagrange multiplier. The ground state electron density must respect the equation:

$$\lambda = \frac{\partial E[\rho(\mathbf{r})]}{\partial \rho(\mathbf{r})} \quad (1.13)$$

Substituting the value of $E[\rho(\mathbf{r})]$ previously obtained in eq. 1.6, the latter equation can be rewritten as:

$$\lambda = \frac{\partial J[\rho]}{\partial \rho(\mathbf{r})} + \frac{V_{Ne}[\rho]}{\partial \rho(\mathbf{r})} + \frac{\partial E_{xc}[\rho]}{\partial \rho(\mathbf{r})} + \frac{\partial T_{ref}}{\partial \rho(\mathbf{r})} = V_{eff} + \frac{\partial T_{ref}}{\partial \rho(\mathbf{r})} \quad (1.14)$$

where, explicating all the contributions to V_{eff} :

$$V_{eff}(\mathbf{r}) = V_{Ne}(\mathbf{r}) + \int \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' + V_{xc}(\mathbf{r}) \quad (1.15)$$

$V_{xc}(\mathbf{r})$ in the latter equation is defined as:

$$V_{xc}(\mathbf{r}) = \frac{\partial E_{xc}[\rho]}{\partial \rho(\mathbf{r})} \quad (1.16)$$

Therefore, the problem is reduced to solving a *Schrödinger-like* equation that, knowing the value of the effective potential V_{eff} , will be a system of i equations of the form:

$$\left[\frac{1}{2m_e} \nabla^2 + V_H(\mathbf{r}) + V_{xc}(\mathbf{r}) + V_{ext}(\mathbf{r}) \right] \psi_i^{KS} = \epsilon_i \psi_i^{KS} \quad (1.17)$$

Once obtained, the monoelectronic wavefunctions ψ_i^{KS} can be used to obtain the electron density $\rho(\mathbf{r})$ from eq.1.10.

The genius of the Kohn-Sham approach is two-fold: first, the theory brings to a tractable independent-particle equation (1.17) that holds the hope of solving interacting many-body problem; second, it separates out the independent-particle kinetic energy and the long-range Hartree terms so that only the exchange-correlation functional $E_{xc}[\rho(\mathbf{r})]$ is left unknown. This term can be reasonably approximated as a local functional of density, and many successful attempts were made over the years. The next few paragraphs will be dedicated to the most famous and used of these approximations.

1.1.3 Local Density Approximation

Since solids can often be considered close to the limit of the homogeneous electron gas, the effects of exchange-correlation are local in character. In this limit, Kohn and Sham proposed [9] the Local Density Approximation (LDA) in which the exchange correlation energy of a *inhomogeneous* system is substituted with the exchange-correlation energy density at each point as if the system could be described as an *homogeneous* electron gas:

$$E_{xc}^{LDA}[\rho] = \int \rho(\mathbf{r}) \epsilon_{xc}(\rho(\mathbf{r})) d^3\mathbf{r} \quad (1.18)$$

Once the local *ansatz* of LDA is made, it follows that the only information needed is the exchange correlation energy of the homogeneous gas as a function of density, since $E_{xc}[\rho]$ is universal. The function $\epsilon_{xc}(\rho(\mathbf{r}))$ was accurately evaluated by the means of Monte Carlo simulations in 1980 [10]. As expected, Local Density Approximation is exact only for homogeneous systems, but it can be considered

accurate in many inhomogeneous cases as well, mostly for systems in which the electron density changes slowly [11].

1.1.4 Generalized-gradient Approximations

Despite the success of LDA functional, many improvements still had to be made. For example, LDA is known to systematically overestimate cohesive energies in solids, while underestimating lattice constants. Over the years, various Generalized-gradient Approximations (GGAs) were developed, with marked improvement over LDA in many cases.

The first step beyond the local approximation is a functional of the magnitude of the gradient of the density $|\nabla\rho|$, the so called *Gradient Expansion Approximation* (GEA), first proposed by Kohn and Sham themselves, then carried out by Herman *et al.* [12] and others. However, since gradients in real materials are so large that the expansion breaks down, GEA did not bring much improvement to LDA, even making the approximation even worse.

The term *Generalized-gradient expansion* (GGA) was coined to denote a variety of functionals that modify the behavior at large gradients in such a way that the desired properties are preserved. These functionals are defined, in a generalized form, as:

$$E_{xc}^{GGA} = \int \epsilon_{xc}(\rho(\mathbf{r}), |\nabla\rho(\mathbf{r})|) \rho(\mathbf{r}) d^3\mathbf{r} = \int \epsilon_x^{hom}(\rho(\mathbf{r})) F_{xc}(\rho(\mathbf{r}), |\nabla\rho(\mathbf{r})|) d^3\mathbf{r} \quad (1.19)$$

where F_{xc} is dimensionless and $\epsilon_x^{hom}(\rho(\mathbf{r}))$ is the exchange energy of the homogeneous gas. F_x is defined as the *exchange enhancement factor* and it is a function of the dimensionless density gradient s , defined as:

$$s_m = \frac{|\nabla^m \rho|}{(2k_F)\rho} \quad (1.20)$$

The analytical form of the exchange enhancement factor F_{xc} is what makes a difference between the different GGA-based functionals that have been proposed over the years. A comparison between the most widely used GGA functionals is given in fig. 1.3.

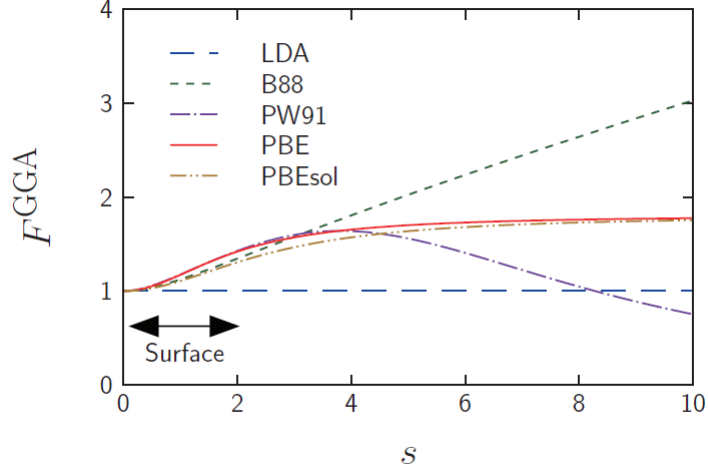


Figure 1.3: Exchange enhancement factor F_{xc} as a function of the dimensionless density gradient s for the most popular GGAs taken from Ref. [13]. It can be noted that, for most materials, in the most relevant range ($0 < s < 3$) all GGA functionals behave similarly and the magnitude of the exchange is increased by factor ≈ 1.3 - 1.6 with respect to LDA.

In this work, since I focused mainly on crystals, the most appropriate functional was chosen to be PBEsol [14], in which F_{xc} is fitted specifically for solids, giving results in better accordance with experimental data.

1.2 Plane waves and pseudopotentials

The next challenge to tackle to be able to solve equation 1.17 for periodic systems with a self-consistent procedure is to expand Kohn-Sham wave functions (ψ_i^{KS}) in a well known and complete basis-set.

1.2.1 Bloch theorem

Plane waves are a valid option to solve differential equation such as Schrödinger equation, especially for periodic system, since they provide at the same time an intuitive understanding and simple algorithms for calculations. The eigenstates of any independent particle Schrödinger-like equation in which electrons move in an effective potential $V_{eff}(\mathbf{r})$ satisfy the eigenvalue equation:

$$\hat{H}_{eff}(\mathbf{r})\psi_i(\mathbf{r}) = \left[-\frac{\hbar^2}{2m_e}\nabla^2 + V_{eff}(\mathbf{r}) \right] \psi_i(\mathbf{r}) = \epsilon_i\psi_i(\mathbf{r}) \quad (1.21)$$

The Bloch theorem states that if $V_{eff}(\mathbf{r} + \mathbf{R}) = V_{eff}(\mathbf{r})$ (i.e. it is lattice periodic) then the wavefunction can be factorized as $\psi_{i,\mathbf{k}}(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}}u_{i\mathbf{k}}(\mathbf{r})$ where $u_{i\mathbf{k}}(\mathbf{r}) = u_{i\mathbf{k}}(\mathbf{r} + \mathbf{R})$ is also lattice periodic. The periodic part of the Bloch wavefunction obeys the orthonormality relation $\langle u_{i,\mathbf{k}} | u_{i',\mathbf{k}'} \rangle = \delta_{i,i'}\delta_{\mathbf{k},\mathbf{k}'}$.

In a solid, it is convenient to require states to obey periodic boundary conditions in an ideally infinite volume Ω , and to be normalized. Using the fact that any periodic function can be expanded in the complete set of Fourier components, we can define all the key elements of eq. 1.21 in the basis of orthonormal plane waves. If $\mathbf{G}$ is a reciprocal lattice vector, then the Bloch wavefunction can be written as a linear combination of plane waves as:

$$u_{i,\mathbf{k}}(\mathbf{r}) = \frac{1}{\sqrt{\Omega_{cell}}} \sum_{\mathbf{G}} c_{i,\mathbf{G}}(\mathbf{k}) e^{i\mathbf{G}\cdot\mathbf{r}} \quad (1.22)$$

where Ω_{cell} is the volume of the unit cell and $\mathbf{k}$ is restricted to the first Brillouin zone. Then the Schrödinger equation for any given $\mathbf{k}$ can be written as the matrix equation:

$$\sum_{\mathbf{G}'} H_{\mathbf{G},\mathbf{G}'}(\mathbf{k}) c_{i,\mathbf{G}'}(\mathbf{k}) = \epsilon_i(\mathbf{k}) c_{i,\mathbf{G}}(\mathbf{k}) \quad (1.23)$$

Inserting eq. 1.22 into eq. 1.21 the Hamiltonian matrix elements are:

$$H_{\mathbf{G},\mathbf{G}'}(\mathbf{k}) = \frac{\hbar^2}{2m_e} |\mathbf{k} + \mathbf{G}|^2 \delta_{\mathbf{G},\mathbf{G}'} + \tilde{V}_{eff}(\mathbf{G} - \mathbf{G}') \quad (1.24)$$

where $\tilde{V}_{eff}(\mathbf{Q})$ is the Fourier transform of $V_{eff}(\mathbf{r})$.

Since the Schrödinger equation 1.23 is defined for each $\mathbf{k}$ separately, each state can be associated with the wavevector $\mathbf{k}$ and all the eigenvalues and eigenvectors for each $\mathbf{k}$ are independent. In the limit of an ideally infinite volume Ω , the $\mathbf{k}$ points become a dense continuum and the eigenvalues $\epsilon_i(\mathbf{k})$ become continuous *bands*. Since every state can be labelled by a well-defined $\mathbf{k}$, it follows that $\mathbf{k}$ is *conserved*, but, since the solutions of eq. 1.23 are periodic in $\mathbf{k}$, $\mathbf{k}$ is conserved modulo addition of any reciprocal lattice vector $\mathbf{G}$.

Among all the advantages that can be enumerated, plane waves are particularly popular because of some useful features:

1. Since Bloch theorem imposes the effective potential V_{eff} to be periodic, it is possible to run the calculations in reciprocal space and then transform them in real space using the fast Fourier transform (FFT).
2. A periodic potential makes $H_{KS}(\mathbf{r})$ a block diagonal matrix in $\mathbf{k}$, and each block can be diagonalized by itself.
3. Plane waves are an orthonormal and complete basis-set, without any overlap integral involved.
4. Plane waves are independent from nuclei positions, and, for an infinite number of plane waves, they practically become a complete basis set. This is in contrast

with localized basis sets where the evaluation of forces and stress is complicated by the presence of extra terms (called Pulay terms).

In principle, to fully describe the system, an infinite basis-set is needed, aim that is impossible to reach. The number of wave-functions must be truncated to a finite number for computational application; the truncation is imposed to the plane wave energy and it is called *cut-off energy*, E_{cut} :

$$\frac{\hbar^2}{2m_e} |\mathbf{k} + \mathbf{G}|^2 < E_{cut} \quad (1.25)$$

A graphical example of truncation in reciprocal space is given in fig. 1.4. It follows that the bigger E_{cut} , the more wave-functions are included in the basis-set, the better the system is described, the heavier the calculation will be.

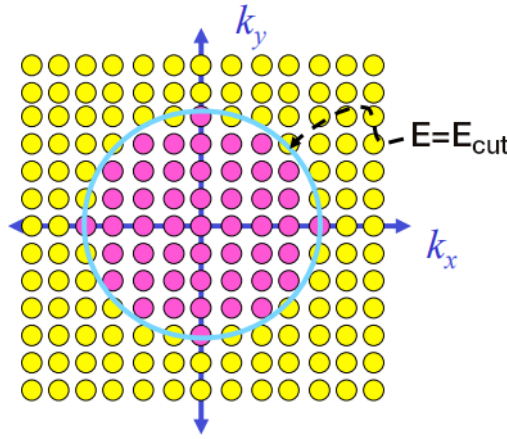


Figure 1.4: Example of truncation in $\mathbf{k}$ -space

Another effective way to reduce the number of plane waves involves the use of pseudopotentials, that are better detailed in the following section.

1.2.2 Pseudopotentials

The fundamental idea behind a *pseudopotential* is replacing one problem with another. The aim is to substitute the strong Coulomb potential of the nucleus and the effect of the tightly bound core electrons with an effective ionic potential acting on the valence electrons that can be described effectively by the use of plane waves basis-set, since pseudo wave-functions can be described with far fewer Fourier modes. Pseudopotentials can be generated in an atomic calculation and then used to compute properties of valence electrons in more complex systems, such as molecules or solids, since the core states remain almost unchanged regardless the nature of interactions between atoms. Furthermore, since pseudopotentials are not unique, one can choose the form that simplifies the calculation and the interpretation of the resulting electronic structure.

First-principles pseudopotentials are derived from an atomic reference state requiring that all electron valence eigenstates have the same energies and densities outside a chosen cut-off radius r_c , so that the real and the pseudo wavefunction and potentials come to match above this critical value, as shown in fig. 1.5.

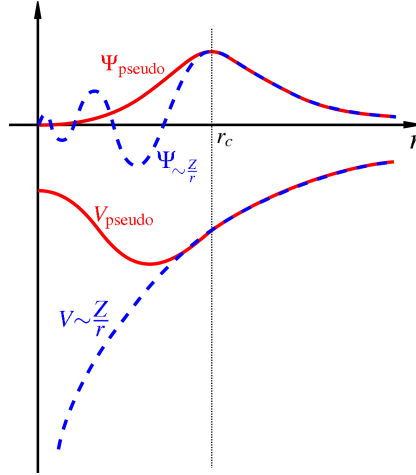


Figure 1.5: Comparison of a wavefunction in the Coulomb potential of the nucleus (in blue) to the one of the pseudopotential (in red).

Pseudopotentials with a larger cut-off radius are more rapidly convergent (*softer*), but they are less accurate to reproduce the same features in different environments (i.e. they are less *transferable*). Depending on the computational need, many different pseudopotentials are available to use:

- **Norm-conserving pseudopotentials:** *norm-conserving* and *ultrasoft* pseudopotentials are the most used in modern plane-wave electronic structure codes. Since they allow the use of basis-set with a lower cut-off to be used to describe the electron wavefunctions, they allow proper convergence even with limited computational resources. The first norm-conserving pseudopotential was proposed by Hamann, Schlüter, and Chiang (HSC) in 1979 [15] and had the following form:

$$\hat{V}_{ps}(\mathbf{r}) = \sum_l \sum_m |Y_{lm}\rangle V_{lm} \langle Y_{lm}| \quad (1.26)$$

where $|Y_{lm}\rangle$ projects a one-particle wavefunction to the angular momentum labeled by l, m and $V_{lm}(\mathbf{r})$ is the pseudopotential that acts on the projected component. Norm-conserving pseudopotentials are constructed to respect two conditions: *inside* the cut-off radius r_c , the norm of each pseudo-wavefunction must be identical to the corresponding electron wavefunction, while *outside* the cut-off radius all-electron and pseudo wavefunctions must be identical.

- **Ultrasoft pseudopotentials:** ultrasoft pseudopotentials relax the norm-conserving constraint to reduce the basis-set size even more at the expense of the accuracy, since a generalized eigenvalue problem is introduced. With a non-zero difference in norms, it can be defined:

$$q_{\mathbf{R},ij} = \langle \phi_{\mathbf{R},i} | \phi_{\mathbf{R},j} \rangle - \langle \tilde{\phi}_{\mathbf{R},i} | \tilde{\phi}_{\mathbf{R},j} \rangle \quad (1.27)$$

where ϕ and $\tilde{\phi}$ are the all-electron and pseudo- wavefunction respectively. In the ultrasoft formalism, the pseudo Hamiltonian now obeys the generalized equation:

$$\hat{H}|\psi_i\rangle = \epsilon_i \hat{S}|\psi_i\rangle \quad (1.28)$$

where the operator $\hat{S}$ is defined as:

$$\hat{S} = 1 + \sum_{\mathbf{R},i,j} |p_{\mathbf{R},i}\rangle q_{\mathbf{R},ij} \langle p_{\mathbf{R},j}| \quad (1.29)$$

In the latter equation, $p_{\mathbf{R},i}$ are the projectors that form a dual basis with the pseudo reference states inside the cut-off radius r_c . They are equal to zero outside.

- **PAW pseudopotentials:** the *Projected Augmented Wave* (PAW) method is a generalization of the pseudopotential and linear augmented-plane-wave methods, and allows DFT calculations to be performed with even greater computational efficiency. It provides a linear transformation ($\hat{T}$) of the pseudo wavefunction ($|\tilde{\psi}\rangle$) to the all-electron wavefunction ($|\psi\rangle$):

$$|\psi\rangle = \hat{T}|\tilde{\psi}\rangle \quad (1.30)$$

where the operator $\hat{T}$ is non-zero only within some spherical augmentation of the region Ω_R enclosing the atom R and can be defined as:

$$\hat{T} = 1 + \sum_i (|\phi_i\rangle - |\tilde{\phi}_i\rangle) \langle p_i| \quad (1.31)$$

where $|\phi_i\rangle$ is a set of all-electron partial waves, $|\tilde{\phi}_i\rangle$ is a set of pseudo partial waves and $|p_i\rangle$ is a set of projector functions. Outside the augmentation regions, the pseudo partial waves are identical to the all-electron partial waves. PAW pseudopotentials find a more vast application for spectroscopic purposes (i.e. XANES, NMR..) where a better description of the core electrons is needed to study electronic transitions.

1.2.3 Quantum Espresso

Structural optimizations and energy calculations for this work of thesis were performed using Quantum Espresso (QE), an integrated suite of open-source computer codes for quantum simulations of materials developed by P. Giannozzi *et al* in 2001 [16, 17]. The method is based on density functional theory, density functional perturbation theory and many body perturbation theory, in the realm of the plane-wave pseudo-potential and projector-augmented-wave approaches. QE owes its popularity to the wide variety of properties of the matter that can simulate and its performance on an increasingly broad array of hardware architectures. The distribution is based on two core packages, PWscf and CP, that perform self-consistent and molecular-dynamics calculations respectively. With Quantum Espresso it is possible to perform different tasks, included:

- Ground state calculations: with QE it is possible to look for self-consistent total energies, forces, stresses and orbitals. Separable norm-conserving and ultrasoft pseudo-potentials are supported as well as many exchange correlation functionals, from LDA to generalized-gradient corrections, to meta-GGA and hybrid functionals. It is also possible to perform noncollinear magnetism and spin-orbit coupling calculations;
- Structural optimization, molecular dynamics and potential energy surfaces calculations;
- Electrochemistry and special boundary conditions
- Response properties (Density Functional Perturbation Theory) calculations: examples of this kind are phonon frequencies and eigenvectors at any wavevector calculations, full phonon dispersion, electron-phonon interactions and many others;
- Spectroscopic properties;
- Quantum transport.

The suite is constantly updating, and it is considered to be a very reliable implementation by thousands of users all around the world.

1.3 Crystal Structure Prediction

Are crystal structures predictable? This question can seem straightforward, but it is actually way more complex to answer than it may appear. Behind an apparently simple question, in fact, there are many hidden predicaments to assess that up to

relatively few years ago made a negative answer the only possible one. Nowadays, given much higher computational power than before, various methods can be applied to get closer to an affirmative answer to the question.

Crystal Structure Prediction (CSP) has been a challenge of the scientific community in the last few decades and it consists in finding the most stable and probable crystal structures of a compound given only the elemental composition. While knowledge of intermolecular valence could be considered satisfactory already thirty years ago, the perspective of being able to design molecular solids with predetermined physical properties that depend on the structure is an appealing and yet challenging purpose still in the present years.

In the early days of X-ray crystallography, guessing at the crystal structure by minimizing intermolecular repulsions was considered a viable method of solving the phase problem, when cell dimensions and diffraction intensities were available. From that perspective, knowing the cell volume implied knowledge of intermolecular attraction and that only mutual avoidance between rigid object had to be figured out. Direct methods made these procedures obsolete, paving the way for new crystal structure prediction techniques which had the ambitious aim to consider not only already experimentally synthesized compounds, but also materials whose synthesis has not yet been accomplished. With the aim of reaching a high level of accuracy in this sense, some fundamental problems and the questions they pose must be tackled [18].

1. *Will a compound crystallize?* Thermodynamics holds that any substance must crystallize given a low enough temperature (or a high enough pressure) and that it is pure. Kinetics, though, puts a limit to these possibilities, since, while dissolution always takes place in the proper solvent, crystal growth in solution is always problematic; melting often occurs at higher temperatures than freezing; a crystal is more easily destroyed than built. Sometimes, well-shaped single crystals are much less likely to occur than disordered, strained or twinned crystals, or even waxes and glasses.
2. *Is this crystal high-melting?* The melting temperature (T_m) is high for high-melting enthalpy and for low-melting entropy. Higher T_m 's are therefore associated to disordered crystals, or solids whose liquids are heavily associated. Correlations between T_m and crystal cohesion should therefore be taken into consideration with caution.
3. *What is the lattice energy?* Over the years, many statistical studies have been performed on the relationship between molecular and crystal properties for the most common families of compounds, either involving hydrogen bonding or not. Correlations were found that allow an estimate of sublimation enthalpies from molecular parameters such as the Van der Waals surface or the number

of valence electrons.

4. *Will the crystal structure be non-centrosymmetric?* Crystal centrosymmetry is sometimes a refinable parameter in X-ray crystal structure analysis and it is often a matter of debate rather than an *a priori* condition. The centrosymmetry of a structure can rarely be predicted, but it was found to be related to some unusual properties of crystals. For these reasons, being able to predict even just the centrosymmetry of the system is an important challenge for CSP techniques.
5. *Will some parts of the molecule take up a predictable orientation in the crystal?* Many studies have been performed to try to identify statistical behavior of chemical recognizable molecular moieties, such as preference approach paths of recurrent substituent with respect to hydrogen bonding or $\pi - \pi$ interactions between aromatic rings. Some broad trends in the dependence of crystal packing from the presence of certain moieties have been identified, but since interactions in crystals of complex molecules are diverse and diffuse, relying only on local effects can be dangerous.
6. *What can be the space group and the number of molecules in the asymmetric unit?* For the crystal chemist, the prediction of the space group can seem a fanciful exercise, if what counts is just an understanding of how molecules arrange themselves in a crystal, but in the answer to this question lies both the *mathematical* and the *chemical* approach to the problem that CSP poses. It was, in fact, demonstrated that the combination of symmetry elements gives rise to exactly 230 independent three-dimensional possible space groups, but, on the other side, crystal symmetry has to do with the possibility of molecules to actually form a stable solid, which depends upon intermolecular forces. No necessary correlation holds between these two views: 230 space groups exist, but molecules cannot freely choose among them. Moreover, there are rather strict conditions that can be met by a limited number of combinations of few symmetry elements, so the choice of space groups is usually restricted for specific classes of compounds: identify the space group can be indeed crucial to rule out some structural possibilities.
7. *What are the cell parameters?* The cell volume can be estimated from molecular volume, and crystal density too can roughly be estimated. If space is to be efficiently used in as condensed phase, there must be a correlation between molecular dimensions and cell parameters. Cell dimensions are a bad identifier of a crystal structure, since the choice is not unique, but they can be indicators of distances between molecular centers of mass, which are the main

quantitative descriptors of crystal geometry and are dictated by the strength and directionality of intermolecular forces.

Up until just a few decades ago, the problems hidden in these questions were big enough to make the scientific community think that no method was ever going to be able to tackle them. In just twenty years, though, computer power has grown exponentially, up to the point that nowadays there are plenty of ways to assess the Crystal Structure Prediction problem and, up to a certain degree of accuracy, solve it.

In the next paragraphs, I will briefly overview the most widely used methods, starting from USPEX (Universal Structure Predictor: Evolutionary Xtallography) code, the method that was used in the present work to predict crystal structures.

1.3.1 Universal Structure Predictor: Evolutionary Xtallography (USPEX) code

One of the best methodologies developed in recent years to address the CSP problem is the USPEX code. Developed by A. Oganov in 2004, it is used worldwide by more than 6000 researchers on a daily basis, since it is considered an efficient and reliable method for predicting crystal structures merging *ab-initio* total-energy calculations and an evolutionary algorithm [19–21]. While in many cases it is possible to solve the crystal structure from experimental data, theoretical structure prediction is crucial for many reasons. First of all, when experimental data are not good enough, especially in high-pressure or high-temperature conditions, theory is the only way to attempt structural resolution. Secondly, theory represents the only way to investigate matter in extreme conditions, which are not reproducible with today’s experimental techniques, such as ultrahigh pressures. Finally, a reliable crystal structure prediction method can be precious to attempt the design of new materials. The search for stable structures, though, is made difficult by the multidimensionality of the free energy surface, since the number of degrees of freedom is $3N + 3$ with N being the number of atoms in the unit cell, with an enormous number of local minima separated by high energy barriers. It is not hard to get a feeling of how big of a number we are talking about; just by making a simple example in simplified conditions, such as a fixed cubic cell of volume V containing N atoms forced to take only discrete positions on a grid with resolution δ , the number C of combinations of atomic coordinates is:

$$C = \frac{1}{(V/\delta^3)} \frac{(V/\delta^3)!}{[(V/\delta^3) - N]!N!} \quad (1.32)$$

This number, regarding of the values chosen for δ and N , is likely to reach a value of the order of magnitude of at least 10^{11} , and it increases exponentially if atoms

are allowed to be different elements, or even just increasing N to a reasonable value. In fact, for example, in a $N = 10$ scenario, the number of possible structures rises to 10^{25} . These numbers are practically impossible to deal with, even for relatively small values of N , but fortunately there is no need to explore the entire free energy surface to locate the global minimum, but only the most promising regions. One can either start already in a good region of configuration space or use a "self-improving" method that locates the best structures. Evolutionary algorithms like USPEX belong to the latter category, since the strength of these kind of simulation is that they do not need any system-specific knowledge aside from the chemical composition and are, indeed, self-improving, meaning that every new generation increasingly better structures are found and used to generate new structures. These features make evolutionary algorithms suitable for crystal structure prediction purposes. The aim of the method is to develop a systematic approach, where a stable structure at given temperature and pressure conditions is found starting from the bare chemical composition. It was developed to be *universal*, meaning that it aims to be applicable to ionic, metallic, covalent or Van der Waals crystals, and different types of structures should be treatable on equal footing. The method should also scale with N , and USPEX can reach good efficiency at least up to $N \approx 40$. The method is also easily parallelizable, with operations running on different processors completely independent one another, guaranteeing the work load to be equally distributed. Searching the global minimum on the free energy surface is often all but an easy task. Free energy landscapes in chemical systems have an overwhelming number of local minima, separated by energy barriers often too high to overcome (fig. 1.6), making them hard to investigate with molecular dynamics or Monte Carlo approaches.

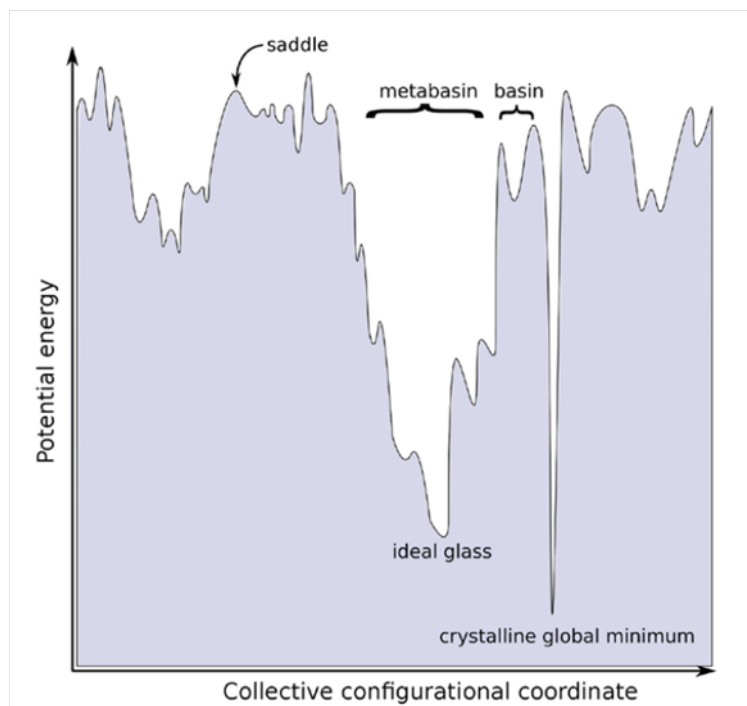


Figure 1.6: An example of a section of free energy surface. It can be observed the great number of minima that can be investigated, and often the global minimum corresponding to the correct crystal structure is so narrow and the energy barriers around it so high that finding it can be a really challenging task.

However, these landscapes have several features that can help in the challenging task of finding the minimum. First of all, only a small fraction of the surface is of any chemical interest; secondly, at the same stable structure usually correspond more than one equivalent minima; it is also true that the deepest minimum is easier to reach than any single local minimum, since it has the largest surface area. Since most of the minima are usually located in the same region of landscape, these factors make it easy to understand that it is not necessary to investigate the entire vastness of the energy surface: what is really crucial to find the global minimum is to investigate the *right section* of the landscape. The problem of global search through a huge number of local minima is replaced by a neighborhood search through a relatively small number of local minima. Usually, this approach works efficiently only if the most stable structure is somehow similar to an input structure which helps to locate the best surface area to investigate. Unfortunately, a reliable starting structure is not always known *a priori*. USPEX method, like others of the same family of evolutionary algorithms, presents a good alternative to this approach, since it mimics *Darwinian evolution* and employ *natural selection* of the fittest and such variation operators as genetic heredity and mutations. This way, evolutionary algorithms can perform well for different types of free energy landscapes, working especially well for surfaces having an overall shape - i.e. those where the global minimum and the deepest local minima are in the same region, as expected for chemical systems.

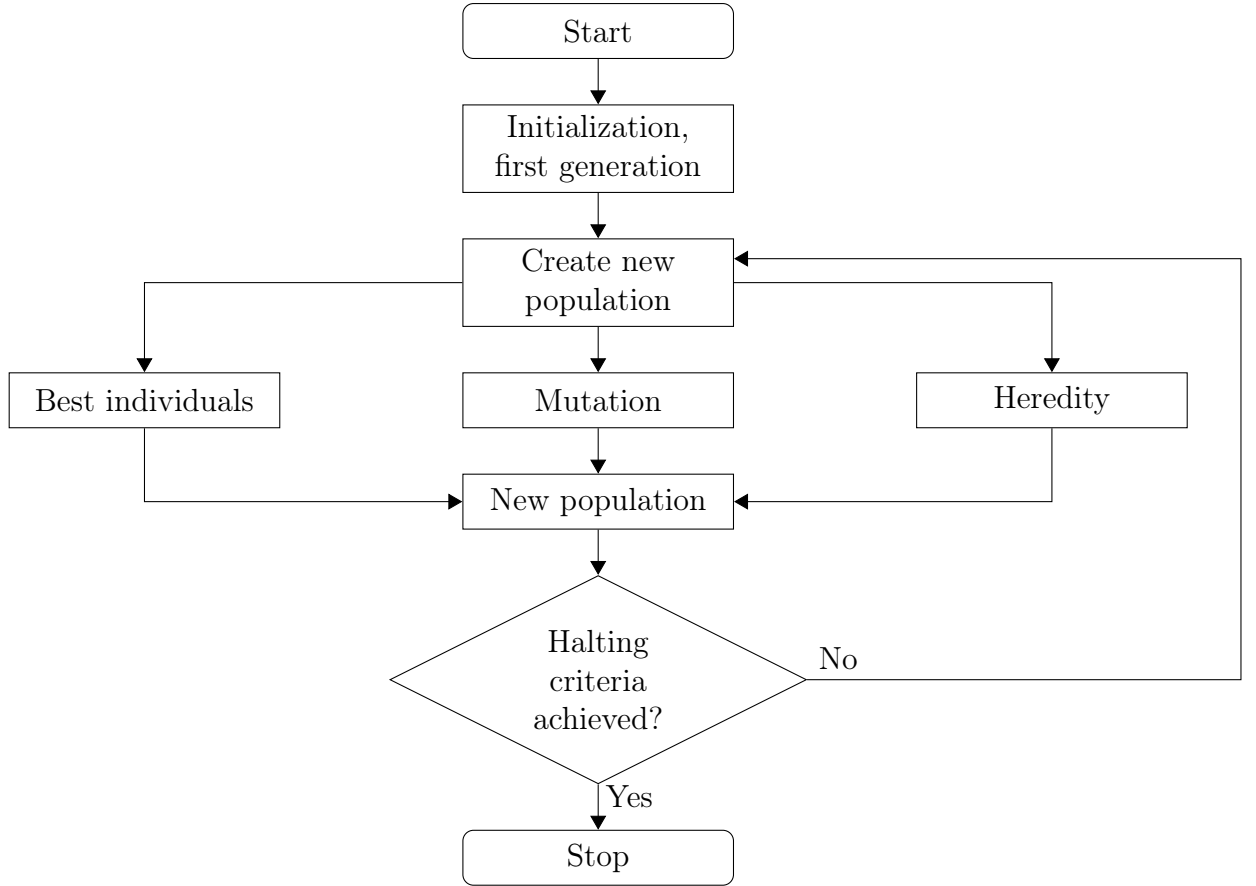


Figure 1.7: A schematic representation of the mechanism behind USPEX code.

The algorithm is implemented in USPEX and has a minimal input: the number of atoms of each type, pressure and temperature conditions, the population size, hard constraints and the criteria by which new populations are built. The procedure (schematically represented in fig. 1.7) is the following:

1. The first generation is produced randomly, although allowing only structures that satisfy the hard constraints. It is also possible to start from a "good guess" input structure provided by the user.
2. Among the locally optimized structures (*ab initio* optimization using first-principles and atomistic simulation codes such as VASP, SIESTA, GULP and QuantumEspresso) a certain number of the worst ones are rejected, and of the remaining structures, the very best are kept by the algorithm and pass directly to the next population, while the others, selected by fitness ranking (i.e. their free energies) participate in the next generation through heredity, atomic permutation and mutation (fig. 1.8).
 - During *heredity* (fig.1.8a), new structures are produced by matching slides of the parents structures, chosen in random directions and with random positions. Heredity of the lattice vector matrix is done by taking a

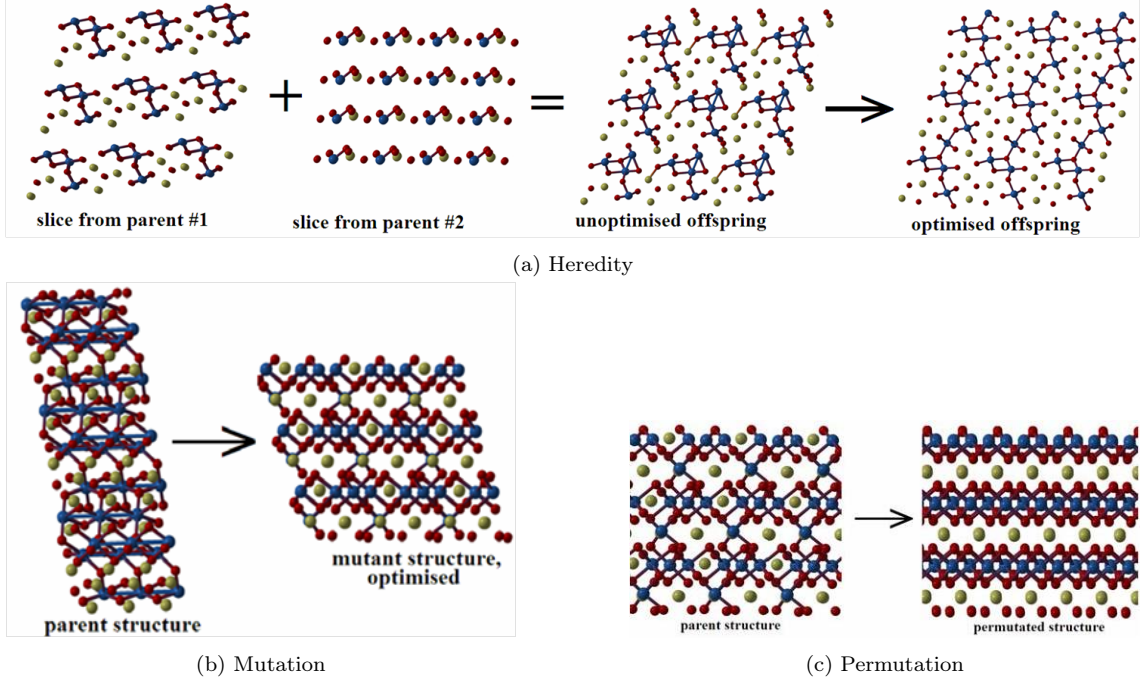


Figure 1.8: Schematic representation of the criteria used by USPEX to generate new generations: (a) Heredity, (b) Mutation and (c) Permutation.

weighted average with a random weight.

- *Mutation* (fig. 1.8b), instead, applies random changes in the cell vectors and/or atomic positions. Lattice mutation essentially incorporates the ideas of metadynamics, since it finds new structures by building up cell distortions of some known structure.
- *Permutation* (fig. 1.8c) consists in switching identities of two or more atoms in a structure; the number of permutations applied is drawn from a uniform distribution.

To avoid pathological lattices, all newly generated structures are rescaled to have a certain volume and then relaxed by local optimization.

3. The simulation is stopped after some halting criterion is met. Usually, for systems with ~ 20 atoms in the cell, convergence to stable crystal structures takes up to ~ 20 generations.

In figure 1.9 is a representation of the algorithm progress in the prediction of the crystal structure of MgSiO_3 at 120 GPa of pressure (20 atoms/cell) for the best structure as a function of generation. It can be noted that after 15 to 20 generations, the code already stabilized the curve on the most promising structures, finding both the stable and low-energy metastable structures in a single simulation with no experimental information to begin with.

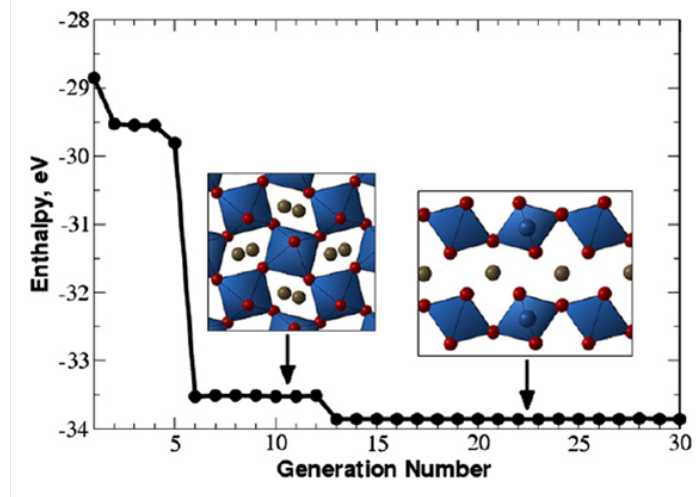


Figure 1.9: Prediction of the crystal structure of MgSiO_3 at 120 GPa (20 at/cell), shown as an example (from [22]). Insets show the perovskite and post-perovskite structures to point out that up to 12th generation the perovskite was found to be the most energetically favoured, and only after the 13th generation the postperovskite structure was found.

1.3.2 Other methods

Even if they were not directly applied in this work of thesis, there exist many other computational methods to solve Crystal Structure Prediction problem that are worth a mention. Many claim the ability to predict the most stable crystal structure given the elemental composition and pressure of temperature conditions, and not all of them are evolutionary algorithms like USPEX. Here is a brief overview of the most widely used nowadays.

- **AIRSS:** Ab Initio Random Structure Searching (AIRSS) is a simple yet powerful approach for Crystal Structure Prediction. The concept was first introduced in 2006 by Pickard and Needs [23], and extensively discussed in the years after. Random structures are generated and then relaxed to nearby local minima, and it has had wide success in the aim of finding the most stable structures in particular by using DFT for the energies. The *sensible* random structures are built to have reasonable densities and atomic distances and they may embody crystallographic, chemical and prior experimental or computational knowledge. This method has been widely adopted in a number of landmark studies in structure prediction, from the structure of SiH_4 under pressure, to providing the theoretical structures, and can be extended to the prediction of clusters, defects in solids, interfaces and surfaces.
- **CALYPSO:** Crystal structure AnaLYsis by Particle Swarm Optimization (CALYPSO) is an efficient structure prediction method developed by Wang *et al.* in 2012 [24]. The approach requires only the chemical composition for a given compound and given external conditions of pressure and temperature to pre-

dict stable and metastable structures and even design new multi-functional materials. The CALYPSO method is based on several major techniques for global structural optimization from scratch, such as particle-swarm optimization algorithm, symmetry constraints on structural generation, bond characterization matrix on selecting and eliminating similar structures and penalty functions. The CALPYSO method comprises four steps: (i) generation of random structures with constraints of symmetry; (ii) local structural optimization; (iii) identification of unique local minima by bond characterization matrix; (iv) generation of new structures by Particle Swarm Optimization (PSO) for iterations.

- GASP: the Genetic Algorithm for Structure and Phase Prediction (GASP) contains a heuristic search code to solve structure prediction problems. It was developed by Ceder group at MIT in 2007 and has widely evolved ever since [25]. It's a genetic algorithm that includes the most successful techniques described in the literature and important new ones, It can search for periodic structures as well as crystal structures and it can be interfaced with many energy optimization codes such as GULP, VASP and LAMMPS. Without parallelization, the code proceeds as follows: (i) create initial parent generation; (ii) create empty offspring generation; (iii) apply promotion and variation operations to create new offsprings; (iv) when enough offsprings are generated, relax each structure and evaluate its fitness; (v) re-develop each offspring and, if successful, add it to the next generation. This iterative process is repeated up until convergence is reached.
- XtalOPT: XtalOPT is an evolutionary algorithm for crystal structure prediction based on a periodic displacement (ripple) operator ideally suited for extended systems [26]. This hybrid operator, which combines two pure operators, makes the potential energy surface easier to explore while simultaneously zooming in on the most promising regions. XtalOpt uses phenotypical representations, meaning the operators responsible for procreation act directly on the actual coordinates and lattice parameters in either fractional or Cartesian space, as opposed to mutating and breeding the individual after encoding it as a binary string.

The previously enlisted are just a few examples of the many softwares employed nowadays to solve the crystal structure prediction problem, which is not considered an impossible task anymore.

1.4 Quantum Theory of Atoms in Molecules

To study the nature of the chemical bonding and analyse the atomic charge in crystals, we made use of Quantum Theory of Atoms In Molecules (QTAIM). In this section I briefly introduce the method and the state of the art of the theory behind it.

Quantum Chemical Topology (QCT) is a branch of theoretical chemistry that makes use of the mathematical theory of topology to partition chemical systems and characterize their properties, focusing mainly on those spatial properties which do not change under deformation. Since the formulation of Density Functional Theory by Hohenberg and Kohn in 1964, there has been a significant effort by the scientific community to describe features of the matter by the use of electron density, not only because it is easier to treat from the computational point of view (see section 1.1.2), but also because the electron density is a quantum observable. The experimental electron density, in fact, can be derived through X-ray studies and compared with the theoretical counterpart that can be obtained through many different approaches. With this purpose in mind, since 1970s Bader *et al.* started investigating the nature of electron density and its topological features, developing the Quantum Theory of Atoms in Molecules (QTAIM) [27]. A topological basin of a scalar function $f(\mathbf{r})$ is defined by two types of non-degenerate critical points (a local maximum and one or more first-order saddles) and by a separatrix $S(\mathbf{r})$ never crossed by gradient lines:

$$\nabla f(\mathbf{r}) \cdot \mathbf{n}(\mathbf{r}) = 0; \forall \mathbf{r} \in S(\mathbf{r}) \quad (1.33)$$

When $f(\mathbf{r})$ is the electron density, the definition of topological basin and that of quantum atom overlap. The expression of the local kinetic energy density is:

$$\begin{aligned} K(\mathbf{r}) &= -\frac{1}{4} \int (\psi^* \nabla^2 \psi + \psi \nabla^2 \psi^*) d\tau' = \\ &= \frac{1}{2} \int (\nabla \psi^* \cdot \nabla \psi) d\tau' - \frac{1}{4} \int (\nabla^2 \psi^* \psi) d\tau' = \\ &= \frac{1}{2} \int (\nabla \psi^* \cdot \nabla \psi) d\tau' - \frac{1}{4} \int \nabla^2 \rho(\mathbf{r}) d\tau' \end{aligned} \quad (1.34)$$

For the divergence theorem, one can also write:

$$\iiint d\tau' \nabla^2 \rho(\mathbf{r}) = \oint \nabla \rho(\mathbf{r}) \cdot d\mathbf{S} \quad (1.35)$$

If one integrates the latter expression in eq.1.34 into a topological basin of the electron density, given the condition in eq.1.33, the local kinetic energy density is given unambiguously. The topology of a generic scalar function of the electron density is defined by four types of non-degenerate critical points, characterized by

the rank (ω) and the signature (σ) of the diagonalized hessian matrix calculated on the point; thus, they are labelled as (ω, σ) . Bader demonstrated [27] that these critical points correspond with elements of chemical structure, and classified them as follows:

- A local maximum of $\rho(\mathbf{r})$ (3,-3) is called *nuclear critical point* or *attractor* and defines an atomic basin along with its gradient region.
- A first-order saddle point of $\rho(\mathbf{r})$ (3,-1) is called *bond critical point* and defines the presence of chemical interaction between two nuclear critical points.
- A second-order saddle point of $\rho(\mathbf{r})$ (3,+1) is called *ring critical point* and defines the presence of a ring-like chemical structure. The critical point is situated in the minimum of electron density situated at the center of the ring plane.
- A local minimum of $\rho(\mathbf{r})$ (3,+3) is called *cage critical point* or *repulsor* and it defines the presence of a cage-like chemical structure. The critical point is situated in the absolute minimum of the cage.

Given these definitions, QTAIM can be easily applied to many fields of chemical structure analysis, including the search for the presence of hydrogen-hydrogen bonding, the calculation of certain physical properties on a per-atom basis, and the analysis of the charge located on each atom in a complex structure. Since the theory is entirely based on electron density, it is easier to couple it with DFT-based theoretical methods and to compare it to experimental data at the same time, making it one of the most versatile methods for chemical topology analysis used nowadays.

1.5 High Pressure experiments

Pressure, along with temperature, is one of the physical parameters that can be accurately varied during modern experiments. The term "high pressure" can be misleading, since it can refer to relatively low pressures, in the order of magnitude of a few bar, up to pressure as high as several hundreds of GPa (1 GPa = 10^5 bar). The highest pressure ever reached in an experiment is reported to be just above 1 TPa (10^7 bar) and it was reached by the means of a diamond anvil cell during an experiment on tin at the European Synchrotron Radiation Facility (ESRF) [28]. Since pressure is defined as force per unit of surface the force is applied to, reaching high pressures can be achieved in two different ways: apply a very large force or reduce the area of the surface to a minimum. Following the former concept is the Large Volume Press (LVP), a device largely used to run modern high-pressure experiments (fig. 1.10).

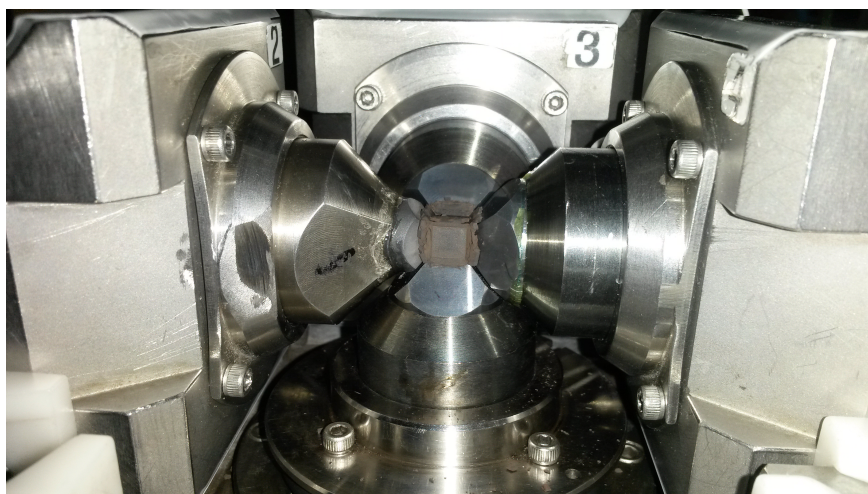


Figure 1.10: Detail of a Large Volume Press, in particular the D-DIA large volume triaxial press at the Earthquake Research Institute in Tokio, Japan. The six anvils of the D-DIA squeeze a cube of boron-epoxy, in which the deformation assembly is located. Most of the anvils are made of tungsten carbide, but for X-ray diffraction experiments two of the four horizontal anvils consist of sintered diamond, which is almost transparent to X-rays. This kind of device can easily reach pressures between 1 and 4 GPa, up to a few tens of GPa.

The LVP consists of hydraulic presses that allow, as suggested by the name itself, the study relatively large samples, especially if compared to other high-pressure experimental techniques. The majority of devices of this kind hold a Walker-type module [29] that allows to reach pressures as high as 25 GPa and temperatures up to 2500°C, since it uses a clever multi-wedge setup to turn the uniaxial force from the hydraulic press into a quasi-hydrostatic pressure on the sample. Most of the anvils are made of tungsten carbide, but they can also consist of sintered diamond, which is transparent to X-rays, making it easier to study the high-pressure experiment. The upper pressure limit is determined by the size of the truncation on the tungsten carbide cube: the smaller the truncation, the higher the reachable pressure. Two pieces of copper are also placed on the surface of the assembled cube to serve as an electrical contact between the tungsten carbide cubes and the steel wedges: this setup allows to resistively heat the sample by the means of an electrical current passing through a graphite sleeve. Temperature is then measured using a thermocouple placed close to the sample. If no thermocouple can be used or if it breaks during the compression, the temperature is usually determined using a power/temperature calibration depending on the machine setup, or it can be calculated from a well defined P - V - T standard using XRPD signal.

The second way to reach pressures in the order of several tens of GPa is by reducing the sample surface to sub-millimeter size, and this is the principle behind the Diamond Anvil Cells functioning. The Diamond Anvil Cell (DAC) makes it possible to study materials under extreme conditions, since it can be used to reach very high pressures, even higher than 100 GPa. Diamond is not only one of the

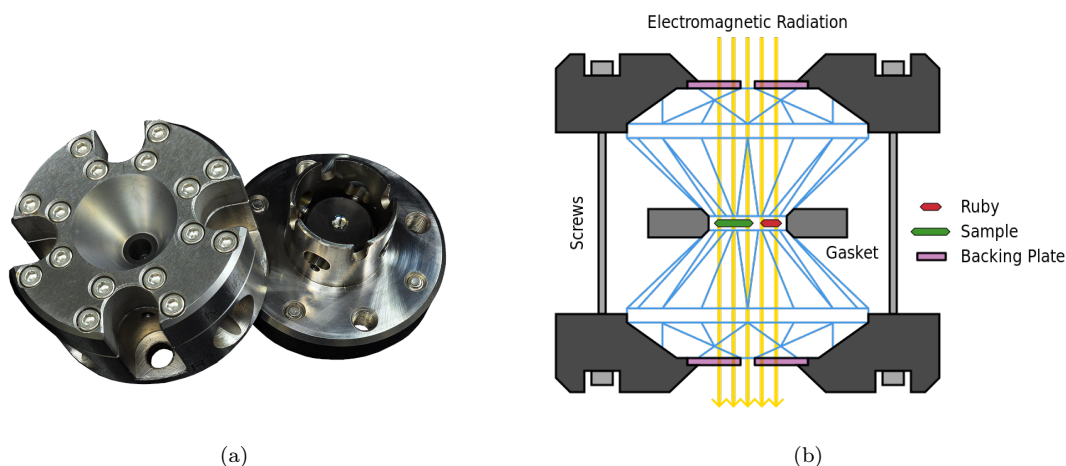


Figure 1.11: (a) Gasket and (b) schematics of the core of a diamond anvil cell. The culets (tip) of the two diamond anvils are typically 100–250 microns across.

hardest materials ever reported on Earth, but it also has some peculiar properties that make it the perfect material for generating high pressure. Diamond is, in fact, transparent to X-ray, both non-conducting and non-magnetic and chemically inert, all characteristics that enable it to be combined with a large variety of experimental techniques. When coupled with laser heating, which can reach temperatures higher than 2000 K, it becomes an exceptional and powerful tool to study a broad range of materials properties under really extreme conditions. There are many different designs of DACs, but the principle behind is similar in all of them: the sample is placed between two diamond surfaces (culets) so that it undergoes very high pressures when the opposing diamond anvils are forced together. Most of DACs display a metal membrane pressurized using screws, as shown in figure 1.11a; a metal gasket with a thickness of approximately $250\ \mu\text{m}$ is indented between the two diamond anvils to a thickness that depends on the pressures that are intended to be reached (typically, an approximate thickness of $40\ \mu\text{m}$ is needed to reach pressures between 30 and 100 GPa).

Pressure can be monitored using a reference material whose behavior under pressure is known, such as ruby fluorescence: this is why a ruby is included in the gasket, as schematically shown in fig. 1.11b. The uniaxial pressure supplied by the DAC is transformed in hydrostatic pressure using a pressure transmitting medium, usually a noble gas like argon or xenon, which is also enclosed in the gasket. Two slits guarantee the light access to the gasket containing the sample; thus, X-ray diffraction, fluorescence, photoluminescence, Raman and other signals can be measured from materials under extreme pressure conditions. Magnetic and microwave fields can also be applied externally to the cell, while very high temperatures can be achieved by the means of laser-induced heating (up to 7000 K). Reaching unbelievable pressures, this setup made it possible to recreate extreme conditions such

as those existing deep inside planets and to synthesize materials and phases never observed before.

Chapter 2

Perovskites under pressure

Perovskites are a large family of structures in the even larger field of materials science, first discovered by Gustav Rose in 1839 in the form of the mineral CaTiO_3 and named after Russian mineralogist Lev Alekseyevich von Perovski. Perovskites are characterized by the general chemical formula ABX_3 : the A-site is occupied by a cation, usually a large alkaline earth metal, the B-site is occupied a smaller transition metal while the X-site is home to an anion, usually oxygen. The ideal structure for perovskites assume is the cubic one, space group $Pm\bar{3}m$ (#221), showed in figure 2.1. This structure is characterized by the formation of corner-sharing BX_6 octahedra, so that the A-site cation is surrounded by twelve anions in octahedral coordination.

Most of synthetic perovskites, though, do not assume the idea structure, but fall into distorted derivatives of it. The distortion can be due to many different factors, mainly the rotation of BX_6 octahedra, the displacement of the B- site cations or a Jahn-Teller distortion. The most common distortion arises from the A-site cation being sufficiently small resulting in a tilting of BX_6 octahedra about the pseudo-cubic axes to accommodate the cations to achieve a more stable structure. This operation lowers the symmetry of the cubic structure, shortening A-X bond length

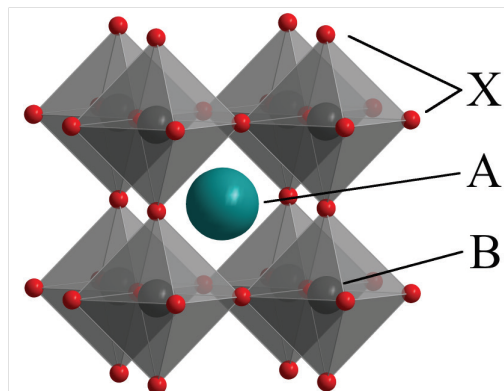


Figure 2.1: The ideal cubic perovskite structure showing the cubo-octahedral coordination of the A-site and B-site cations.

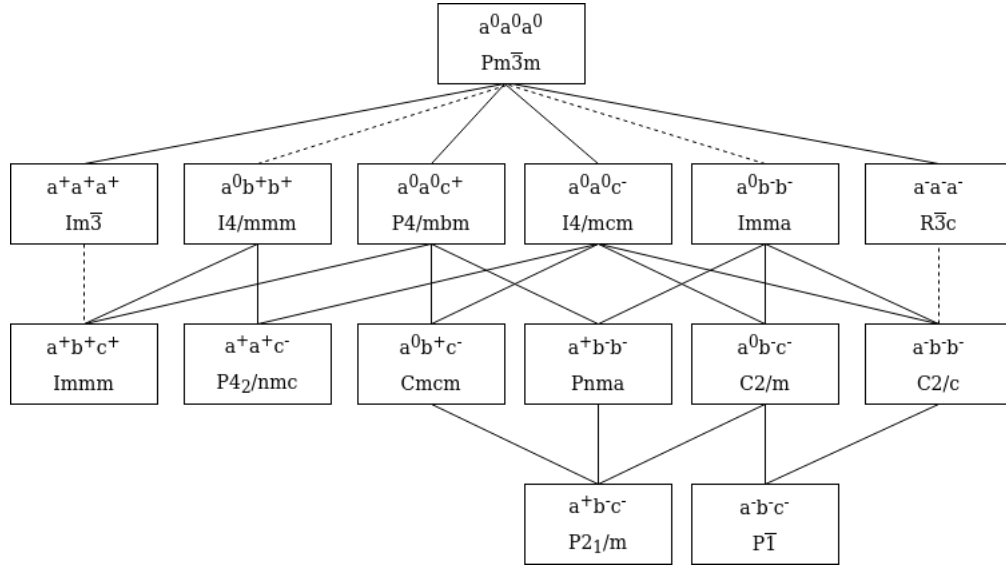


Figure 2.2: Schematic representation of the group-subgroup relationships between the 15 space groups associated with octahedra tilting in perovskites. A dashed line joining a group with its subgroup indicates that the corresponding phase transition is required by Landau theory to be first order, while a solid line indicates a second order phase transition. Figure adapted from [30].

and changing the A-site coordination, without, however, breaking the corner sharing connectivity between BX_6 octahedra. The type of distortion that can occur strongly depends on the radius of the ions forming the structure. The type of distortion can be predicted to some extent by the means of the Goldschmidt tolerance factor, t , which can be calculated knowing the ionic radii of the species involved as:

$$t = \frac{R_A + R_X}{\sqrt{2}(R_B + R_X)} \quad (2.1)$$

The X anion is usually oxygen, most of metallic elements are stable in a perovskite structure if the Goldschmidt factor is in the range of 0.75-1.0. Moreover, the tolerance factor can be used as an indicator to predict which type of perovskite structure one combination of elements is going to assume. The cubic structure, since it has A-site and B-site cations of the ideal size, has t in the range of 0.9-1.0. When A-site ions are too small to fit into B-site ion interstices the structure tends to distort into an orthorombic or a rhombohedral structure, and the Goldschmidt tolerance factor falls into the range of 0.71-0.9. If, instead, A-site ion is too big, or B-site ion is really small, the tolerance factor can even be greater than 1, and the resulting structure tends to be hexagonal or tetragonal.

Even if the value of t is not an unambiguous indication to the distortion type, the tilting of the octahedra lowers the symmetry of the cubic space group in a predictable way. In 1998, Howard and Stokes [30] evaluated the group-subgroup relationship between the 15 space groups involved as a consequence of the tilting

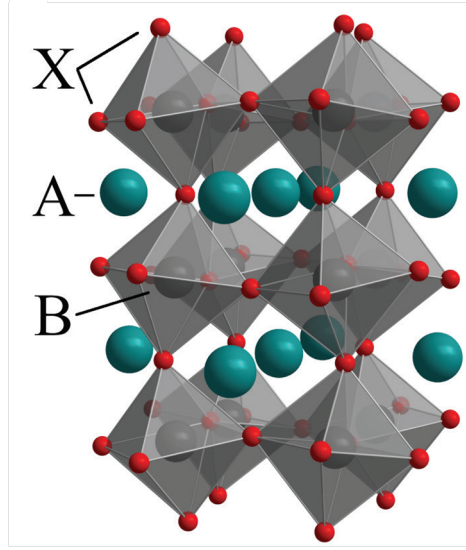


Figure 2.3: The orthorhombic perovskite structure, space group $Pbnm$ (#62)

of octahedra, as shown in figure 2.2. Changing temperature, pressure conditions and eventually the composition, it is possible to drive the phase transition from one group to the linked subgroup, following the theoretically predicted sequence. Among these derivatives of the cubic structure, the orthorhombic perovskite structure is one of the most common, and it is shown in figure 2.3.

These conformation is characterized by a much more pronounced tilting of the octahedra with respect to the cubic perovskite. The octahedral tilting is expressed by the means of the three tilting angles, θ , ϕ and Φ , which represent the rotations of the octahedra about the pseudo-cubic axes, $[110]_p$, $[001]_p$ and $[111]_p$ respectively. For the space group $Pbnm$, Glazer's notation indicates the presence of two anti-phase tilts of equal magnitude (a_x^- and a_y^-) about the $[100]_p$ and $[010]_p$ pseudo-cubic axes, respectively. The $[110]_p$ or θ -tilt can be considered the resultant of these two tilts, while the c_z^+ tilt is equivalent to the ϕ -tilt ($[001]_p$). In general, if $a_x^- \approx a_y^-$, then only two angles (θ and ϕ) are required to describe the tilting of the octahedra about all three axes. This condition is usually satisfied and these angles are, by definition, approximately equal in space group $Pbnm$. Even if the tilting angles are more accurately obtained from the atomic positions, they can also be estimated from the unit cell parameters. In fact, for orthorhombic perovskites with no distortion of the BX_6 polyhedra, the unit cell dimensions can be written as:

$$\begin{aligned} a &= \sqrt{2}a_p \cos\theta \cos\phi \\ b &= \sqrt{2}a_p \cos\phi \\ c &= \sqrt{2}a_p \cos\theta \end{aligned} \tag{2.2}$$

where a_p is the dimension of the pseudo-cubic cell. Since a_p is related to the

mean B-X bond length by $a_p = 2(d_{B-X})$, it can be written:

$$\begin{aligned} d_{B-X} &= \frac{bc}{4a} \\ \cos\theta &= \frac{a}{b} \\ \cos\phi &= \frac{\sqrt{2}a}{c} \\ \cos\Phi &= \frac{\sqrt{2}a^2}{bc} \end{aligned} \tag{2.3}$$

From the latter equation it can be deduced the value of the tilting angle around the triad axis (Φ), which is a useful parameter when comparing different materials:

$$\Phi = \cos^{-1} \left(\frac{\sqrt{2}a^2}{bc} \right) \tag{2.4}$$

This parameter is a robust method of evaluating the octahedral tilting from powder X-ray diffraction (XRPD) in those cases where the atomic positions cannot be efficiently refined. Since the octahedra are often not regular, this method usually underestimates the tilt angles.

Post-perovskite structure

The first post-perovskite was reported in 1965 by Rodi and Babel, who discovered the structure of CaSiO_3 (space group $Cmcm$, #63), but the name was given after one of the silicate mineral MgSiO_3 , which is one of the most abundant constituents of various types of igneous rocks and metamorphic rocks in Earth's mantle. The structure was first called *silicate perovskite* after the discovery that MgSiO_3 has a perovskite structure at ambient pressure, but then it undergoes a structural transition to the CaIrO_3 -type structure under high pressure and high temperature conditions [31]. The term *post-perovskite* refers to the observation that this type of structure is observed as a structural transition *after* the perovskite structure in MgSiO_3 , as pressure and temperature are increased.

The post-perovskite structure, shown in figure 2.4, still has the same BX_6 octahedra that characterize the perovskite structure, but the tilting is much more pronounced. This implies that the octahedra in this structure are corner-sharing only in one direction, along the c -axis, while they are edge-sharing along the a -axes. The final impression is that the structure is layered along the b -axis, with sheets of connected BX_6 moieties stacked in layers separated by the A-site cation.

Since it was discovered in 2004, the post-perovskite structure had been of great interest for the scientific community, since it was predicted to have high electrical

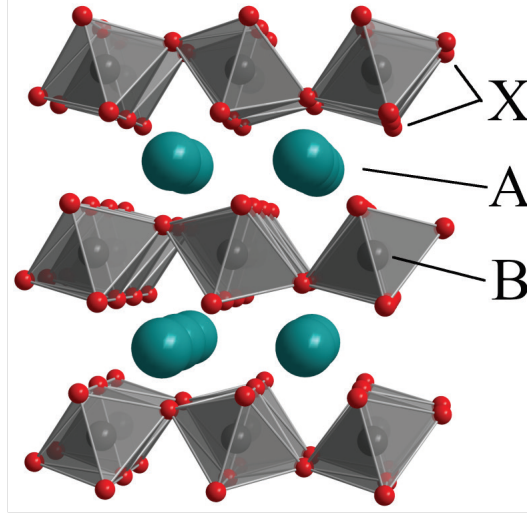


Figure 2.4: The post-perovskite structure, space group $Cmcm$ (#63)

conductivity, perhaps two orders of magnitude higher than perovskite's conductivity [32], in addition to having all the interesting features deriving from its particular structure, such as the anisotropy in compressibility and elastic properties. The main problem with post-perovskites is the difficulty encountered when quenching the structure at ambient conditions, which makes it hard for experimentalists to study the properties. This is the reason why the search for novel post-perovskite structures that can be quenched at ambient conditions is of great interest nowadays and in the last decades several ABO_3 perovskites have been found to undergo a structural transition to a $CaTiO_3$ -type structure under pressure [33–36].

2.1 $SrRuO_3$

Driven by the success of new experimental methods to study perovskites under very high pressures, we started looking for novel post-perovskites phase transitions in strontium perovskites $SrMO_3$ ($M = Ru, Ge, Os$). Perovskites with $4d$ transition metals, in fact, have attracted growing attention for their particular electronic and magnetic properties, highly sensitive to variations in the crystal structure. The alkaline-earth ruthenates, in particular, show a variety of appealing physical properties that strongly depend on the nature of the alkaline-earth cation. This is the reason why the first compound that was investigated is $SrRuO_3$, which displays an orthorhombic perovskite structure with a rather large Curie temperature of 160-165 K and a magnetic moment of $1.63(6) \mu_B/Ru$ at 10 K [37]. This material is also an itinerant weakly correlated ferromagnet, which is rather unusual for perovskites with a $4d$ -element as the B-site of the structure [38]. These are just a few of the appealing properties that, in the last few decades, led to a wide interest in using thin-films $SrRuO_3$ as a conductor in multilayer oxide electronics [39]. At ambient

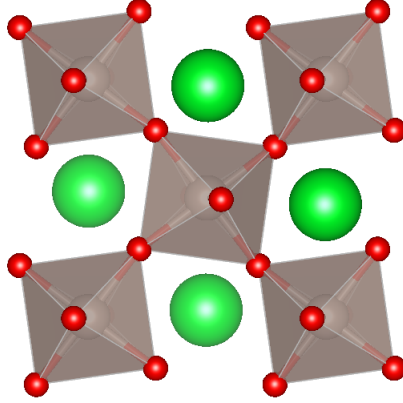


Figure 2.5: At ambient pressure, SrRuO_3 displays the orthorhombic $Pbnm$ (#62) structure. Strontium atoms are the green ones, surrounded by layers of RuO_6 octahedra. Ruthenium is shown as the grey atom in the center of the RuO_6 octahedra, while oxygen atoms are in red.

pressure, SrRuO_3 adopts the orthorhombic perovskite structure (space group $Pbnm$) shown in figure 2.5.

For this compound, two independent studies have predicted a perovskite to post-perovskite transition at 32 GPa [40] and 40 GPa [41] respectively, by the means of Density Functional Theory (DFT) calculations, while three independent experimental studies [42–44] conducted experiments on SrRuO_3 up to 54 GPa but never observed any structural transition to a post-perovskite structure. Zhernenkov *et al.* observed two structural transitions at 21 GPa and 38 GPa to lower symmetry structures. Trying to shed light on transitions occurring under high pressures for this material, we performed DFT variable-cell structure relaxations as a function of pressure using Quantum Espresso [16,17] employing different functionals to model which one fitted best with experimental data from high pressure experiments performed by collaborators Camilla Hjort Kronbo, Louise Ring Jensen and Martin Bremholm. We used double-projector, norm-conserving ONCV [45, 46] pseudopotentials including semicore states (i.e. $4s^24p^65s^2$ for Sr and $4s^24p^65s^24d^6$ for Ru). We used a plane-wave cut-off of 80 Ry and up to $6 \times 6 \times 4$ k-points. Since SrRuO_3 is a weakly-correlated ferromagnetic metal at ambient pressure, we set up a spin-polarized ferromagnetic (FM) state. The symmetry of the optimized structures were determined by the means of the FINDSYM utility [47]. Experimentally, polycrystalline SrRuO_3 was synthesized by collaborators by a conventional solid state reaction of stoichiometric amounts of Ru and SrCO_3 in an alumina crucible for 10 hours at 950 °C. Then the sample was ground, pressed to a pellet and heated twice for 10 hours at 1200 °C. High pressure PXRD experiments at room temperature were performed at the Advanced Photon Source (APS) using a photon energy of 37 keV ($\lambda=0.3344$ Å) and an X-ray beam size of $3 \times 5 \mu\text{m}^2$.

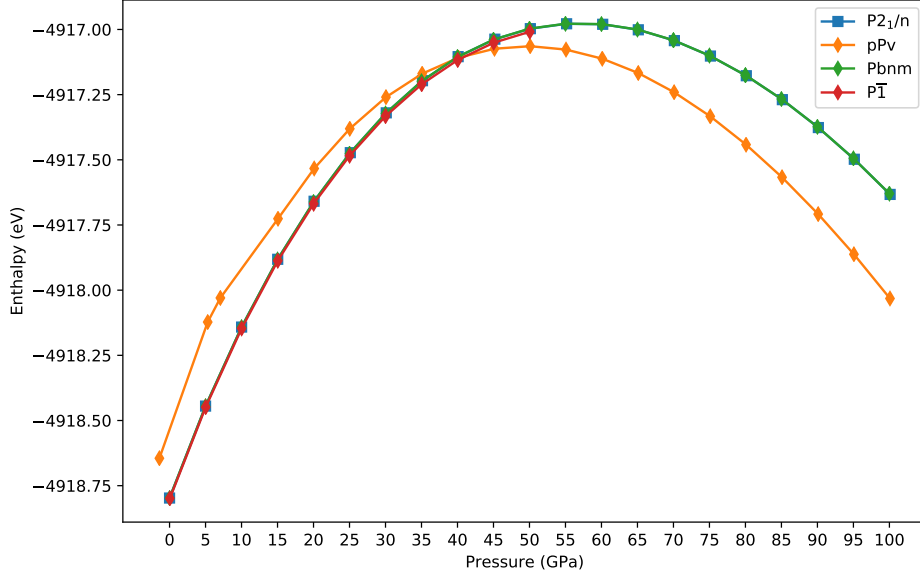


Figure 2.6: Enthalpy (H_0) as a function of pressure for the four SrRuO_3 structures explored. To help visualize the transition pressure, volume is corrected with a fixed volume $V_0=50 \text{ \AA}^3$, which is the mean value per formula unit over this range of pressure. This way it can be clearly seen that we observe a transition from perovskite $Pbnm$ structure to a post-perovskite $Cmcm$ structure at ~ 40 GPa of pressure.

Results and discussion

We performed structural relaxations as a function of pressure using Quantum Espresso, optimizing the structure of the four more plausible structures for this compound: perovskite orthorhombic $Pbnm$, perovskite monoclinic $P2_1/n$, perovskite triclinic $P\bar{I}$ and the post-perovskite $Cmcm$. In figure 2.6 are shown the results for the enthalpy of the four structures explored. Since the enthalpy grows very quickly as a function of pressure, it can be very hard to distinguish different curves, since they would all appear as straight steep lines. To better visualize the enthalpy difference between the structures, the enthalpy is shown as:

$$H_0 = E + P(V - V_0) \quad (2.5)$$

where V_0 is the average volume per unit formula over the considered range of pressures and is kept fixed for all the structures. This way, what would look like indistinguishable straight lines appear as clearly different curves with a maximum in V_0 .

A structural transition was observed at ~ 40 GPa, since the $Cmcm$ post-perovskite structure becomes energetically favoured. These results were obtained by the use of PBE functional and are coherent with the similar results obtained by Cai *et al.*

in ref. [41] also by theoretical means. On the contrary, collaborators observed an unexpected transition to a monoclinic $P2_1/n$ phase [48] between ~ 22 GPa and ~ 28 GPa, and this structure persists up to the highest investigated pressure point of 88 GPa. From theoretical calculations, this latter transition is not detected: curves corresponding to $Pbnm$ and to $P2_1/n$ polymorphs are, in fact, superimposed and thus not distinguishable one another, nor can be underlined any transition to a triclinic $P\bar{1}$ phase. Theoretical and experimental crystal data obtained for perovskite and post-perovskite phases of SrRuO_3 are listed in table 2.1. It can be noticed that theoretical data for the perovskite $Pbnm$ phase are in good agreement at lower pressures, confirming that at ambient condition the crystal is indeed orthorhombic. Increasing the pressure to ~ 40 GPa, however, calculation deviates significantly from experimental data, with a difference as high as 4%. On the other hand, calculations predict a phase transition to a post-perovskite structure, which is characterized by a much shorter a -axes cell parameter with a corresponding increase in the b -axes.

	Perovskite				Post-perovskite
	Exp. ^a	Exp. ^a	Cal. ^b	Cal. ^b	Cal. ^b
	10 GPa, 6K	42 GPa, 6K	10 GPa	40 GPa	40 GPa
Space group	$Pbnm$ (#62)	$P2_1/n$ (#14)	$Pbnm$ (#62)	$Pbnm$ (#62)	$Cmcm$ (#63)
Cell parameters					
a (Å)	5.48192	5.33511	5.46134	5.22400	3.09596
b (Å)	5.40583	5.11355	5.49593	5.32751	9.18030
c (Å)	7.70531	7.33943	7.77166	7.50959	7.24395
Volume/f.u. (Å ³)	57.0855	50.0495	58.3169	52.4934	51.4716
^a Ref. [48]					
^b This work, using PBE functional.					

Table 2.1: Experimental (Exp.) and calculated (Cal.) crystallographic data of perovskite and post-perovskite phases of SrRuO_3 .

Fig.2.7a shows the lattice parameters of perovskite $Pbnm$ SrRuO_3 structure as a function of pressure. The c parameter was reduced to $c_u = c/\sqrt{2}$ to make it comparable to a and b , so that the new reduced cell is pseudo-cubic. It can be clearly noticed that the a and c_u axes of the pseudo-cubic cell coincide at low pressures and then diverge as the pressure increases. On the other hand, fig.2.7b shows that the axial ratio b/a and c_u/a increase as a function of pressure, a behavior that has been observed in many other cases of perovskite to post-perovskite phase transitions, such as for MgGeO_3 , MnGeO_3 [33] and NaMgF_3 [49].

These lattice parameters trends under high pressure indicate that pressure itself enhances the orthorhombic structural distortion of SrRuO_3 , which drives the transition to the post-perovskite phase occurring at ~ 40 GPa. Although this transition

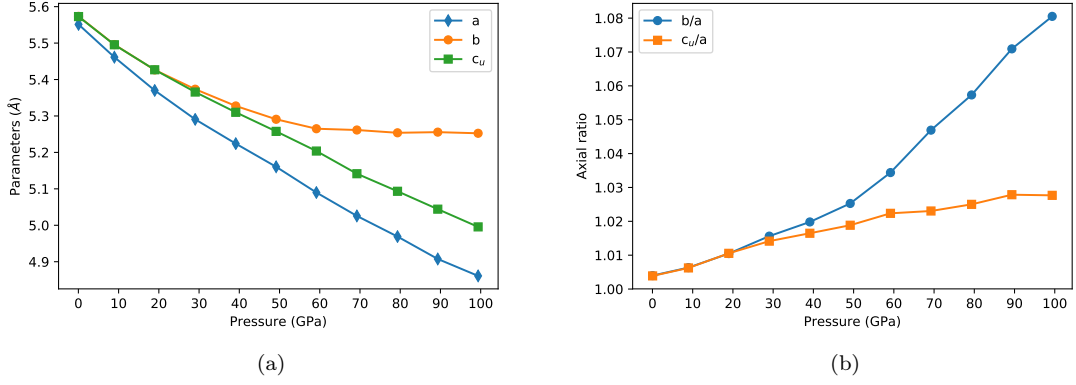


Figure 2.7: (a) Trend of the unit cell parameters and (b) changes in the axial ratios b/a and c_u/a of $Pbnm$ $SrRuO_3$ as a function of pressure. The cell parameter c is plotted as $c_u = c/\sqrt{2}$ to fall in the same range as a - and b -axes.

pressure is higher than that of parent structures (such as $CaRuO_3$, which is 13-27 GPa [35]), it is in good agreement with previously performed theoretical calculations on this material in literature [40,41]. Analysis of the trend of the volume as a function of pressure (fig.2.8) highlights a volume drop from $52.49 \text{ \AA}^3$ of the $Pbnm$ phase to $51.47 \text{ \AA}^3$ of the $Cmcm$ post-perovskite phase, a volume change of -1.95%, which is close to those of $CaRuO_3$ (-1.7%) and $CaIrO_3$ (-1.4%) [35] and coherent with what obtained by Cai *et al.* [41].

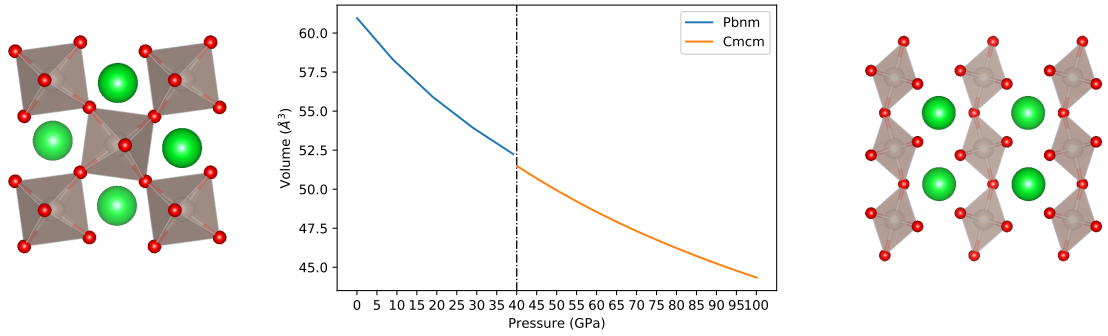


Figure 2.8: Volume per formula unit as a function of pressure for the perovskite phase up to 40 GPa and for the post-perovskite phase from 40 GPa to 100 GPa. The corresponding crystal structures are shown on the left ($Pbnm$) and on the right ($Cmcm$).

Such a sizable volume drop suggests that the perovskite to post-perovskite transition is a first-order phase transition.

Although these results may seem promising, experimental data shows no evidence of a structural transition to a post-perovskite structure occurring up to the highest

pressure explored of 87 GPa. XRPD diffraction data seem to suggest instead a second order phase transition to a lower symmetry perovskite structure, a monoclinic $P2_1/n$, occurring between 22.7 GPa and 27.8 GPa, driven by the collapse of the magnetic moment per Ru ions going from $2\mu_B$ to $\sim 1\mu_B$ and then to zero as a function of pressure [48]. I tried to adopt a new computational strategy to run more accurate calculations and find the functional that fit best experimental data. Since PBE [50] functional was not in good agreement with high-quality diffraction data, I tested three more functionals to seek for a better understanding of the system: LDA [9], which is known to slightly underestimate volumes and transition pressures, PBEsol [14], which is a modification of PBE functional especially fitted for solids, and the recently developed ACBN0 [51]. The latter in particular is a "pseudo-hybrid" density functional which defines the Hubbard U and J terms based on the bare Coulomb and exchange interactions and a renormalized occupation matrix. It has the advantage of a great flexibility with respect to unique Hubbard sites at the price of a very low computational cost compared to the main DFT calculation, which makes this functional very well suited for high-throughput applications. Furthermore, it was reported [52] to significantly improve the description of transition metal perovskites with respect to PBE and other hybrid functionals. For the investigation of SrRuO_3 behavior under high pressures, a Hubbard U of $U_{\text{Ru}}=2.4$ was applied on ruthenium atoms and $U_{\text{O}}=7.25$ on oxygen atoms. Since the majority of the experimental data that can be found in literature refers to the orthorhombic perovskite structure, the $Pbnm$ structure was fully relaxed again over the range of pressures between 0 GPa and 100 GPa employing the aforementioned four functionals. Results for the volume are shown in fig.2.9. Experimental data sets are obtained from two different works conducted on SrRuO_3 . The first one is from Zhernenkov *et al.* [44], who conducted the high-pressure experiments up to 60 GPa at the temperature of 6K and observed a first structural transition to a monoclinic $P2_1/n$ phase between 10 GPa and 21 GPa, and then a second transition to a triclinic $P\bar{1}$ phase. The second one, instead, is from Jacobsen *et al.* [43] who performed room temperature high-pressure structural studies on SrRuO_3 using two different pressure media: argon, which is the data set labelled in figure as "exp2", and a 4:1 mixture of methanol:ethanol, which is the data set labelled as "exp3". Up to the highest pressure investigated (34 GPa), they observe no structural transition from the perovskite $Pbnm$ phase.

Analysis of the performance of the different functionals tested shows that the higher values for volumes come from PBE functional, which is known to slightly overestimate cell parameters, while the lower values are associated with LDA functional, which is as well known to underestimate volumes instead. PBEsol data is found to lie at intermediate values between the two aforementioned functionals, which makes it a good compromise that can give a better description of the systems

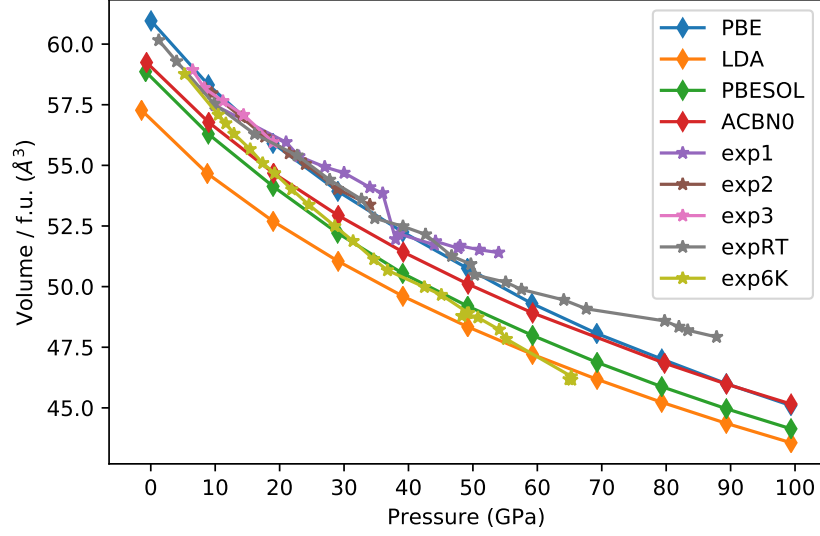


Figure 2.9: P-V relation for orthorhombic $Pbnm$ phase calculated with different functionals and compared to different sets of experimental data. "exp1" set refers to study conducted by Zhernenkov *et al.* in [44] while "exp2" and "exp3" sets are both from the work of Jacobsen *et al.* in [43]. "expRT" and "exp6K" sets are both from high quality diffraction data performed by collaborators [48], the former at room temperature and the latter at 6K.

taken into exam. Despite the expectations, ACBN0 functional seems to work well at low pressures, falling closer in values to PBEsol results, but then the data diverges, getting closer to PBE results at high pressures, meaning that combined effects of Hubbard U on ruthenium and oxygen atoms improve structural parameters only at low pressure.

Moreover, it can be noticed that different experimental data sets return quite different results. As expected, diffraction data obtained at room temperature results in a more expanded unit cell and thus in a greater volume. Experiments conducted at low temperature, instead, fall in the same range of the DFT data sets, even though the experimental curve drops with a more pronounced slope, starting off at higher volumes at low pressure and quickly falling to lower volumes at high pressures.

Overall, it can be deduced that the functional which better describes high-quality diffraction data is undoubtedly PBEsol, since the curves of these two sets of data are almost superimposed, mostly at intermediate pressures. A comparison of the lattice parameters obtained experimentally at 6K and PBEsol results is shown in fig. 2.10. Values of c parameters are plotted as reduced to make the cell pseudo-cubic, with $c_u = c/\sqrt{2}$.

Cell parameters decrease rather smoothly as the pressure increases and no crossover between the curves is observed, neither for experimental nor for calculated data set. Aside from the range of pressures lower than 10 GPa, PBEsol seem to follow the

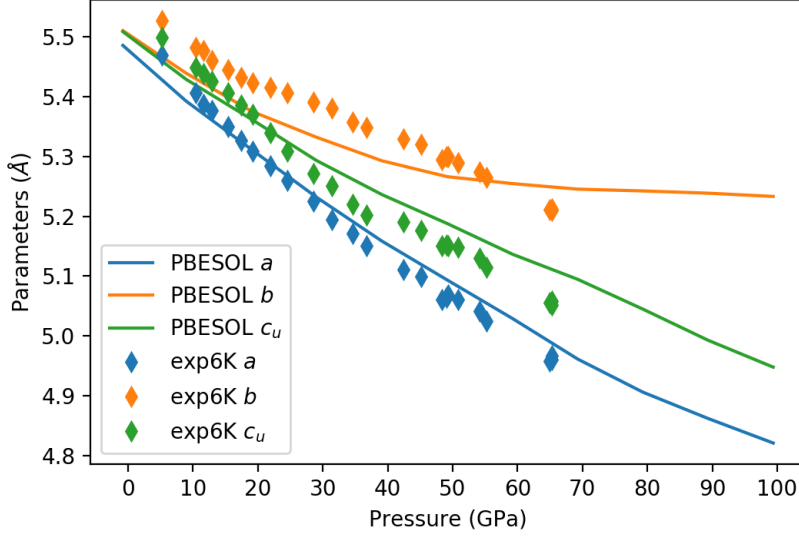


Figure 2.10: Refined unit cell parameters as a function of pressure for $Pbnm$ phase of $SrRuO_3$ at 6K experiment [48](symbols) compared to calculated unit cell parameters using PBEsol functional (lines). To make a pseudo-cubic unit cell, values of c parameters are shown as $c_u = c/\sqrt{2}$.

same trend as experimental data and the values, mostly for a and c unit cell parameters, are in good agreement.

In conclusion, none of the functional tested was able to reproduce the transition to a monoclinic $P2_1/n$ phase that was observed experimentally, while predicting a definite transition to a $Cmcm$ post-perovskite phase at ~ 40 GPa of pressure that is however not observed from high-quality diffraction data. The $SrRuO_3$ was taken as benchmark system to test the performance of four different functionals and PBEsol was found to be the most reliable to tackle crystal structures, as the data obtained with this functional were in good agreement with experimental data.

2.2 $SrGeO_3$

Perovskite and perovskite-related structures have been of major interest in both materials science and geoscience research areas also because a significant percentage of the Earth's mantle is made of silicate ($ASiO_3$) compounds, which under the great pressure existing at those depths, present indeed perovskite-related structures. For these reasons, investigations of ternary silicates ($ASiO_3$) compounds and their physical properties have been of prior interest of the scientific community, especially coupled with extensive study of ternary germanates ($AGeO_3$) structures. The latter ones, in fact, are often used as a model for the former ones since they undergo structural transition to similar phases when high pressures and temperatures are involved, but at less extreme conditions [53–57]. We decided to concentrate the attention on

SrGeO₃ because many analogies can be made with parent silicate structures, especially SrSiO₃ and CaSiO₃. Moreover, the cubic perovskite of SrGeO₃ is a promising new transparent electronic conductor [58] which are sought for a variety of optoelectronic applications and was recently found to be a superior electron-transporting layer for high-performance perovskite solar cells [59].

SrGeO₃ has a Goldschmidt tolerance factor of $t = 1.04$. For ABX₃ compounds a similar value usually suggests that SrGeO₃ would crystallize as a hexagonal BaTiO₃-like perovskite structure with face-sharing octahedra. Although the structure was first reported to be indeed hexagonal [60,61] more recent studies confirmed it to be monoclinic pseudo-wollastonite at ambient pressure [62]. Pseudo-wollastonite SrGeO₃ undergoes a transition into a cubic perovskite structure at 6 GPa of pressure and 1100°C. By analogy, the corresponding silicate, SrSiO₃, was predicted to transform in the same perovskite structure, but only at a pressure of 38 GPa and a temperature of 1700°C [63,64]. SrGeO₃ has also been considered a good model for CaSiO₃ for many years, since the two compounds have a similar Goldschmidt tolerance factor ($t = 1.08$ for the silicate) and both are predicted to undergo a structural transition to a triclinic walstromite phase (fig.2.11c) before transforming into the perovskite phase at higher pressures and temperatures [54,56,65]. Together with Camilla H. Kronbo and Martin Bremholm, collaborators from Aarhus University who performed all the experiments, we wanted to gather more information on SrGeO₃ structures and make a coherent study of the structural properties as a function of pressure. Results are published on the Journal of Alloys and Compounds [66].

Experimentally, monoclinic pseudo-wollastonite SrGeO₃ ($C2/c$) was synthesized by collaborators by a conventional solid-state reaction, grinding together and then pressing to a pellet stoichiometric quantities of SrCO₃ and GeO₂ powders. The pellet was then placed in an alumina crucible and sintered at 1100°C for 10h. A fraction of the pseudo-wollastonite sample was transformed into the triclinic walstromite ($P\bar{1}$) phase using an in-house large volume multi-anvil press. The pressure was increased to 4 GPa at room temperature and then heated up to 1000°C. Another fraction of the pseudo-wollastonite sample was transformed into the cubic perovskite ($Pm\bar{3}m$) with a similar procedure by the means of a large volume press. The pressure was increased to 6 GPa at room temperature, then the sample was heated up to 1100°C and then quenched at room temperature.

High pressure PXRD data for pseudo-wollastonite and perovskite polymorphs of SrGeO₃ were collected at the European Synchrotron Radiation Facility (ESRF) ($\lambda=0.3738$ Å, beamsize $\sim 3 \times 3$ μm²) while triclinic walstromite phase was measured at the Advanced Photon Source (APS) ($\lambda=0.3344$ Å, beamsize $\sim 5 \times 7$ μm²). From the computational perspective, we first performed a fixed composition US-

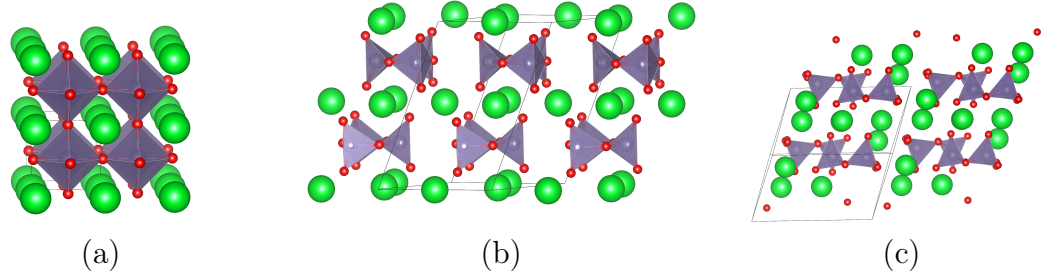


Figure 2.11: (a) Cubic (b) pseudo-wollastonite (c) wallstromite structures of SrGeO_3

PEX (v9.4.4) search on 4-6 SrGeO_3 unit formulas. The initial USPEX population was composed of 30 randomly generated structures and we allowed up to 40 generations, employing the standard genetic algorithms (heredity, random generation, soft mutation, permutation, lattice mutation) [20, 21, 67]. We performed many runs with different external pressures applied (0 GPa, 20 GPa, 30 GPa, 100 GPa). To reduce computational cost, we employed the local-basis code SIESTA [68] with norm-conserving pseudopotentials from the Martins-Trouiller table and the SZP basis set, and we used PBE exchange correlation functional. At the end of the USPEX runs, we selected the most stable structures and further relaxed them in steps of 2-5 GPa up to 50 GPa of pressure using the plane-wave pseudo-potential code Quantum Espresso [16, 17]. We used PBEsol exchange-correlation functional and ultrasoft pseudopotentials from the GBRV library [69, 70] including semicore states (i.e. $4s^2 4p^2 5s^2$ for Sr and $4s^2 3d^{10} 4p^2$ for Ge). A plane-wave cutoff of 45 Ry and up to 1000 k -points per reciprocal atoms (resulting in $6 \times 6 \times 4$ k -point grid for the largest cell) were used, sufficient to converge the total energy by 1 mRy. We chose to employ PBEsol functional as it has been shown to give a better description of the structural parameters of oxygen perovskites with respect to other functionals. The symmetry of the relaxed structures was determined using the FINDSYM utility [47].

Results and discussion

At ambient pressure, SrGeO_3 crystallizes in the monoclinic pseudo-wollastonite structure ($C2/c$). Two high-pressure polymorphs, monoclinic wallstromite ($P\bar{1}$) and cubic perovskite ($Pm\bar{3}m$), were synthesized using a large volume press. The structures of the three polymorphs are shown in fig.2.11. First reported by Hilmer *et al.* [60, 61] to present a hexagonal layered order-disorder structure, the pseudo-wollastonite phase (fig.2.11b) was later found to be monoclinic [62] with a pseudo-hexagonal cell. It consists of an alternate stacking of ternary rings of GeO_4 moieties and closed-packed strontium atoms along [001] in a six layer polytype structure. The triclinic wallstromite phase (fig.2.11c), instead, is characterized by GeO_4 tetrahedra arranged in three membered rings moieties, that occur in layers with alternating

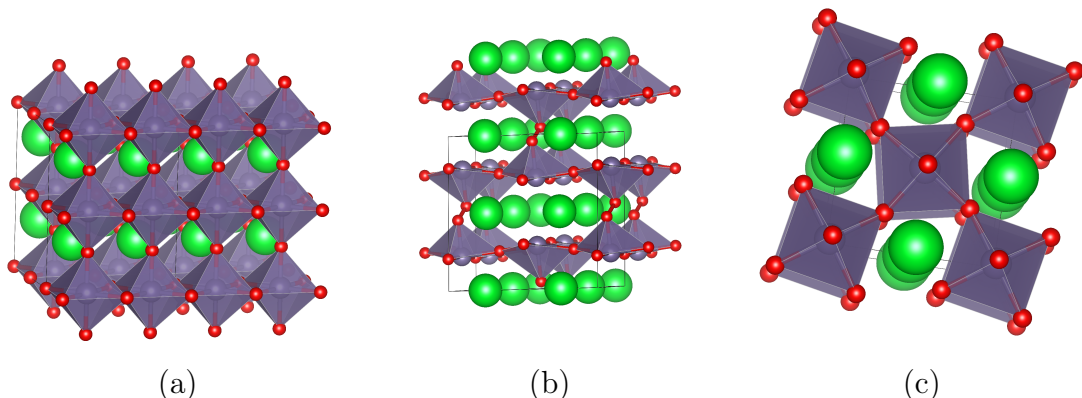


Figure 2.12: (a) EA182 (b) EA216 and (c) EA548 structures resulting from USPEX fixed composition run. These three phases were found to be the most stable in the last generation pool.

rings pointing in opposite directions, and there are three unique Ge sites for both ring types. Finally, the crystal structure of the cubic perovskite phase (fig.2.11a) consists of an ordered network of GeO_6 octahedra with strontium atoms in the network cavities surrounded by twelve oxygen atoms in a cubo-octahedral coordination. The obtained *in-situ* high pressure PXRD patterns for the pseudo-wollastonite and the walstromite structures show a short transition between 10 GPa and 12 GPa, but then a collapse is observed into what seemed to be an amorphous phase, since the diffraction peaks disappear with increasing pressure and only a very broad characteristic remains [66]. However, since the diffraction pattern seemed to suggest the transition to a short-living phase that was very hard to refine, we performed a fixed-composition USPEX run to seek for unknown phases that maybe we wrongly not taking into account. We performed the calculations at different external pressures, but USPEX simulation at 20 GPa, 30 GPa and 100 GPa all converged to a full population of perovskite or perovskite-related structures, that did not fit the experimental diffraction data of the unknown phase. A fixed composition USPEX run at 0 GPa, instead, resulted in a more varied combination of phases. The three most stable and promising structures that resulted from the USPEX run are shown in fig.2.12. To distinguish the different structures, original labels from USPEX run are kept.

The first structure, labelled EA182 (fig.2.12a) is a compact *Pma2* orthorhombic phase with edge-sharing GeO_6 octahedra with strontium atoms occupying interstitial positions. The second structure, labelled EA216 (fig.2.12b) presents layers of GeO_5 moieties linked through oxygen-oxygen bonding. Finally, the third structure, labelled EA548 (fig.2.12c) is a *Pmna* orthorhombic phase with corner-sharing GeO_6 octahedra. In the interest of finding if one of these structures could fit in the picture of SrGeO_3 phase transitions under high-pressure, we fully relaxed the structures using Quantum Espresso, employing PBEsol functional, in the range of pressure

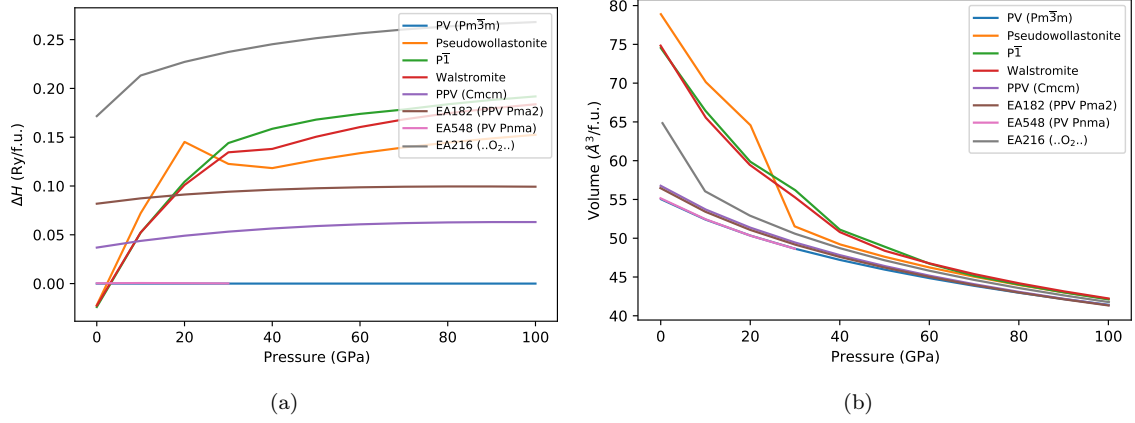


Figure 2.13: (a) Enthalpy difference for all the phases involved. Results are shown with respect to the enthalpy of the cubic $Pm\bar{3}m$ perovskite phase. (b) Volume per formula unit for all the structures involved.

between 0 GPa and 100 GPa. For completeness, we also tested the $Cmcm$ post-perovskite structure and the three phases that were experimentally synthesized (i.e. $C2/c$ pseudo-wollastonite, $P\bar{1}$ walstromite and $Pm\bar{3}m$ cubic perovskite). Results for the enthalpy and for the volume are shown in fig.2.13.

From the plot of the enthalpy (fig.2.13a) it can be noticed that all the structures resulting from the USPEX calculation are found to be less stable than the three phases experimentally synthesized. Structures presenting GeO_4 corner-sharing moieties are the most stable at ambient pressure, but quickly destabilize in favor of a more compact perovskite phase, which is found to be the favoured structure up to the highest pressure investigated. Moreover, from the plot of the volume (fig.2.13b) it can be noticed that, above the pressure of ~ 20 GPa, all structures appear to collapse, converging to the same volume as the perovskite structure. This observation suggests that less compact structures, namely pseudo-wollastonite and walstromite phases, are likely to undergo amorphization at high pressure, because they might not have the time to rearrange the coordination of germanium from GeO_4 to GeO_6 . It can also be noted that all structures resulting from the USPEX run show the same curve slope, both from the enthalpy and from the volume perspective, and USPEX failed to predict pseudo-wollastonite and walstromite even if the run was conducted at ambient pressure. From this observations it can be conclude that USPEX is more likely to return compact structures that expanded, less symmetric structures, at least in the specific case of SrGeO_3 .

Once we ruled out possible novel structures, we extracted enthalpies and structural parameters of pseudo-wollastonite, walstromite and perovskite structures to verify and compare the results experimentally obtained by collaborators. As shown in fig.2.14, the DFT calculated enthalpies for the three polymorphs clearly highlight that pseudo-wollastonite and walstromite structures are more stable at 0 GPa than

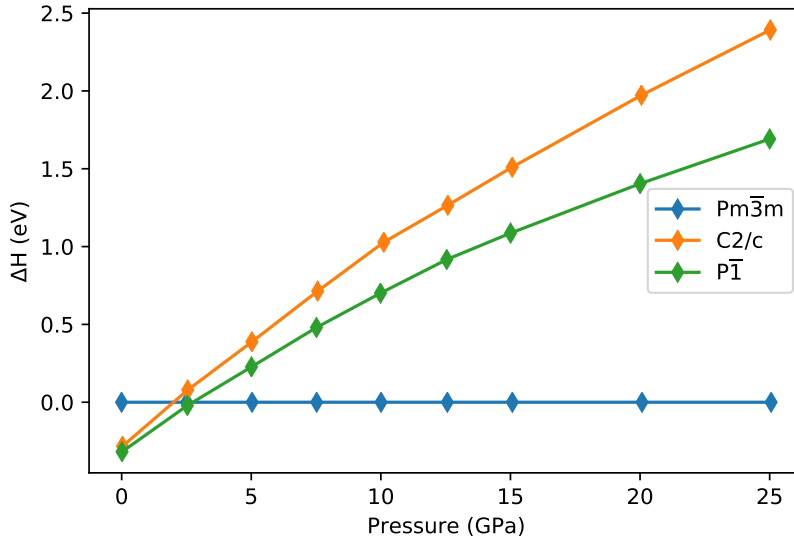


Figure 2.14: Enthalpy difference between $Pm\bar{3}m$, $C2/c$ and $P\bar{1}$ phases of $SrGeO_3$, with respect to the perovskite phase, in the pressure range between 0 GPa and 25 GPa.

the perovskite phase since the former ones lie lower in enthalpy than the latter.

The $C2/c$ and the $P\bar{1}$ structures are so close in energy at ambient pressure, though, that is really hard to tell which one is the most stable at 0 GPa. Relying on experiments performed by collaborators and pre-existing literature, we know that $SrGeO_3$ crystallizes in the pseudo-wollastonite structure at ambient pressure, but the walstromite structure can be obtained already at 1 GPa of pressure. At ~ 5 GPa, the perovskite structure already becomes the most stable and continues to be up to the highest pressure investigated. Transition from monoclinic and triclinic structures to cubic, though, requires heating to high temperatures, since the energy barrier to overcome for the transition to happen is too high. None of the experiments performed, neither from collaborators nor from literature, could observe the transition to the perovskite structure without employing heating, obtaining distorted amorphous polymorphs instead.

To compare the behavior of structural parameters of the monoclinic $C2/c$ phase under pressure, DFT structural relaxations were performed up to 50 GPa with 2.5-5 GPa steps. Calculations converged well up until ~ 25 GPa, but above that limit the pseudo-wollastonite structure was not stable anymore, undergoing a phase transition due to the severe mechanical stress applied. Since experimental data suggests that $C2/c$ phase is likely to go amorphous anyway between 10 GPa and 12 GPa, in fig.2.15 are shown the results for cell parameters and volume up to 25 GPa of pressure.

It is evident that the structure is more compressible along a and b axis than along the c axis. This is due to the topology of pseudo-wollastonite structure, since a

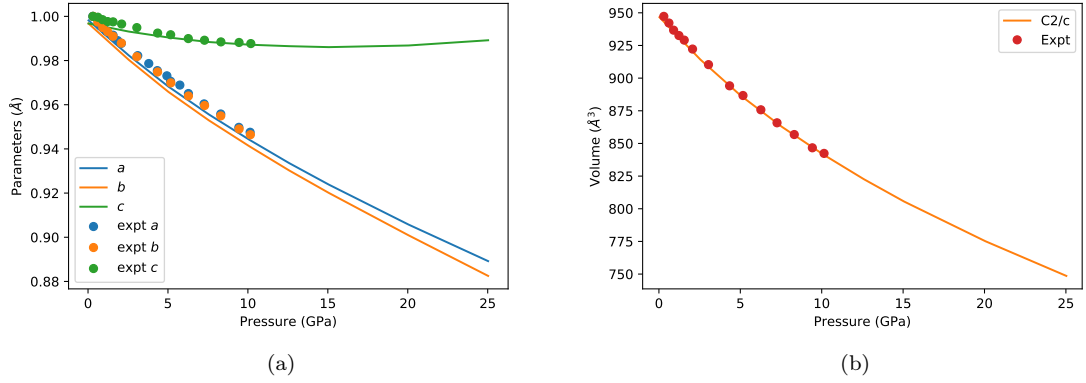


Figure 2.15: (a) Trend of the unit cell parameters and (b) trend of the volume per formula unit of pseudo-wollastonite $C2/c$ SrGeO_3 as a function of pressure. Parameters are normalized with respect to cell parameters of the experimental ambient pressure unit cell to appreciate the comparison.

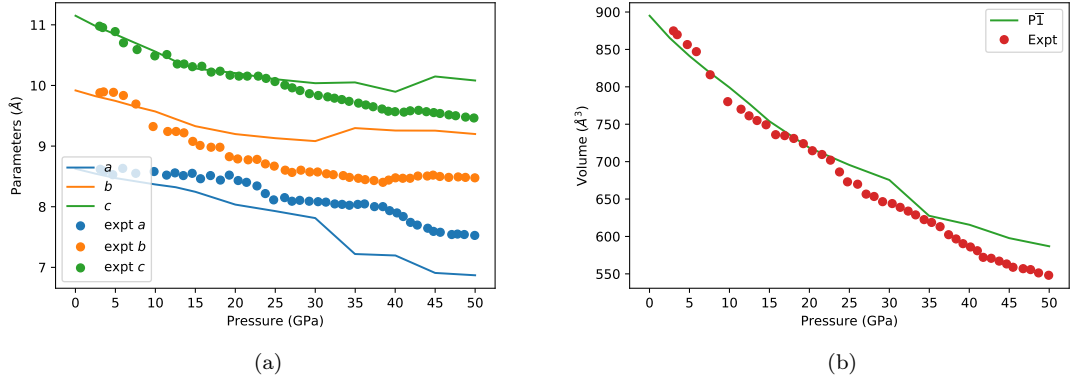


Figure 2.16: (a) Trend of the unit cell parameters and (b) trend of the volume per formula unit of walstromite $P\bar{1}$ SrGeO_3 as a function of pressure.

considerable amount of empty space is left among the ternary rings of GeO_4 moieties in between closed packs layers of strontium atoms. The anisotropic compression is therefore due to the structure being much less densely packed along the a and b axes. Moreover, the calculated trend fits really well with experimental results, both for cell parameters (fig.2.15a) and volume (fig.2.15b), enhancing that PBEsol functional works indeed really well in predicting structural properties for perovskites. A direct comparison of volumes at ambient pressure is shown in tab.2.2.

The *in-situ* PXRD patterns for the walstromite $P\bar{1}$ structure [66] show two major phase transitions, the first one occurring between 10 and 12 GPa, and the second one between 34 and 38 GPa. It is difficult to make reliable conclusions about what happens to the structure since the triclinic phase has almost no symmetry restrictions and the data quality was not good enough to refine a definite structure. DFT calculated structural parameters compared to experimental results are illustrated in fig.2.16.

The compression of the unit cell axes (fig.2.16a) shows that the least compressible axis in the structure is the c axis, which is the direction along which the three-membered rings of GeO_4 tetrahedra are sandwiched between layers of Sr atoms (fig.2.11c). This behavior under pressure is similar to that already observed for the pseudo-wollastonite phase. As occurred for the $C2/c$ phase, also the walstromite structure lacks of structural stability above 30 GPa, making the calculation at higher pressures hard to bring to convergence. Above ~ 30 GPa, in fact, the triclinic phase stability breaks and the compound undergoes a structural transition, as also predicted experimentally. The DFT data is therefore reliable for the description of the walstromite phase only up to 30 GPa of pressure. As show in fig.2.16a, theoretical data depart significantly from diffraction data between 30 and 35 GPa, that fits with the experimental observation of a structural transition in that same range of pressure. The calculated DFT data are also shown to slightly diverge from experimental data already between 10 and 15 GPa, that can be rationalized observing that the first structural transition for walstromite phase was seen already between 10 and 12 GPa, on top of diffraction quality being too low to make a precise refinement. These profound differences are less marked when comparing data for the volumes (fig.2.16b). Calculated and experimental data, in fact, look fairly smooth and fit well up until ~ 30 GPa of pressure, at which theoretical data seem to suggest a first-order phase transition, underlined by the evident volume drop, which is not present in the experimental data set. Given the poor quality of the diffraction data and the lack of symmetry restrictions associated with the triclinic structure, it is very difficult to solve the observed phase transitions for the walstromite structure. Even though DFT predicted a phase transition to the cubic perovskite phase at ~ 5 GPa (fig.2.14), PXRD diffraction pattern seem to suggest that the structure transforms into a semi-amorphous state instead, since it loses most of long-range symmetry during compression but keeps some translational symmetry in the crystal structure.

Finally, results regarding the cubic perovskite phase are shown in fig.2.17.

Collaborators run the *in-situ* high-pressure PXRD experiment up to ~ 45 GPa of pressure, and corresponding diffraction data are shown as a comparison to DFT calculated parameters and volume. In a study by Gramsch *et al.* [71] it was investigated the possibility of a high-pressure phase transition to a less symmetric structure (tetragonal or orthorhombic), like it is observed to happen for the ideal perovskite structure of SrTiO_3 at 6 GPa [72]. They observed no structural transition up to the highest investigated pressure of 55 GPa, but at the time concluded that it could be due to quality data being too poor. Nevertheless, collaborators observed no structural transition up to 45 GPa of pressure, as evident from the smoothness of the volume trend (fig.2.17b) and of the a parameter (fig.2.17a), be-

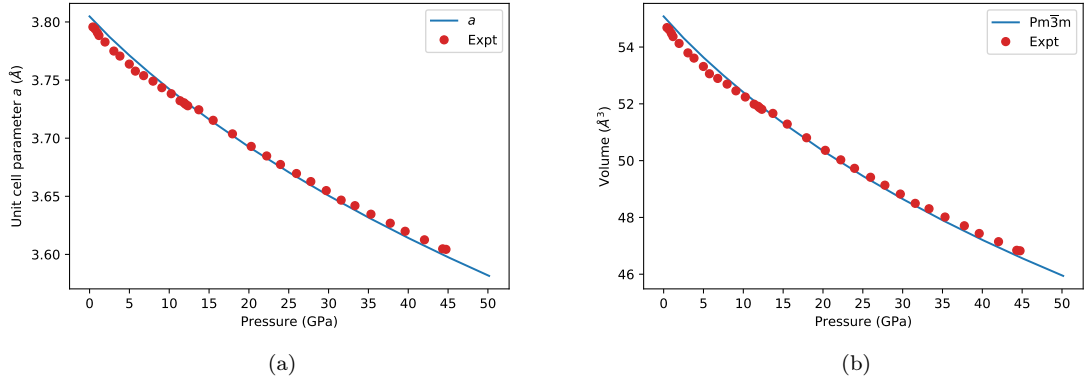


Figure 2.17: (a) Trend of the unit cell parameters and (b) trend of the volume per formula unit of ideal perovskite $Pm\bar{3}m$ SrGeO_3 as a function of pressure.

sides the small anomaly at ~ 13 GPa which is considered an experimental artifact due to a change in the compression rate. Both experiments and DFT calculations agree that the perovskite $Pm\bar{3}m$ structure of SrGeO_3 does not distort to a lower symmetry upon compression. The two sets of data are seen to fit really well up to the highest investigated pressure of 50 GPa.

	$C2/c$	$P\bar{1}$	$Pm\bar{3}m$
	0 GPa	2 GPa	0 GPa
Volume ($\text{\AA}^3$) Exp. ^a	951.5(5)	874.77(4)	54.716(17)
Volume ($\text{\AA}^3$) Cal. ^b	946.6621	865.256	55.0802

^a Ref.

^b This work, using PBEsol functional.

Table 2.2: Experimental (Exp.) and calculated (Cal.) volume data for the three phases of SrGeO_3 . Values for walstromite structure are taken at the pressure of 2 GPa since no experimental data is reliable at ambient pressure due to the severe instability of the triclinic phase.

In conclusion, PBEsol is confirmed to be a good functional for these class of crystals, since it was found to match really well high-quality experimental diffraction data, as also underlined by a close comparison of the volumes in tab.2.2. SrGeO_3 is theoretically predicted to undergo two structural phase transitions, from pseudowollastonite $C2/c$ to walstromite $P\bar{1}$ at ~ 1 GPa, and then to ideal perovskite $Pm\bar{3}m$ at ~ 5 GPa. Unfortunately, poor quality diffraction data together with the amorphization of the investigated structures made the transitions impossible to verify experimentally, even though DFT was able to reproduce diffraction data really well. Looking for new SrGeO_3 polymorphs by the means of USPEX fixed composition run, on the other hand, did not give the desired results, since the structures re-

sulting from the calculation were found to be less stable than the three phases experimentally investigated. Strangely, USPEX run at 0 GPa did not predict neither pseudo-wollastonite nor walstromite structures, returning more compact and symmetric phases instead. Nevertheless, all USPEX runs with a fixed external pressure greater than ambient pressure (i.e. 20 GPa, 30 GPa and 100 GPa) inevitably converged to a full 30-membered population of perovskite structures, confirming that the ideal perovskite is indeed the most stable phase for SrGeO_3 at high pressure.

2.3 HgPbO_3

In recent years the scientific community has been seeking for new materials for assisting the development of multifunctional devices, especially from the technological point of view, such as crystals that can simultaneously perform magnetic, electronic and optical functions. Ferroelectric lattice instability and metallic conductivity coexisting in materials such as LiOsO_3 [73] and LaNiO_3 [74] open the doors to the whole new concept of "polar metal", which is no longer hypothetical but rather multifunctional. Li *et al.* recently demonstrated [75] by the means of *first-principles* calculations that ferroelectricity can also coexist with a Weyl semimetal. They predicted this phenomenon to occur when HgPbO_3 loses its centrosymmetry as a result of a structural transition from $R\bar{3}c$ to $R3c$, and this is the reason why this compound in particular was further studied in recent years [76] and it is still of great interest. Ternary oxide HgPbO_3 was first synthesized by Sleight and Prewitt in 1973 [77]. The high-pressure synthesis required 3-6.5 GPa of pressure and a temperature of 600-1000°C. They found the resulting structure to be rhombohedral, although it was not clear whether it was centrosymmetric or not. Experimental studies conducted in more recent years [76] claim, based on single-crystal X-ray diffraction data as well as the powder synchrotron X-ray, that HgPbO_3 structure at room temperature cannot be described by either $R\bar{3}c$, $R3c$ or $R\bar{3}m$ space groups, but could be refined as $R\bar{3}m$, confirming that the compound is possibly centrosymmetric at room temperature. Moreover, since the first synthesis attempt in the early seventies, HgPbO_3 is supposed to behave alike the parent mercuric oxide HgTiO_3 , since they were found to have similar crystal structures [77]. HgTiO_3 system was studied by the means of first-principles DFT calculations by Lebedev *et al.* [78] which ran a systematic study on this compound under pressure, analyzing structural transitions and mechanical behavior of all the different phases explored. Along with collaborators from Martin Bremholm's group at Aarhus University, we tried to shed a light on the nature of HgPbO_3 compound, focusing especially on the structural properties and the phase transitions occurring when increasing pressure. We performed a systematic study starting from the work of Lebedev *et al.* on HgTiO_3 , while collaborators synthesized

the compound under pressure trying to understand better contradictory literature up to date.

From the computational point of view, we performed DFT variable-cell structure relaxations as a function of pressure up to 40 GPa using Quantum Espresso [16,17] employing PBE and PBEsol functionals, since they proved to be the ones that fit best experimental data for these type of compounds. We used double-projector, norm-conserving ONCV [45, 46] pseudopotentials including semicore states. We used a plane-wave cut-off of 45 Ry and up to 6x6x6 k-points. The symmetry of the optimized structures were determined by the means of the FINDSYM utility [47]. Experimentally, HgPbO₃ was synthesized by collaborators by a high-pressure synthesis in in-house large volume press at 6 GPa and 1000°C for 1 hour, and quenched afterwards. High pressure PXRD experiments at room temperature were performed at the Advanced Photon Source (APS) using a photon energy of 37 keV ($\lambda=0.3344$ Å) and an X-ray beam size of 3x5 μm^2 .

Results and discussion

Following all the literature existing on HgPbO₃, many different phase were tested to find which one is the most stable over the range of pressure between 0 GPa and 40 GPa. In particular, we explored $R3c$, $R\bar{3}c$, $R\bar{3}$ and $Pbnm$ polymorphs, which are the most stable structures that resulted from Lebedev *et al.* for HgTiO₃, and furthermore $R\bar{3}m$, since it is the refined structure obtained by Chen *et al.* [76] out of both single-crystal and powder-synchrotron XRD studies. Moreover, collaborators found a phase transition at ~ 7 GPa that could be refined both as cubic $Pm\bar{3}m$ or orthorombic $Pbnm$ so we also investigated the cubic structure. All the aforementioned phases were fully optimized with Quantum Espresso employing PBEsol functional with a step of 2 GPa in the range between 0 and 20 GPa and a step of 5 GPa between 25 and 40 GPa. Results for the stability are shown in fig.2.18, with the enthalpy displayed as the difference with respect to the orthorombic $Pbnm$ phase.

Enthalpy values for $R\bar{3}m$ and $Pm\bar{3}m$ phases are not shown since they are way less stable than the other four plotted. Rhombohedral $R\bar{3}m$ structure is in fact ~ 1.4 eV higher in enthalpy than orthorombic $Pbnm$, while cubic $Pm\bar{3}m$ is more than 2 eV less stable, as reported in table 2.3. Corresponding curves are therefore not plotted to appreciate the much lesser enthalpy difference between the other phases taken into examination. Calculations show that the highest contribution in the change in $H = E + PV$ is given by the PV term, and thus, as the pressure increases, the phase with a minimum volume per unit formula becomes more stable. This is the case of the $Pbnm$ phase, as shown in table 2.3, while the ilmenite $R\bar{3}$, which at ambient pressure was the lowest total energy, is characterized by the largest volume per unit

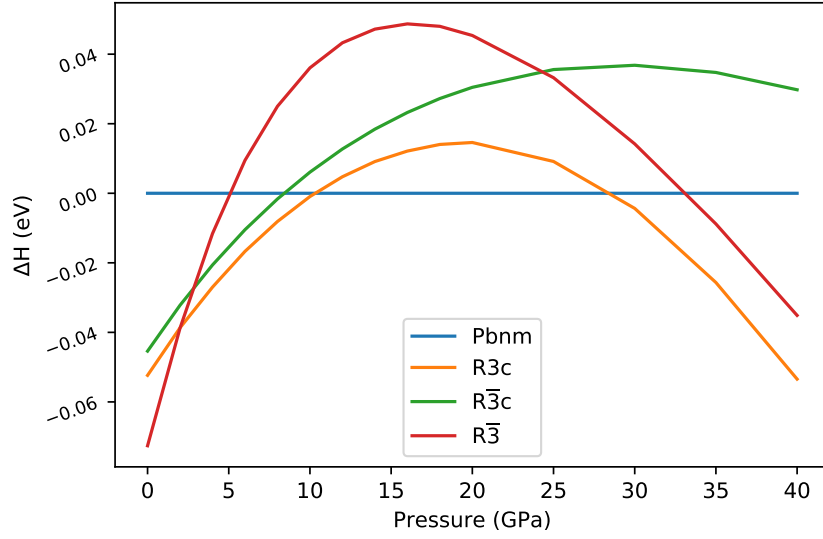


Figure 2.18: Enthalpy difference between $R\bar{3}$, $R3c$, $R\bar{3}c$ and $Pbnm$ phases of HgPbO_3 , with respect to the orthorhombic phase, in the pressure range between 0 GPa and 40 GPa.

formula among the four most stable structures. Following the enthalpy sequence arising from fig. 2.18 it can be noted that at ambient pressure HgPbO_3 has indeed an ilmenite $R\bar{3}$ crystal structure, which quickly undergoes a phase transition to a rhombohedral $R3c$ phase at ~ 2 GPa. Moreover, with increasing pressure, another phase transition occurs to an orthorhombic $Pbnm$ phase.

Space group	Energy (eV)	Volume / f.u. ($\text{\AA}^3$)
$Pm\bar{3}m$	0	73.067
$R\bar{3}m$	-0.493	78.282
$Pbnm$	-2.059	69.031
$R\bar{3}c$	-2.104	70.188
$R3c$	-2.111	70.244
$R\bar{3}$	-2.132	72.037

Table 2.3: Volume per formula unit as a function of pressure. The most stable structure is displayed in each pressure range. The dashed lines indicate the transition pressures from one phase to the other.

Following the enthalpy sequence arising from fig.2.18 it can be noted that at ambient pressure HgPbO_3 has indeed an ilmenite $R\bar{3}$ crystal structure, which quickly undergoes a phase transition to a rhombohedral $R3c$ phase at ~ 2 GPa. Moreover, with increasing pressure, another phase transition occurs to an orthorhombic $Pbnm$ phase, which is consistent with what Lebedev *et al.* observed to be the case of HgTiO_3 . Surprisingly, this orthorhombic $Pbnm$ phase is observed to loose stability as pressure increases, up until the rhombohedral $R3c$ phase returns to be the most stable, at a pressure of ~ 30 GPa.

Analysis of the volume trend in fig.2.19 shows that all phase transitions are accompanied by an abrupt change in the unit cell volume at the transition pressures (2.03%, 0.76% and 0.96%, respectively), meaning that they could all be classified as first order phase transitions.

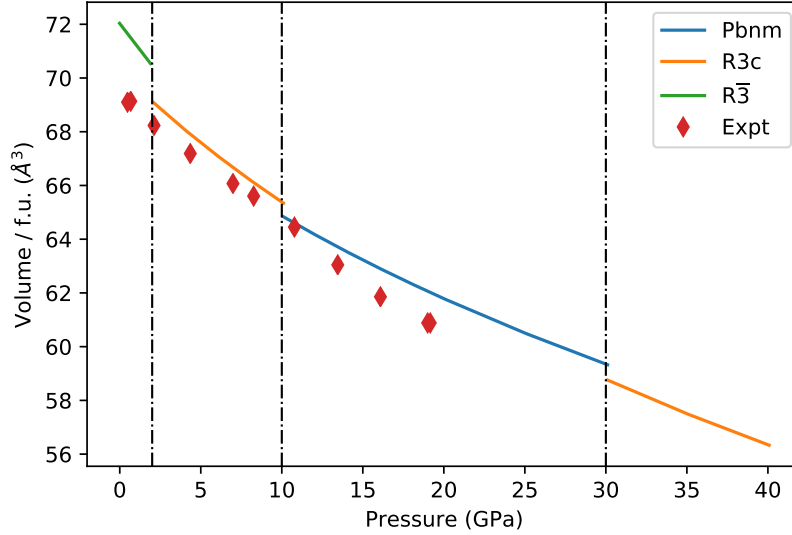


Figure 2.19: Plot of the volume per formula unit of the four phases investigated showed in the specific range of pressures where they are found to be more stable. Dashed lines represent the pressures at which a structural phase transition is predicted to occur. Symbols indicate high pressure experimental data obtained by collaborators.

Plotted together with computational results are preliminary experimental data from high-pressure XRD experiments performed by collaborators up to 20 GPa of pressure. Even though DFT seems to fit well with experimental results, the latter curve seems to show a steeper slope. New experiments are to be performed at even higher pressures to see if we can reach an even better agreement.

In conclusion, first-principles calculation within the DFT revealed that HgPbO_3 undergoes two structural transition when high-pressure is applied, following the sequence $R\bar{3} \rightarrow R3c \rightarrow Pbnm \rightarrow R3c$. The first one, from the ilmenite $R\bar{3}$ phase to a rhombohedral $R3c$ phase, occurs at pressures as low as 2 GPa, which is probably the reason why the former phase was never observed experimentally. The synthesis of the crystal structure of HgPbO_3 is in fact performed by the means of a large volume press at pressures between 4 GPa and 6 GPa, already above the first transition pressure. The second structural transition takes place at ~ 10 GPa from the rhombohedral phase to an orthorhombic $Pbnm$ phase, which is coherent with what Lebedev *et al.* observed to be the case of the parent compound HgTiO_3 . Up to 20 GPa, the highest pressure explored in [78], in fact, the two compounds behave the same way, undergoing the same first-order phase transitions. However, when the pressure is further increased, we observe a loss of stability of the $Pbnm$ phase, which ends

up falling back into a more compressed $R3c$ phase. This phenomenon was never observed before, neither for HgPbO_3 nor for HgTiO_3 , and could be due to Hg cations playing a substantial role in the structure, not acting like a mere filler anymore, while substantially changing the electronic structure and even bonding to closer oxygens atoms. Further analysis of electronic DOS will be necessary to confirm this hypothesis. Even though experimental data seems to point to $R\bar{3}m$ [76] structure to be the most favourable at ambient pressure, DFT calculations found the total energy of such phase to be much less stable than $R\bar{3}$ structure even with a higher volume per formula unit, meaning that the large difference in enthalpy between the two phases would only increase with increasing pressures. Analogously, refinement from high-pressure diffraction data from preliminary experiments performed by collaborators suggests that HgPbO_3 could transition from $R3c$ to a $Pm\bar{3}m$ phase when pressure is applied, but analysis of DFT results shows that the cubic structure is so energetically unfavoured that should not be considered a possible high-pressure phase for this compound.

Conclusion and outlook

One of the main conclusion of this chapter is that the PBESOL functional can reproduce reasonably well the equation of state and the structural properties of the three ABO_3 materials studied here, in addition to many other perovskites (see also the Appendix).

The three materials studied in this chapter show differences and analogies. SrRuO_3 is a perovskite starting from ambient pressure. On the contrary at ambient pressure SrGeO_3 prefers to form GeO_4 tetrahedra like silicate structures. From DFT calculations HgPbO_3 (like HgTiO_3) would like to crystallize in the layered $R\bar{3}$ structure. However these SrGeO_3 and HgPbO_3 structure are less compact than the corresponding perovskites (i.e. the volume per unit formula is larger than that of the perovskite). This is a large price to pay and they transform into perovskites at small pressure. The SrGeO_3 perovskite structure is so much stable with respect to the other structures that USPEX was unable to find other polymorphs at 10 and 20 GPa. Indeed USPEX found a number of defectives perovskites, stacking faults and shear crystallographic phase. Despite the apparent failure, this is success! (*uspe*x means *success* in Russian).

A very interesting observation is that both SrRuO_3 and HgPbO_3 have two phases with the same symmetry at low and high pressure. SrRuO_3 goes from orthorhombic to monoclinic and to orthorhombic again. HgPbO_3 goes from trigonal to orthorhombic to trigonal again. This phenomenon cannot be supported by a simple geometrical order parameter. The explanation must be of electronic origin. In fact

the phase transitions of SrRuO_3 are clearly induced by the collapse of the magnetic moment. The phase transitions of HgPbO_3 are more subtle: I didn't find any discontinuity in the lattice parameters and bond lengths of the Pnma and trigonal phases and the system is a metal in the whole pressure range. This requires further investigations.

While SrGeO_3 can be synthesized by conventional solid state reactions, HgPbO_3 can only be synthesized at high pressure (6 GPa) and high temperature. Unfortunately there must be a high kinetic barrier to transform the perovskite into the $\text{R}\bar{3}$. It would be interesting to find an alternative synthetic route or use different precursors in order to synthesize SrGeO_3 at ambient pressure. Similarly the formation of SrRuO_3 post-perovskite, predicted by DFT at ~ 40 GPa, was not observed in the most recent experiments, likely due to the high energy barrier.

Chapter 3

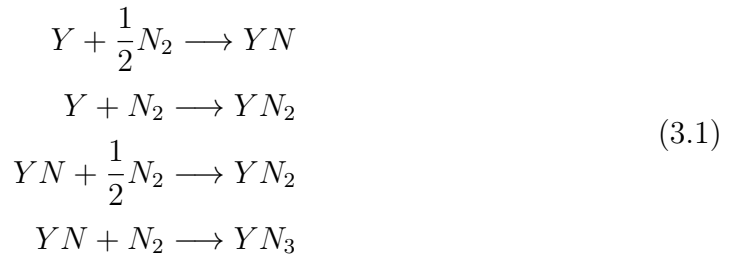
Metal Nitrides

Transition metal nitrides have attracted much interest of the scientific community for their intriguing properties and technological application, including high refractivity [79], superconductivity [80] and electrocatalytic activity [81, 82]. Most M_xN_y transition metals nitrides exhibit metallic properties and present a $N : M \leq 1$ ratio, with M being the transition metal involved. On the other hand, nitrogen-rich transition metal pernitrides, that can be synthesized at high-pressures, exhibit even more intriguing properties, if compared to the corresponding nitrides or even to parent oxides [83–85]. PtN_2 compound, for example, was found to have an extraordinarily high bulk modulus of (372 ± 5) GPa while having a molar volume oddly larger than the starting materials ($Pt + \frac{1}{2}N_2$) at pressures above 12 GPa [86].

In particular, I focused my attention on nitrides displaying a trivalent rare-earth cation since, besides the intriguing properties associated with nitrogen-rich nitrides, they bring the attention on the peculiar nature of nitrogen bonding, especially when it comes to dinitrides. The mononitrides with a trivalent rare-earth cation are reported to form simple packed structures under pressure (B1, B2, B10) [87–89] with a suggested formal oxidation state configuration $M^{3+}N^{3-}$, resulting in small to wide band-gap semiconductors [90]. On the contrary, several valence configurations have been proposed [91] to explain the nature of the nitrogen chemical bonding and its relation to the physical properties of MN_2 materials. Tetravalent cations form compounds with formal oxidation $M^{4+}(N_2)^{4-}$ that are called *pernitrides* and are characterized by a N–N bond length of ~ 1.42 Å. Divalent cations form compound with formal oxidation state $M^{2+}(N_2)^{2-}$ that are called *dinitrides* and display a significantly shorter N=N bond length of about 1.23 Å. The case of a trivalent rare-earth cation does not seem to fit in any of the two definitions, and the understanding of the nature of N $\cdots$ N bond in this case is not so intuitive. In a recent work, Wessel et al. [91] rationalized the nature of the nitrogen bonding in LaN_2 compound, suggesting a possible mechanism for the formation of this non-trivial structure. Indeed, forcing the N_2 moiety away from the -2 and -4 oxidation states, could be an

effective way towards the formation of long nitrogen chains.

I focused on YN_x system ($x = 2, 3$) and the structural properties and transition occurring at high pressures of the resulting compounds. I choose yttrium as a proxy for the lanthanide series because it has only +3 oxidation state, contrary to most transition metals. The Y-N system was experimentally studied by mixing metallic yttrium and gaseous nitrogen at the pressure of 50 GPa by the means of a diamond anvil cell and then laser-heated up to 2200 K. In this case, nitrogen was used both as a reactant and as a pressure transmitting medium. Many mechanisms were proposed for the formation of yttrium pernitrides, but an accredited one goes through the formation of YN, which then reacts with N_2 again due to the great pressure applied.



To rationalize which reactions are the most favored to occur, I first run a variable composition USPEX [19] search to seek for the most stable compositions of the Y-N system, finding that YN_3 is a very good candidate for yttrium nitrates among the less nitrogen rich ones, together with YN_2 , which is not as stable but it is interesting to investigate for all the aforementioned reasons.

I then computed a fixed composition USPEX (v9.4.4) run for both species, fully relaxing the resulting structures with Quantum Espresso [16,17]. I then computed thermodynamic and dynamical stability of these structures compared to the decomposition reactions to seek for structural transitions of interest in the range of pressures investigated, finding new phases that feature longer nitrogen chains in the crystal structure. Finally, I also studied the electronic structure and the dynamical stability of the structures I found.

3.1 Variable Composition

The variable composition USPEX run was performed employing an initial population of 40 individuals and up to 25 generations were allowed. The external pressure was set at 100 GPa, which is about double the highest pressure applied in the synthesis experiments. To reduce the computational cost, I used the local-basis code SIESTA [68], with norm-conserving pseudopotentials from the Martins-Trouiller table with SZ basis set, 50 meV energy shift and a mesh cut-off of 250 Ry. The calculation

was run using PBE exchange correlation functional [50]. Results of the variable composition run are shown in fig.3.1.

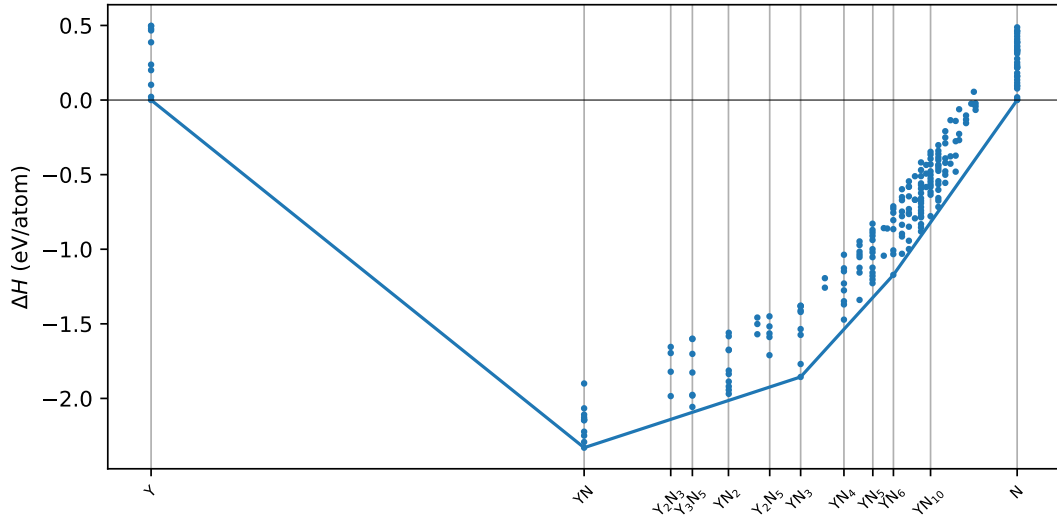


Figure 3.1: Results of the variable composition USPEX run on Y-N system. The dots represent every possible phase that resulted from USPEX prediction, while the solid line represents the convex hull. The closest a phase is to the convex hull, the more stable that composition is.

Since the enthalpy of phases with a different composition cannot be directly compared, the stability is expressed in terms of position with respect to a convex hull (the solid line in figure). If a resulting phase (the dots in figure) with a certain composition lies on the convex hull, the structure is stable and favoured. Otherwise, if the phase lies above the convex hull it means that, at the external conditions imposed in the calculation, that phase would decompose into the two closest phases that lie on the convex hull. Results of the USPEX run show that, of the many possible compositions, both YN_2 and YN_3 are among the closest to the convex hull, making them good candidates to be deepened in and verify the validity of the process illustrated in scheme 3.1.

3.2 YN_2

I focused the attention on yttrium dinitride (YN_2) and its formation under pressure mainly because it was chosen to be a good candidate as a proxy for lanthanides, for it has the advantage of being trivalent, avoiding the multiple valence character of some lanthanides ions. Moreover, from a computational point of view, yttrium displays empty highly-localized $4f$ orbitals, thus avoiding complications such as magnetism and strong correlation that arise when in presence of partially filled f orbitals.

First, I applied an ab-initio Crystal Structure Prediction method [19] to seek for the most stable YN_2 polymorphs up to 100 GPa, about double the highest pressure

that is expected to lead to the experimental synthesis of yttrium pernitrides, and then I computed the thermodynamic and dynamic stability of the obtained polymorphs down to ambient pressure and with respect to the decomposition reaction $\text{YN}_2 \rightarrow \text{YN} + \frac{1}{2}\text{N}_2$. Then I compared nitrogen bond lengths and bulk moduli to a set of existing compounds in order to rationalize the nature of chemical bonds and to understand which formal valence better describes the chemistry of these compounds. I performed a fixed composition USPEX (v9.4.4) search on four YN_2 unit formula. The initial USPEX population was composed of 40 randomly generated structures and I allowed up to 25 generations, employing the standard genetic algorithms (heredity, random generation, soft mutation, permutation and lattice mutation) [20, 21, 67]. Once again, I employed the local-basis code SIESTA [68], with norm-conserving pseudopotentials from the Martins-Trouiller table and the SZP basis set with a 50 meV energy shift. The mesh cutoff was 250 Ry. I used the PBE exchange correlation functional [50]. At the end of the USPEX run, I selected the 20 most stable structures, after pruning those I found equivalent by symmetry. These structures were further relaxed down to ambient pressure in steps of 10 GPa with the plane-wave pseudopotential code Quantum Espresso [16, 17]. I used the PBE functional, ultra-soft pseudopotentials from the GBRV library [70], wave function/-density cutoffs of 45/450 Ry and up to $6 \times 6 \times 6$ k-points. The electronic density of states was computed on a finer k-point mesh. The phonon density of states were computed using the density functional perturbation theory (DFPT) method [92] with a density cutoff of 900 Ry.

Results and discussion

Within the maximum pressure range of 100 GPa, I found three stable polymorphs among all the structures produced by USPEX (fig. 3.2). The other higher energy polymorphs usually differ from the the most stable one by the stacking of the layers, and are not reported here because they were found to be much less stable than the three investigated. I note that even though the polymorphs appear like layered structures, the inter-layer interaction is not Van der Waals (vdW) or dispersion. This would require further DFT investigation employing vdW-corrected functionals (i.e. vdW-DF, rVV10), which can describe both vdW and non-vdW bound solids. However I have observed that the energy difference between polymorphs having different stacking is larger than it would be if it was due to van der Waals interactions. Moreover, at high pressure, the distance between cations and anions is strongly reduced and the main interaction is Pauli repulsion and electrostatic attraction.

At ambient pressure, I predict that YN_2 adopts the ThC_2 (space group $C2/c$ [93]) crystal structure (Fig. 3.3a), characterized by alternating layers of Y and N_2 dimers. Upon increasing the pressure the structure undergoes a structural phase transition

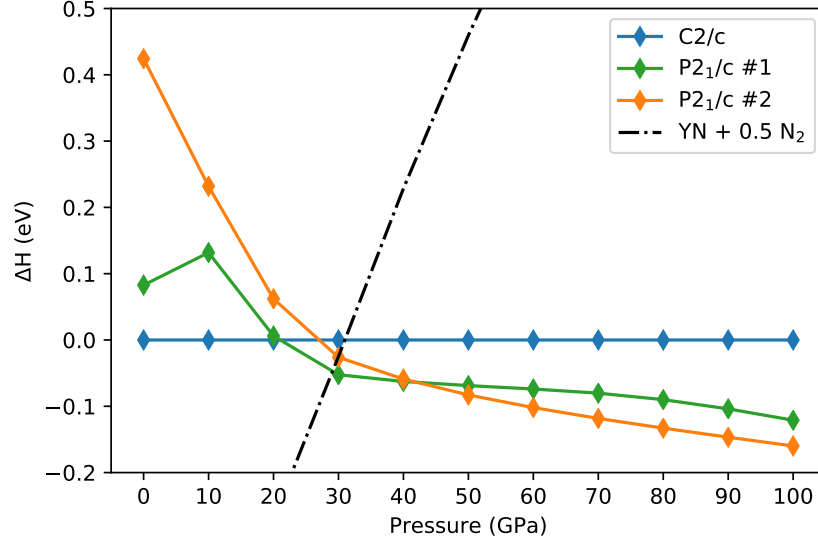


Figure 3.2: Calculated enthalpy as function of pressure, of the three most stable YN_2 polymorphs, relative to the enthalpy of the ThC_2 -type structure. The dashed line marks the enthalpy of bulk YN (B1 structure) plus $\frac{1}{2}\text{N}_2$ (ϵ - N_2 structure).

at ~ 20 GPa into a more compact $P2_1/c\#1$ structure (Fig. 3.3b), still with N_2 dimers, but with no evident alternate layers of Y and N_2 . Then, at ~ 40 GPa, the structure turns into another monoclinic phase with the same symmetry ($P2_1/c\#2$), but featuring N_4 moieties (Fig. 3.3c).

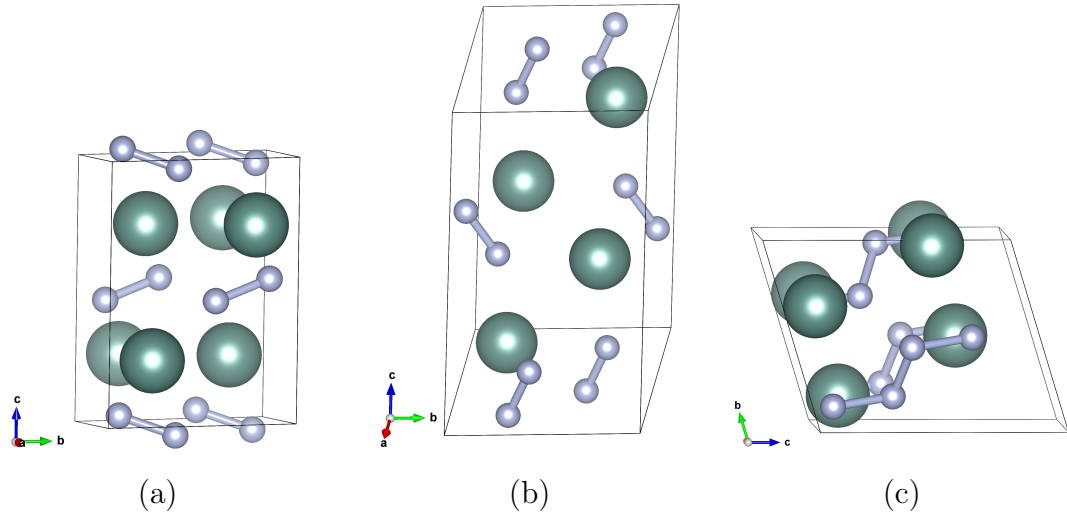


Figure 3.3: Fully optimized YN_2 structures. (a) $C2/c$ (ThC_2) structure at 0 GPa. (b) $P2_1/c\#1$ structure at 30 GPa. (c) $P2_1/c\#2$ structure at 50 GPa. The green spheres are the Y ions, the small gray spheres are the N ions.

The N_4 chains persist up to the highest investigated pressure of 100 GPa. The lattice parameters and the Wyckoff positions of the structures at 0, 30, 50 and 100 GPa are listed in Tab. 3.1.

Fig. 3.4 shows the volume of the structures investigated. The volume is observed

Phase	Pressure	Lattice	Sites	Coordinates
$C2/c$ (s.g. 15)	0 GPa	a=6.0492 Å b=4.2245 Å c=6.2247 Å $\beta = 74.64^\circ$	4e 8f	Y: 0.0000, 0.2276, 0.2500 N: 0.2260, 0.5389, 0.5389
$P2_1/c\#1$ (s.g. 14)	30 GPa	a=4.3842 Å b=4.7349 Å c=7.7441 Å $\beta = 134.50^\circ$	4e 4e 4e	Y: 0.6205, 0.7824, 0.9175 N: 0.0289, 0.9216, 0.3154 N: 0.7500, 0.2130, 0.4771
$P2_1/c\#2$ (s.g. 14)	50 GPa	a=5.6303 Å b=4.6147 Å c=4.5694 Å $\beta = 108.80^\circ$	4e 4e 4e	Y: 0.7723, 0.0131, 0.1563 N: 0.8210, 0.5166, 0.1802 N: 0.4336, 0.0820, 0.3679
$P2_1/c\#2$ (s.g. 14)	100 GPa	a=5.4306 Å b=4.4185 Å c=4.3994 Å $\beta = 106.90^\circ$	4e 4e 4e	Y: 0.7695, 0.0232, 0.1518 N: 0.8262, 0.5283, 0.1761 N: 0.4333, 0.0844, 0.3666

Table 3.1: Lattice parameters, space group and Wyckoff positions of the YN_2 structures, at selected pressures.

to decrease as a consequence of the great pressure applied. In addition, a noticeable volume drop is seen for both the first structural transition (20 GPa, 3.25%) and the second structural transition (40 GPa, 1.07%). Clearly, the volume drop of the second transition is lower and both structural transitions are probably of first-order.

In Fig. 3.2 I also report the enthalpy of bulk YN (B1 structure, which is by far the most stable one) $+\frac{1}{2}N_2$. For sake of simplicity, I took the $\epsilon-N_2$ polymorph to model solid nitrogen in the whole pressure range as it is reported to be the most stable polymorph between 13 GPa and 69 GPa. I found that in this pressure range, below 30 GPa the $P2_1/c\#1$ is not thermodynamically stable and it decomposes into YN and N_2 . To establish that the predicted structures are dynamically stable, I calculated the phonon dispersion on a q -point mesh of $3 \times 3 \times 3$. In Fig. 3.5 I report just the phonon density of states, rather than the phonon dispersion since all structures are monoclinic. From Fig. 3.5 I found that the ThC_2 -structure is dynamically unstable at ambient pressure. Inspection of the unstable phonon modes, reveals that the stable structure would display a long wavelength modulation of the relative distance between the Y and N_2 sublattices. However, the $P2_1/c\#1$ structure is thermodynamically unstable against the decomposition, as shown previously. Therefore, this lattice modulation, akin to a charge density wave instability would be extremely difficult to observe in experiments. On the contrary, the other two structures are dynamically stable since all the phonon frequencies are real and positive. An interesting feature is that the nitrogen contributes mainly to the high energy optical modes at frequencies 1000 cm^{-1} and above. In the low energy region, there

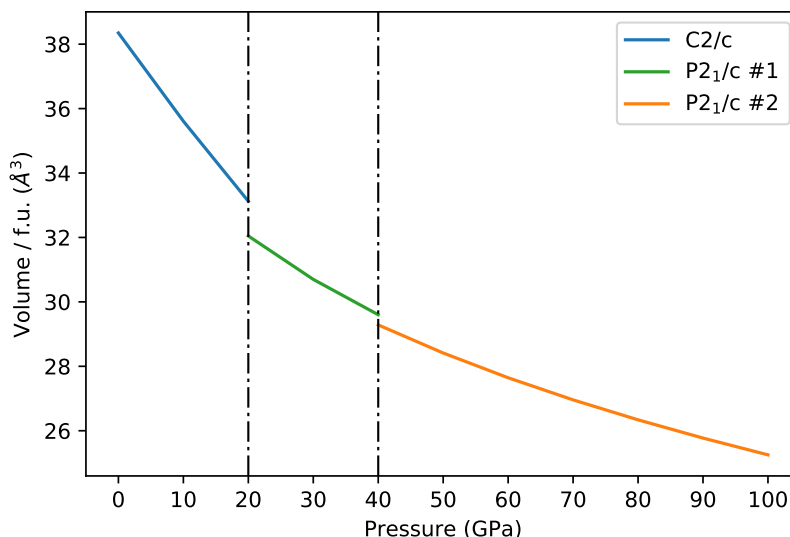
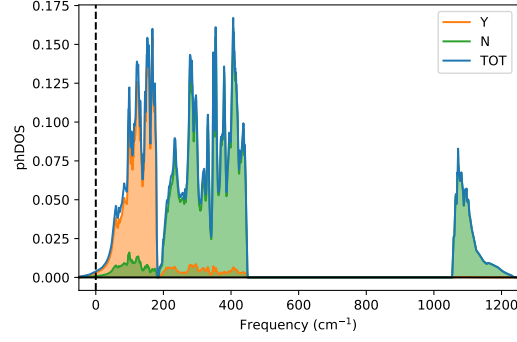


Figure 3.4: Calculated volume per formula unit as function of pressure. The vertical lines indicate the transition pressures.

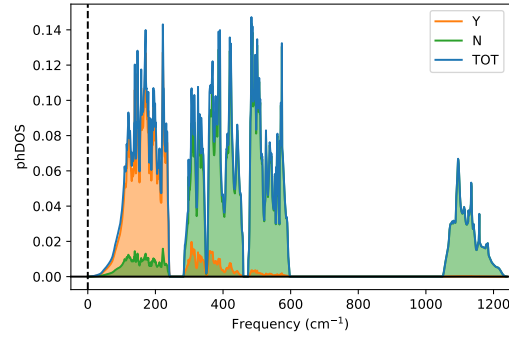
is still a noticeable separation between Y and N vibrations. Indeed the heavy Y ion contributes mainly to the lowest energy phonon (below 200 cm^{-1}), whereas the intermediate energy region is largely characterized by vibrational modes involving nitrogen only.

In Fig. 3.6 I report the projected electronic density of states of selected structures, with respect to the Fermi level. The $C2/c$ (0 GPa) and $P2_1/c\#1$ (30 GPa) structures are metallic and their valence band has a large N $2p$ character. The Y states instead contribute mainly to the empty states. From the electronic structure point of view the formal valence of these polymorphs is closer to $Y^{+2}(N_2)^{2-}$ (fig.3.7a) rather than to $Y^{+4}(N_2)^{4-}$ (fig.3.7b), i.e. closer to the *dinitride* structure. The presence of a unique $N\cdots N$ bond length indicates that bond disproportionation (i.e. $(Y^{3+})_2(N_2)^{2-}(N_2)^{4-}$) does not takes place. This is conceivable since the electronic screening of the metallic state tends to delocalize the charge carriers and suppresses the ionic character. The situation changes upon increasing the pressure above 50 GPa, following the formation of the N_4 moieties. The electronic density of states is semimetallic, with a low density of states up to $\sim 2\text{ eV}$ above the Fermi level. This can be explained by the formal valence $(Y^{3+})_2(N_4)^{6-}$, in which the N_4 moiety has 6 extra electrons (i.e. 26 valence electrons). The 26 valence electrons (13 electron pairs) could be naively arranged as 3 single bonds and 10 lone pairs as shown by the Lewis structure with single N–N bonds as shown in Fig. 3.7c. Moreover, the $(N_4)^{6-}$ moiety fulfills the $6n + 2$ Wade rule in n -member linear chains. However the Lewis structure does not reflect the actual charge distribution and chemical bonding. In fact the $(N_4)^{6-}$ anion is planar, indicating a partial multi-center π bonding. In

(a)



(b)



(c)

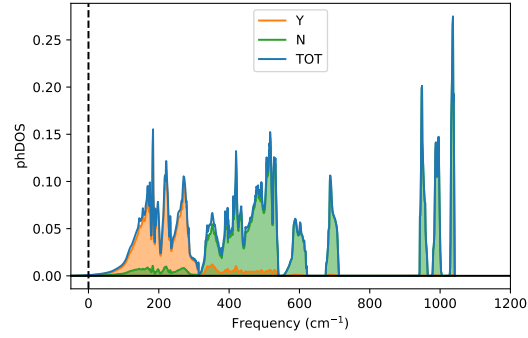


Figure 3.5: Calculated phonon density of states of the three structures. (a) $C2/c$ phase at 0 GPa; (b) $P2_1/c\#1$ phase at 30 GPa; (c) $P2_1/c\#2$ phase at 50 GPa. The Y and N contributions to the phonon density of states are indicated by the orange and green shaded areas, respectively.

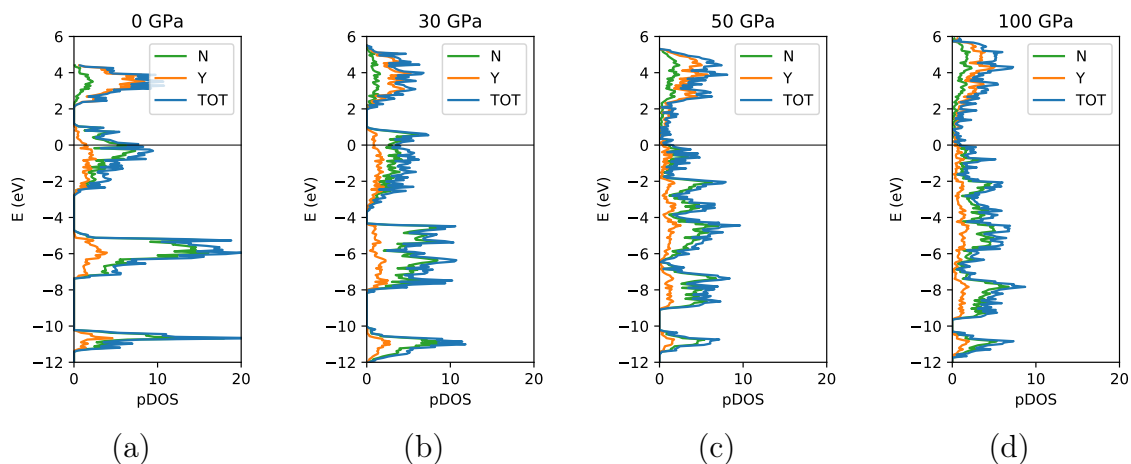


Figure 3.6: Projected electronic density of states of selected polymorphs and pressure. (a) $C2/c$ at 0 GPa. (b) $P2_1/c\#1$ at 30 GPa. (c) and (d) $P2_1/c\#2$ at 50 and 100 GPa. The Fermi level is denoted by the black horizontal line.

principle this structure would possess a finite band gap, but the increased overlap due to the external pressure tends to close the gap. Notice also the increase of the band width of the occupied states and the larger hybridization between Y and N states. Whereas the low pressure phases can be described as intermetallic, the high pressure phase could be described more as a salt-like, Zintl phase. This hypothesis could be confirmed or disproved by advanced chemical bond analysis [94, 95]. Interestingly, a $(N_4)^{6-}$ anion in the planar *cis* conformation is found in the USPEX search but its enthalpy is larger than that of the *trans* conformation.

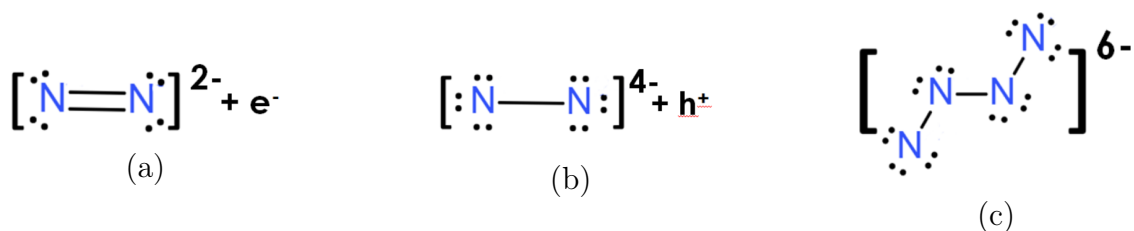


Figure 3.7: The simplest Lewis structures that can be proposed for the $N\cdots N$ moieties investigated. The easiest to rationalize is (c), the $(N_4)^{6-}$ moiety with only σ bonds found in the $P2_1/c\#2$ structure, while (a) and (b) represents the two possible electronic distributions for the $N\cdots N$ dimers found in the ThC_2 -like and in the $P2_1/c\#1$ phases.

It is interesting to study the behavior of $N\cdots N$ bond length as a function of pressure and compare to other di-nitrides. The ThC_2 -like structure at ambient pressure has a $N\cdots N$ bond length of 1.33 Å, which is intermediate between a single and a double bond (see Tab. 3.2). Indeed, when the cation is divalent (like in the dinitrides as BaN_2), N_2 is better described in the form $(N=N)^{2-}$, whereas if the cation valence is higher (like in the pernitrides as PtN_2), the N_2 moiety is best described as $(N-N)^{4-}$. In this particular case, however, the situation is more challenging to

Structure	N–N bond length / Å	Ref.
BaN ₂	1.23	Ref. [91]
PtN ₂	1.41	Ref. [91]
OsN ₂	1.43	Ref. [96]
IrN ₂	1.30	Ref. [97]
LaN ₂	1.30	Ref. [91]
YN ₂ , <i>C2/c</i> , 0 GPa	1.33	this work
YN ₂ , <i>P2₁/c</i> #1, 30 GPa	1.32	present work
YN ₂ , <i>P2₁/c</i> #2, 50 GPa	1.42, 1.44	present work
YN ₂ , <i>P2₁/c</i> #2, 50 GPa	1.39, 1.40	present work

Table 3.2: Nitrogen-nitrogen bond lengths in various pernitrides and dinitrides, reported from literature as well as calculated in the present work for YN₂, as a function of pressure.

rationalize, since there is no evidence of the yttrium cation being either divalent or tetravalent: it is always reported as trivalent. This consideration brings us to consider two different options to rationalize the valence of these compounds: the first possibility is to have static fluctuations in the N₂ bond lengths, where some N···N longer bonds are longer than others averaging out to around 1.33 Å; the second possibility is to have an electron forming a partially filled band. The analysis of the DOS in Fig. 3.6 seems to suggest the second scenario. This has been already proposed to be the case of LaN₂ [91]. After the first structural transition, the situation remains similar, with a N–N bond length of 1.32 Å.

The situation changes dramatically after the second transition, at 40 GPa, with the formation of N₄ chains. The bond lengths, in fact, increase significantly with respect to lower pressures: the central bond is 1.42 Å and the two others are 1.44 Å. Indeed, the (N₄)^{6−} moiety can be described by a single Lewis formula with all single N–N bonds (fig.3.7c). As a consequence, the system is a closed shell and the solid is semimetallic. At the very high pressure of 100 GPa the N-N bond lengths in N₄ moiety become 1.39 and 1.40 Å.

Wessel and collaborators [91] observed that mechanical hardness and bulk modulus are larger in pernitrides than in dinitrides, due to the different character and filling of N₂ orbitals. I calculated the bulk modulus of the three YN₂ polymorphs by fitting to the Birch-Murnaghan 3rd order equation of state [98]. The results are reported in Tab. 3.3, and compared to other dinitrides and pernitrides from literature. Indeed, the low pressure YN₂ phases display a bulk modulus larger than the dinitride BaN₂ and similar to that of LaN₂. Interestingly, upon the formation of N₄ chains, the bulk modulus increases by ~60 GPa.

Regarding superconductivity one could estimate T_c from the BCS formula $T_c = 1.134 T_D \exp [1/(N_0 g)]$ which links the superconducting temperature to the Debye temperature T_D (which is high in hard materials), to the density of states at the Fermi level N_0 and to the average electron phonon coupling g . These dinitrides

Structure	Bulk Modulus (GPa)	Ref.
BaN ₂	46	Ref. [99]
SrN ₂	65	Ref. [99]
PtN ₂	256	Ref. [99]
OsN ₂	358	Ref. [97]
IrN ₂	428	Ref. [100]
LaN ₂	86	Ref. [99]
YN ₂ , <i>C2/c</i>	117	present work
YN ₂ , P2 ₁ /c#1	118	present work
YN ₂ , P2 ₁ /c#2	174	present work

Table 3.3: Bulk moduli in various pernitrides and dinitrides, reported from literature as well as calculated in the present work for YN₂ with EosFit [101] (Birch-Murnaghan, 3rd Order).

are not super-hard materials compared to transition metal mono-nitrides [102,103]. There is no particular reason to expect a large electron phonon coupling and the density of states at the Fermi level is not very large. As a consequence, I expect that YN₂ T_c to be smaller than that of the mono-nitrides and much smaller than the superconducting hydrides. [104]

My methods can be applied to study the formation and stability of the series of LnN₂ compounds (Ln=La..Lu). I expect that as the size of the cation is reduced the phase transition will occur at higher pressure and new compact structures might be found. Lanthanide cations with multiple oxidation states (i.e. Ce, Pr, Sm, Eu, Tb, Tm, Yb) will represent a challenge for DFT and one must employ advanced techniques like dynamical mean field theory (DMFT). [105]

3.3 YN₃

Another appealing structure that arose from the USPEX composition search is yttrium trinitride which is on the convex hull at 100 GPa. This trinitride is interesting because it is ~ 2 eV/atom stable with respect to phase separation. The other nitrogen-rich compound on the convex hull (i.e. YN₆) are less stable and are expected to be more similar to pure solid nitrogen.

Results and discussion

A first fixed composition USPEX run enhanced the presence of several polymorphs of yttrium trinitride, most of which show long - if not infinite - nitrogen chains stable at very high pressures. When relaxed down to ambient pressure, though, it can be observed a general loss of stability in favor of structures that lack of long chains, but present N-N dimers equally distributed in the crystal. In figure 3.8 is showed the

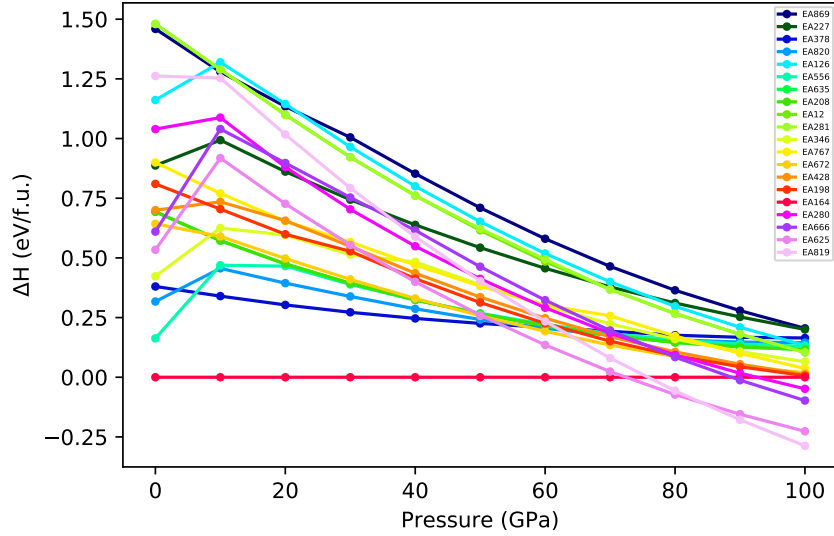


Figure 3.8: Relative enthalpy of the twenty most stable structures resulting from the USPEX fixed composition search.

enthalpy of the twenty most stable structures that arose from the fixed composition USPEX search, relative to the one labelled EA164 which was found to be the most stable at ambient pressure.

It can be noticed that at pressures higher than 60 GPa most structures investigated tend to be closer in enthalpy, then significantly diverging from the most stable one when the pressure is lowered down to ambient pressure. Moreover, at pressures higher than ~ 70 GPa, EA164 is not the most stable structure anymore, undergoing a phase transition first to EA625 and afterwards to EA819. A closer analysis of the three most stable structures gives a better picture of the structural transitions that the compound undergoes. A plot of the enthalpy including only EA164, EA625 and EA819 structures better shows the pressures at which structural transitions occur, as show in figure 3.9.

At high pressures, the structure which displays the lower enthalpy is a monoclinic $C2/c$ structure that features infinite nitrogen chains, as shown in figures 3.10 and 3.11. The infinite chain could be an artefact of the number of unit formulas used in the calculation, but we can be fairly positive that the chains would not be shorter than twelve atoms in any case.

When pressure is released, though, the infinite nitrogen chain tends to break, forming shorter chains twelve atoms long. The resulting phase is a triclinic $P1$ phase shown in figure 3.12.

The lack of symmetry is due to the different orientations of the chain, that gives the impression that the longer chain of the monoclinic structure found at 80 GPa randomly broke when pressure was lowered. This intermediate phase survives a range of lesse than 10 GPa before breaking apart at ~ 72 GPa, letting then the for-

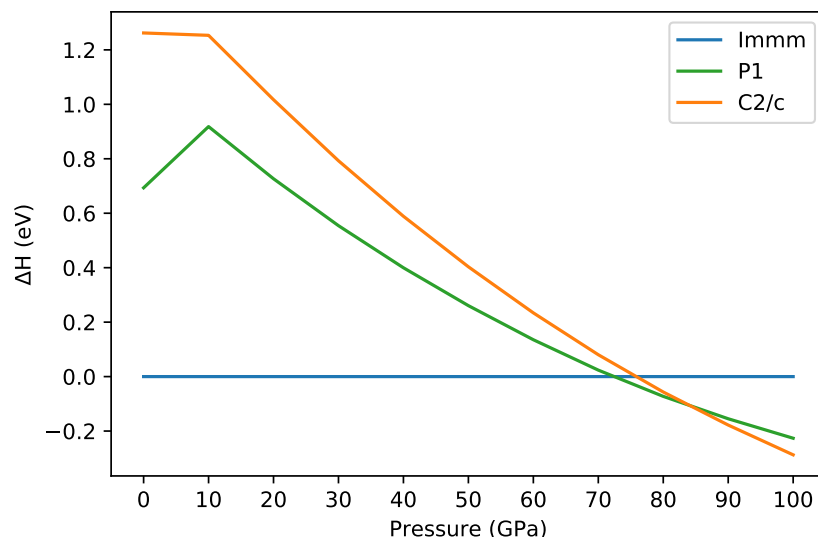


Figure 3.9: Relative enthalpy of the three most stable structures that arose from the USPEX fixed-composition run, with respect to *Immm* phase.

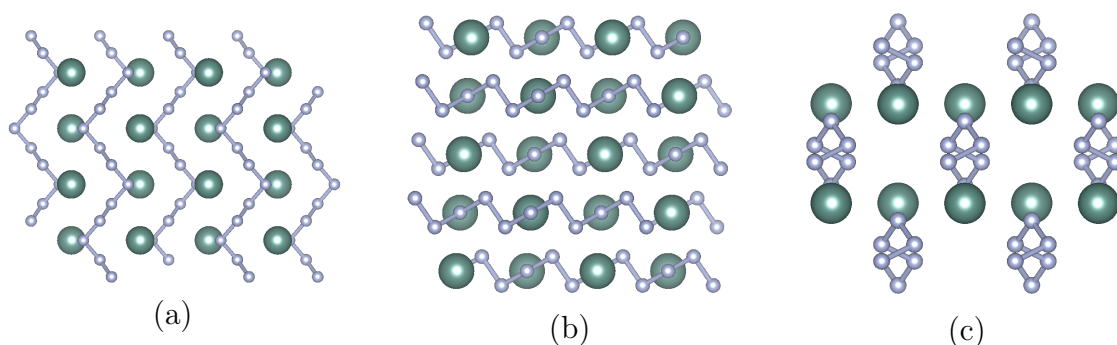


Figure 3.10: Fully optimized *C2/c* structure shown along the three different axes: (a) along the *a*-axis, (b) along the *b*-axis and (c) along the *c*-axis.

mation of an orthorhombic *Immm* structure in which nitrogen is arranged in layers of N-N dimers. This phase persists down ambient pressure, being markedly energetically favoured than any other. This structure, labelled EA164 from the USPEX search, is shown in figure 3.13.

Interestingly, I do not observe a gradual shortening of the chains: the twelve nitrogen chain in the triclinic structure abruptly breaks into dimers in a first order transition made evident from the great volume difference existing with the orthorhombic parent (figure 3.14). There is no evidence of structures showing chains of intermediate length and this is probably due to the valence. Since yttrium is always trivalent, in fact, the structure fits well in the formulation $\text{Y}_2(\text{N}_2)_3$, which displays Y^{3+} cations and N_2^{2-} dimers. Longer chains are thus unstable and tend to break apart as soon as pressure is released.

It is interesting to study the trend in the $\text{N} \cdots \text{N}$ bond lengths, since it varies significantly with increasing pressure, upon the formation of longer chains. At ambient

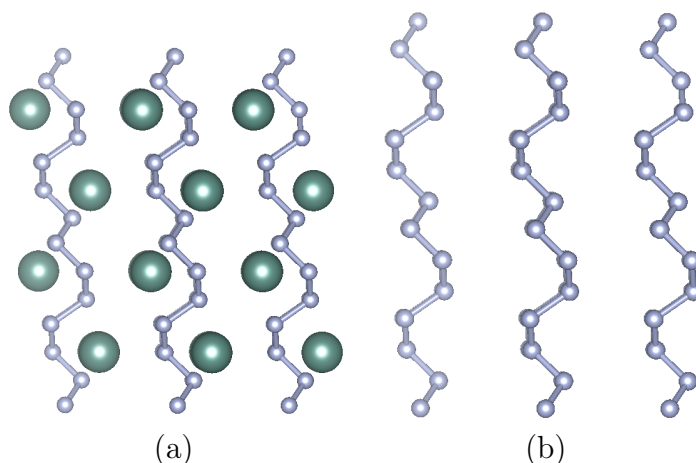


Figure 3.11: A better perspective on the infinite nitrogen chain that the $C2/c$ structure displays (a) including yttrium atoms and (b) without yttrium atoms.

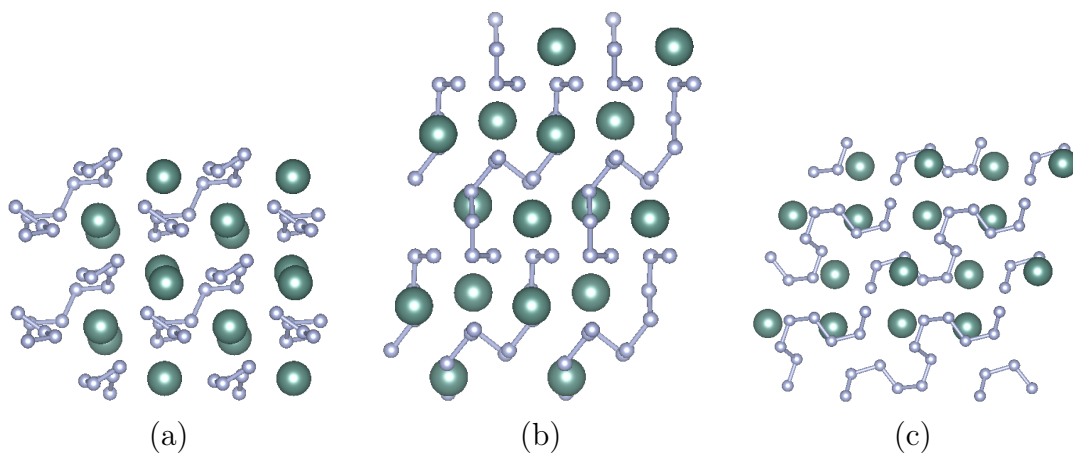


Figure 3.12: Fully optimized $P1$ structure shown along the three different axes: (a) along the a -axis, (b) along the b -axis and (c) along the c -axis.

pressure, in fact, the compound behaves as a dinitride, showing N_2 dimers that can be rationalized as double bonded. Dimers in the $Immm$ structure show $N \cdots N$ bond length that varies between $1.196(9) \text{ \AA}$ and $1.269(4) \text{ \AA}$ depending on the position of the dimer in the crystal. These $N \cdots N$ bond lengths are indeed comparable with that of a $N=N$ double bond, as expected from the valence of the species involved $Y_2^{3+}(N_2^{2-})_3$.

Upon the formation of 12 nitrogen chains, the $N \cdots N$ bond lengths increases up to values closer to a single $N-N$ bond, oscillating between $\sim 1.53 \text{ \AA}$ and $\sim 1.35 \text{ \AA}$ along the chain. It is interesting to notice that there seems to be a specific trend in the bond lengths, symmetric with respect to the central bond - the longest one, $1.561(4) \text{ \AA}$. This trend is shown in figure 3.15.

When the transition to monoclinic $C2/c$ occur, upon the formation of infinite chains, $N \cdots N$ bond lengths remain in the range between $1.45 \text{ \AA}$ and $1.53 \text{ \AA}$, still compatible with single bonded nitrogen atoms. In this case, a different trend in the

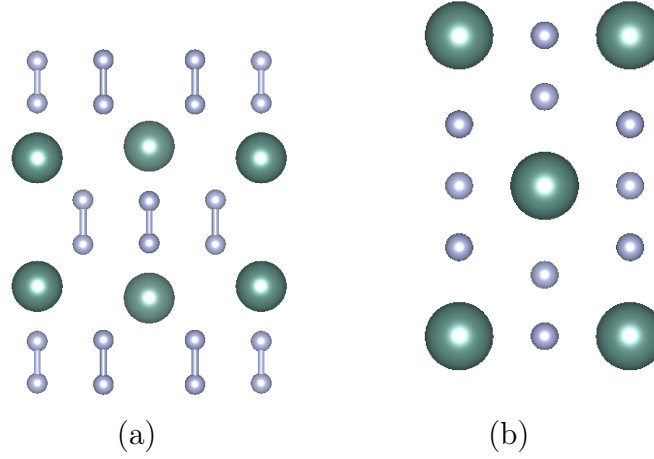


Figure 3.13: Fully optimized *Immm* structure shown along two different axes: (a) along the *a*-axis, (b) along the *c*-axis.

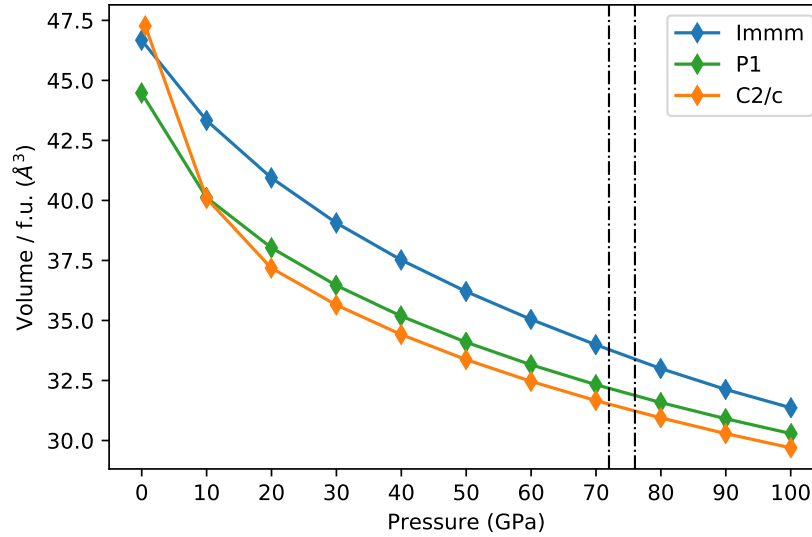


Figure 3.14: Volume as a function of pressure. The dotted lines indicate the pressures at which structural transitions occur.

bond lengths is observed, as shown in figure 3.16.

In this case, the trend is much more regular, showing two adjacent bond long exactly the same (1.455(6) Å) followed by a longer one (1.530(7) Å). This scheme is repeated all along the infinite chain. These bond length alternations (BLA) are not simply the well known Peierls distortions for the following reasons: (i) the BLA is quite large even without employing hybrid functionals (differently from what is shown in Ref. [106] for an infinite nitrogen zig-zag chain); (ii) both the *s* and *p* orbitals of nitrogen are involved with different degree of hybridization; (iii) moreover the classical picture of single, double and triple bonds is probably just a simplification, and more complex reality emerges as shown in Ref. [95, 107] for finite size nitrogen chains.

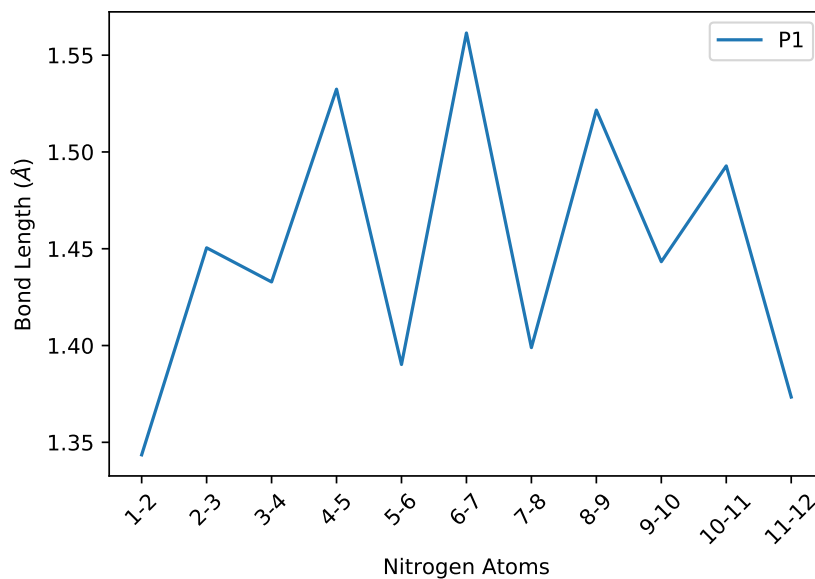


Figure 3.15: Trend of the N...N bond length along the N₁₂ chain in the triclinic *P1* structure. Labels refer to the position of the nitrogen atom in the chain.

Summary and outlook

I found by crystal structure prediction the most stable structures of YN₂ up to 100 GPa. At low pressure, the system adopts the ThC₂ structure like LaN₂. Unfortunately this structure is thermodynamically unstable with respect to the decomposition into YN and solid N₂ and dynamically unstable at ambient pressure. This structure is characterized by N₂ dimers and, upon increasing pressure, it transforms into a monoclinic polymorph (*P2₁/c*#1) with no evident N₂ layers. By comparing the nitrogen bond length and the bulk modulus, I arrive at the conclusion that both *C2/c* and *P2₁/c*#1 predicted polymorphs can be categorized as *dinitrides* and the N₂ chemical bond is closer to a double N=N bond. Finally, above 40 GPa, N₄ moieties are formed and the structure is semimetallic. I verified the dynamical stability of the two high pressure structures by computing the phonon density of states. Experimentally there is a clear evidence of a novel crystalline phase of YN₂ at 50 GPa and the refinement of PXRD data seem to agree with the *P2₁/c*#1 structure I found. I hope to be soon able to report on this in a joint paper with the experimental collaborators in Aarhus.

My work is the first step towards studying the formation and stability of LnN₂ compounds (Ln=La..Lu). As the first approximation, one in principle one can substitute Y with every other lanthanide ion in all the structure generated by USPEX and compute the enthalpies in the whole pressure range. This will provide a tentative phase diagram for each LnN₂ compound that will provide useful indication for future high pressure experiments. As shown in Ref. [89] for the mono-nitrides, the B1→B2/B10 transition pressure increases along the lanthanide series. In other

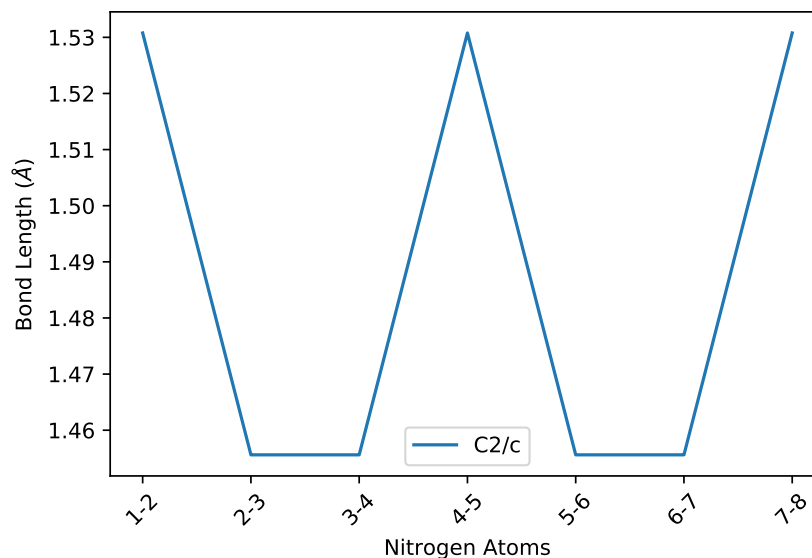


Figure 3.16: Trend of the N...N bond length along the infinite chain in the monoclinic *C2/c* structure. Labels refer to the position of the nitrogen atom in the chain.

words the late lanthanide nitrides might undergo structural phase transitions at pressure larger than 100 GPa and would be of scarce interest as energy materials. Of course USPEX must be re-run for the lanthanide ions which can have a +2 or +4 formal valence in addition to the +3.

It is interesting to observe that “unhappy” formal valence of N_2 in YN_2 lead to the formation of N_4 chains stable at intermediate pressure. On the contrary the “happy” YN_3 compound form infinite nitrogen chains at 100 GPa that will break easily by decreasing the pressure. This show how chemistry and pressure conspire against each other!

Final Considerations

I tackled many different projects during my PhD, especially focusing on the mechanical properties and the structural transition of perovskite crystals and the interesting features belonging to transition metals nitrides. I employed the advanced computational methods featured in Quantum Espresso and USPEX algorithms to both confirm experimental results obtained by collaborators and suggest new possibilities.

The three perovskite-like structures investigated in chapter 2 have very different properties and structures, both at ambient pressure and at very high pressures, but some analogies can be found in the predicted behavior when pressure is applied. Perovskite and perovskite-like structures, in fact, tend to undergo structural transitions to more compact phases, usually metallic. Even if comparing the results from different materials could seem worthless since they display very different features, analysis of the overall trend of calculation outputs helped to define the best functional to be used for the study of this kind of crystals. PBEsol functional, in fact, was found to be the one which best reproduced the equation of state and the structural properties of the investigated compounds, if compared to high-quality PXRD data from high-pressure experiments.

Investigation of yttrium nitrides in chapter 3, instead, featured an extensive use of crystal structure prediction algorithms, USPEX in particular, to predict structures and properties of nitrides little studied before. Even though the initial purpose was to explore nitrides of the lanthanides series, compounds of yttrium were found to be even more interesting than lanthanides parents, since they feature the formation of longer nitrogen chains. Moreover, YN_2 is characterized by the presence of nitrogen dimers in the structure of ambiguous bonding nature, since, given the fixed valence of yttrium cation, it is hard to define whether nitrogen atoms are single or double bonded. It will be interesting to deepen in this peculiar feature also by other means, such as applying QTAIM techniques, to get even clearer results.

This PhD thesis summarizes the projects that are already concluded. Three of them have been already published [48,66,108] and others are in preparation or to be submitted. During this three years, however, I also worked on many other different projects, most of which are briefly illustrated in this thesis appendixes. This "works

in progress" are to be concluded in the following months, in the strong hope that the global sanitary emergency that world faced during the last year will soon be a problem belonging to the past, so that nothing will slow down new scientific discoveries anymore.

Appendix A

Other results and side projects

In this appendix I report on few side projects that I did during my PhD, most of them in collaboration with the experimentalists in Aarhus. I also report here extra calculations and data as supporting information for the thesis chapters.

A.1 Which XC functional for perovskites and post-perovskites?

In Fig. A.1, A.2, A.3 I report the EOS and lattice parameters of several perovskites that were studied experimentally before I started my PhD, calculated with LDA, PBE and PBESOL functionals.

As expected the PBESOL results are always bracketed by LDA (which underestimates the volume) and PBE (which overestimates it). At low pressure (below 20-30 GPa) the agreement of PBESOL with experiments is very good. Note that in these perovskites either the a or c lattice parameters are less “compressible” with respect to the others. In the case of SrIrO_3 the values of a and c cross around 25 GPa and the precise indexing of PXRD reflections might become problematic. The experimental data reported for SrOsO_3 show a different behaviour among different experimental runs and are currently being re-analyzed. SrOsO_3 appears to undergo a phase transition at 40 GPa, probably towards a monoclinic phase. This is work in progress.

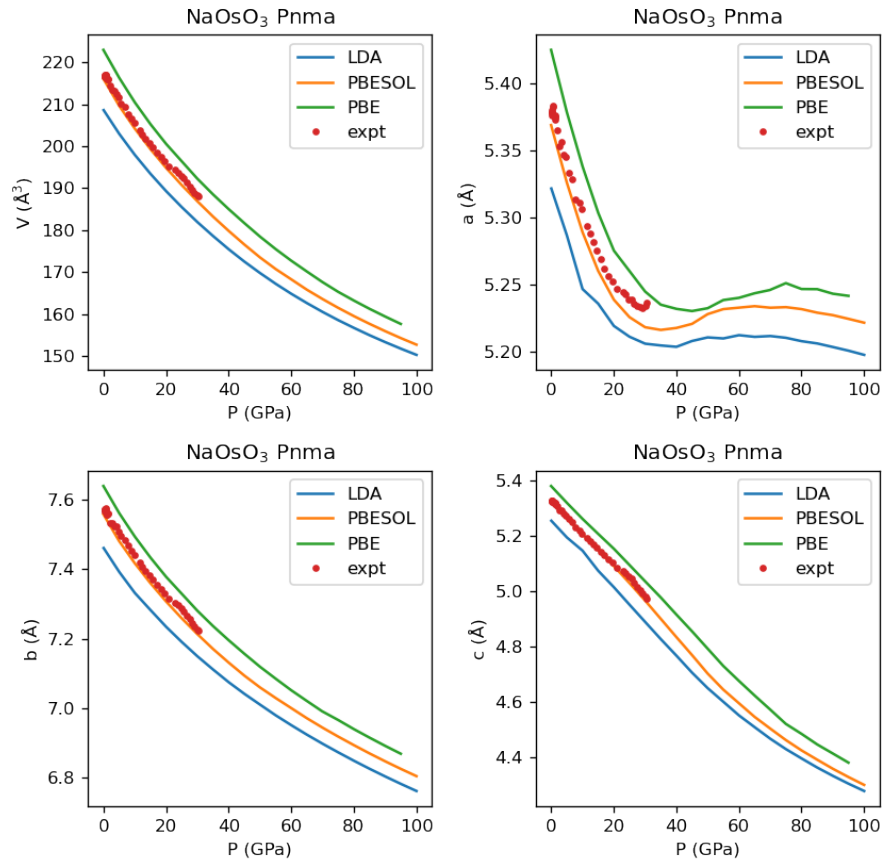


Figure A.1: EOS and lattice parameters of NaOsO₃ in the Pnma structure.

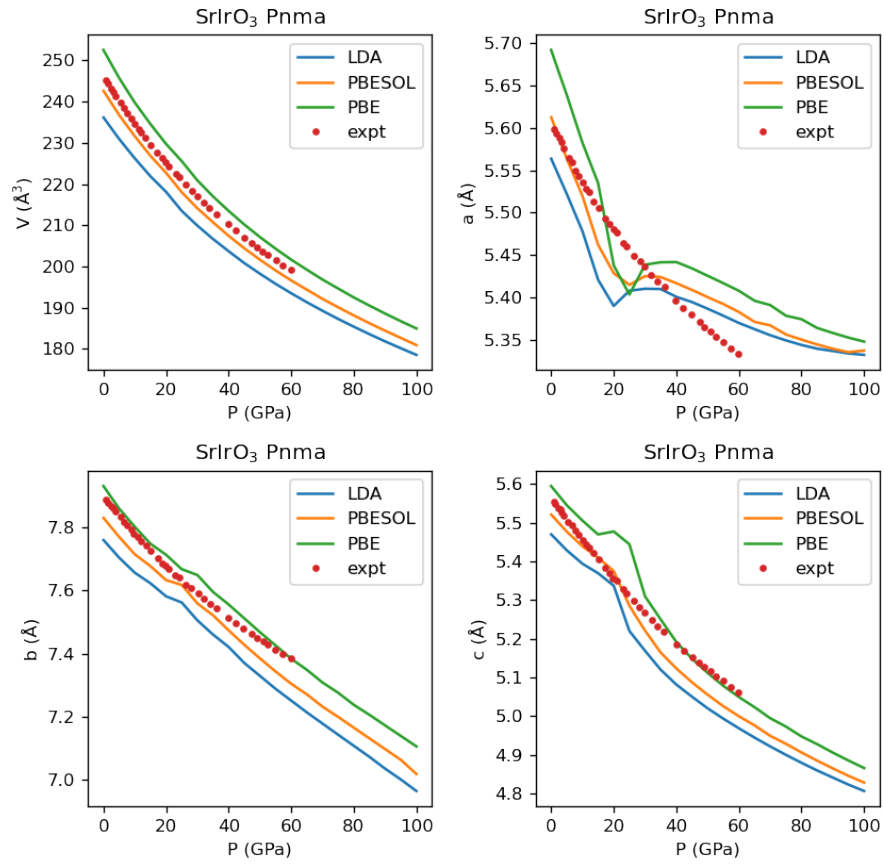


Figure A.2: EOS and lattice parameters of SrIrO₃ in the Pnma structure.

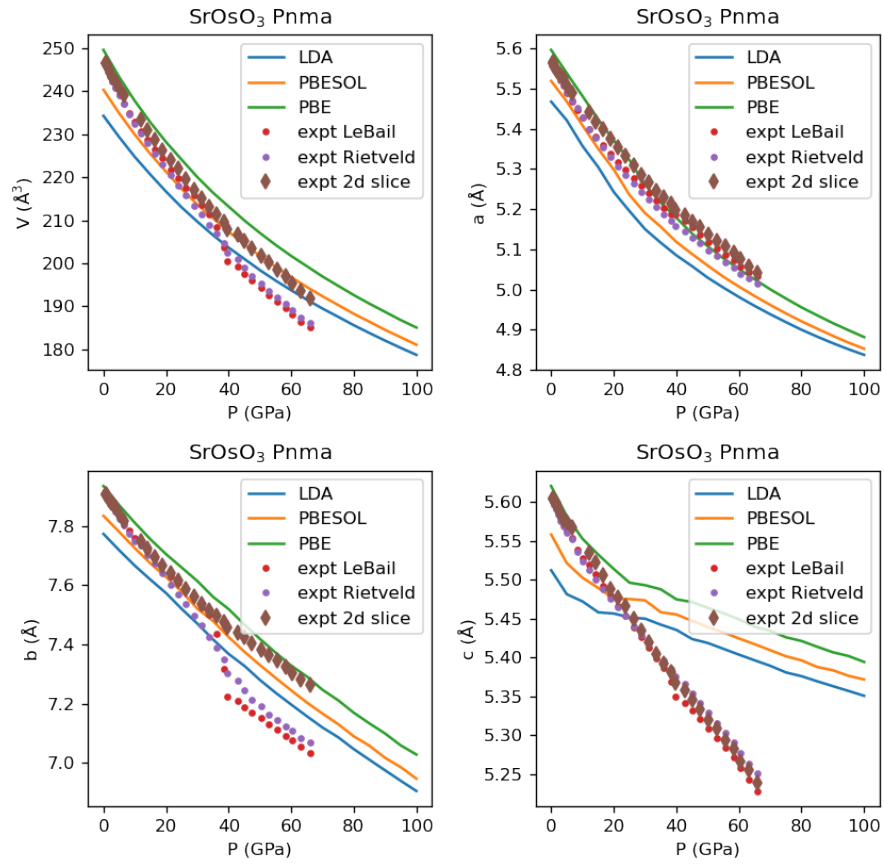


Figure A.3: EOS and lattice parameters of SrOsO₃ in the $Pnma$ structure.

	a (expt)	b (expt)	c (expt)	V (expt)	a (calc)	b (calc)	c (calc)	V (calc)
NaOsO ₃	5.3763	7.5658	5.3239	216.55	5.3690	7.5587	5.3234	216.04
					-0.14%	-0.09%	-0.01%	-0.24%
SrRuO ₃	5.5263	7.7767	5.4695	235.06	5.5101	7.7899	5.4853	235.45
					-0.29%	+0.17%	+0.29%	+0.17%
SrIrO ₃	5.5986	7.8869	5.5532	245.21	5.6123	7.8300	5.5207	242.61
					+0.25%	-0.72%	-0.59%	-1.06%
PbRuO ₃	5.5692	7.7455	5.6621	244.24	5.5493	7.7162	5.6420	241.59
					-0.36%	-0.38%	-0.35%	-1.09%
SrOsO ₃	5.6021	7.9052	5.5619	246.31	5.5584	7.8343	5.5186	240.31
					-0.78%	-0.90%	-0.78%	-2.44%

Table A.1: Experimental and calculated (PBESOL) lattice parameters of selected perovskites. Lattice parameters are in Å, volume is in Å³.

In tab. A.1 I report the PBESOL calculated lattice parameters at ambient pressure (except for MgSiO₃) for selected perovskites. Note that the deviation between PBESOL and experimental value is in the order of 1%. However the volume of SrOsO₃ is underestimated by 2.44%. The calculations were spin polarized and ferromagnetic. In the case of SrOsO₃ I also tried non-magnetic and antiferromagnetic ordering but this additions had no appreciable effect on the lattice parameters.

	a (expt)	b (expt)	c (expt)	V (expt)	a (calc)	b (calc)	c (calc)	V (calc)
MgSiO ₃	2.4560	8.0420	6.0930	120.34	2.4623	8.0607	6.1201	121.47
					+0.26%	+0.23%	+0.45%	+0.94%
CaIrO ₃	3.1430	9.8569	7.2924	225.92	3.1758	9.6526	7.2630	222.65
					+1.04%	-2.07%	-0.40%	-1.45%
CaPtO ₃	3.1261	9.9198	7.3506	227.94	3.1397	9.8174	7.3213	225.67
					+0.44%	-1.03%	-0.40%	-1.00%
CaRuO ₃	3.1150	9.8268	7.2963	223.34	3.1412	9.6115	7.2190	217.96
					+0.84%	-2.19%	-1.06%	-2.41%
CaRhO ₃	3.1013	9.8555	7.2643	222.03	3.1123	9.6814	7.2504	218.47
					+0.36%	-1.77%	-0.19%	-1.61%
NaIrO ₃	3.0397	10.3576	7.1766	225.95	3.0734	10.2535	7.1426	225.09
					+1.11%	-1.01%	-0.47%	-0.38%
NaOsO ₃	2.8321	10.6928	7.3342	222.10	2.7572	10.7067	7.3136	215.90
					-2.64%	+0.13%	-0.28%	-2.76%
SrOsO ₃	3.1529	10.8220	7.2710	248.09	3.2688	9.9784	7.3994	241.35
					+3.68%	-7.79%	+1.77%	-2.72%

Table A.2: Experimental and calculated (PBESOL) lattice parameters of selected post-perovskites. Lattice parameters are expressed in Å, while volume is in Å³. MgSiO₃ data are at 121 GPa. All other perovskites are at ambient pressure.

In tab. A.2 I report the PBESOL calculated lattice parameters at ambient pressure (except for MgSiO₃) for several post-perovskites. Note that the deviation between PBESOL and experimental value is the order of 1-2%, slightly worse than that for perovskites. The most striking result is that *b* lattice parameter of SrOsO₃ is underestimated by ~8%. This result looks like an outlier and re-examination of

PXRD data is under way. The results in the table rule out possible problems with osmium pseudopotential. The calculations were spin polarized and ferromagnetic. In the case of SrOsO_3 I also tried non-magnetic and antiferromagnetic ordering but this had no appreciable effect on the lattice parameters.

A.2 Which XC functional for the spin density?

In principle, DFT is an exact theory but in practice approximations to the exchange-correlation (XC) functional must be made. Therefore DFT accuracy and predictive power are strongly dependent on the choice of the XC functionals. Moreover, being a mean field theory, DFT is not self-interaction free and no XC functional to date is able to cancel exactly the Hartree term. The problem of the self-interaction is particularly severe for highly localized orbitals, like the d and f orbitals. The self-interaction leads to an excessive wavefunction delocalization and closes band gaps in many insulating systems. To solve these drawbacks, one should employ generalized DFT methods, such as DFT+U or hybrid functionals (i.e. mixing of DFT and Hartree Fock methods). One relevant question is if and how these methods improve the description of other measurable quantities such as the charge and spin density. Another relevant question is if it possible to determine DFT parameters from experiments. For instance, the authors of Ref. [109] were able to determine the Hubbard U parameters of NiO from quantitative convergent-beam electron diffraction experiments.

We performed total energy calculations of ferromagnetic YTiO_3 and SrRuO_3 at the experimental lattice and geometry reported in Refs. [110] and [111, 112] using norm-conserving pseudopotentials with a plane wave expansion of 120 Ry to integrate accurately the charge and spin density. The QTAIM charge/spin populations were calculated with Critic2 [113]. The valence shell charge concentration (VSCC) points were located with Critic2 by searching the outermost minima of the laplacian of the charge density within a distance of 2 au from the individual Ti and Ru ions. We applied the rotationally invariant Hubbard U correction on top of the PBESOL functional. We set up two different schemes of “+U” corrections: (1) we applied a $U=0.5$ eV to the d orbitals of the transition metal atoms; (2) we applied the U correction both to the metal d and oxygen p orbitals. For the scheme (2) we calculated self-consistently the Hubbard U values using the ACBN0 method (using the stand alone `acbn0.py` script in the PAOFLOW package [114, 115]). Finally, we performed a more expensive calculation using the HSE06 screened hybrid functional.

Method	q(Y)	q(Ti)	q(O1)	q(O2)	m(Y)	m(Ti)	m(O1)	m(O2)	Tot. magn.
U = 0 eV	2.1101	1.9066	-1.3325	-1.3423	0.0594	0.7974	0.0521	0.0456	1.0000
U = 1 eV	2.1131	1.9198	-1.3387	-1.3474	0.0549	0.8161	0.0461	0.0414	1.0000
U = 2 eV	2.1182	1.9336	-1.3448	-1.3537	0.0457	0.8348	0.0396	0.0399	1.0000
U = 3 eV	2.1220	1.9496	-1.3510	-1.3605	0.0376	0.8511	0.0342	0.0386	1.0000
U = 4 eV	2.1243	1.9671	-1.3574	-1.3673	0.0316	0.8647	0.0299	0.0369	1.0000
U = 5 eV	2.1255	1.9854	-1.3636	-1.3739	0.0272	0.8764	0.0264	0.0350	1.0000
ACBN0	2.2678	2.0992	-1.4481	-1.4597	0.0450	0.8208	0.0458	0.0442	1.0000
HSE06	2.2343	2.0259	-1.4127	-1.4239	0.0273	0.8513	0.0369	0.0422	1.0000
expt. PND	N/A	N/A	N/A	N/A	-0.047	0.715	0.016	0.004	0.704
PBE0	N/A	N/A	N/A	N/A	0.015	0.852	0.036	0.049	0.998

Table A.3: QTAIM charges and spin densities of YTiO_3 . O1 is the apical oxygen, while O2 are the basal oxygens. Experimental polarized neutron diffraction (PND) results and PBE0+QTAIM results are from Ref. [110].

A.2.1 YTiO_3

YTiO_3 is a ferromagnetic perovskite with a Curie temperature of 5 K and crystallizes in the GdFeO_3 Pnma structure with large TiO_6 octahedra tilting (19°). The Ti-O-Ti angles are $\sim 144^\circ$ on the ac plane and 140° along the b axis. The distance between the Ti and apical O along the b axis is the shortest (2.0167 Å), while the Ti-O distances in the ac plane are alternatively short and long, 2.0178 Å and 2.0754 Å [110]. Fig. A.4 shows the spin density isolines on the ac plane passing through the Ti ions. The oxygen atoms directly bound to the Ti ions are located 0.44 Å above and below the plane.

The atomic charges and spin densities integrated in the Bader basins of the charge density are reported in Tab. A.3. The effect of the Hubbard U on the Ti ion is to concentrate both the charge and spin density on the metal ions. Interestingly, the ACBN0 method yielded $U(\text{Ti-3d})=0.26$ eV and a large value on oxygen, $U(\text{O-2p})=8.31$ eV.

The calculated atomic charges are far from the formal valence charges (Y:+3, Ti:+3, O:-2). The sum of the partial charges, integrated on a real space mesh, differs by 10^{-4} electrons from the total number of electrons per unit formula. The total spin magnetization per unit formula is $1 \mu_B$ with 80%–86% of it located on the Ti ion. This situation corresponds to a Ti^{3+} ion in the $t_{2g}^1 e_g^0$ configuration. Note that the spin density around the oxygen atoms shows a negative shell near the ion, surrounded by a region of positive spin density. The size of this negative spin region is large when the U is applied to the Ti ion whereas it is reduced with ACBN0. The ACBN0 atomic charges and spins are close to those obtained with the hybrid HSE06 and PBE0 functionals. Note that the small magnetic moment on the O1 (apical) ion is initially larger than those of the O2 ions at $U=0$ but the situation changes for $U>3$ eV. The larger magnetic moments on the basal O2 ions is also suggested by the experimental data but this is not the case for ACBN0.

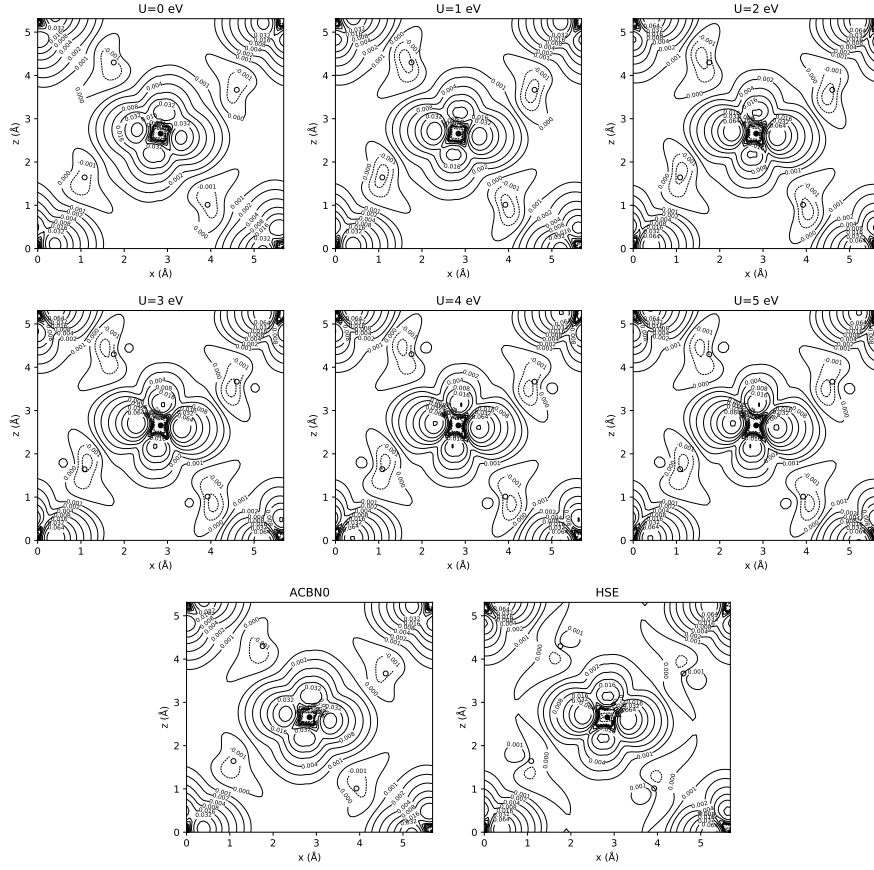


Figure A.4: Isodensity contour of the spin density of YTiO_3 plotted on the ac plane. The Ti ion is in the center of the cell. The projection of the O2 ions are indicated by open circles (the O ions are $0.44 \text{ \AA}$ above and below the cut plane. The isovalues are $\pm 0.001 \cdot 2^n$ with $n = 0 \dots 7$.

The spin density and the VSCC are reported in Fig. A.5. The analysis of the laplacian of the charge density shows that there are six VSCC points, located $\sim 0.37 \text{ \AA}$ from the Ti ion, which corresponds to the outer $3d$ shell of Ti. When $U(\text{Ti})$ is small (less than 2 eV), the VSCC are arranged as a nearly regular octahedron. The VSCC octahedron is rotated such that two VSCC are in the O1-Ti-O2 plane and the remaining four VSCC are located in plane tilted by $\sim 40^\circ$ from the Ti-O2-O2' plane. For small values of $U(\text{Ti})$ the six VSCC correspond to the six lobes of the spin density, showing that the spin density is given by a superposition of the t_{2g} orbitals. When the Hubbard U on Ti is larger than 2 eV and the system becomes insulating, the VSCC octahedron changes its shape and it becomes highly distorted: four VSCCs are found in correspondence of the four spin density lobes, while the two remaining VSCC are located close to the Ti-O1 bond. This is reflected by the values of the laplacian (curvature of the charge density): when $U(\text{Ti})$ is small, the laplacian at the VSCC ranges from -9.3 to -10.0 au^{-5} meaning that the charge density is concentrated nearly equally at the VSCC. When $U(\text{Ti})$ is larger than 2 eV, the laplacian is more negative (-12.5 au^{-5}) at the four VSCC corresponding to the spin density lobes, while it is less negative (-8.7 au^{-5}) at the two remaining VSCC. Therefore, in YTiO_3 the curvature of the charge density distribution gives a direct indication of the shape of the spin density.

Not surprisingly the small $U(\text{Ti})=0.26 \text{ eV}$ found by the ACBN0 method yields a spin density with six lobes and the VSCC form a nearly regular octahedron. However the ACBN0 charge density around the Ti atom is more concentrated with respect to the $U=0$ case: the laplacian at the six VSCC ranges from -9.4 to -11.2 au^{-5} and this is due to the fact that the ACBN0 Bader charge on Ti is $\sim 10\%$ larger than that computed with $U=0$. In the HSE06 case the spin density shows four large lobes and 2 small ones that become visible with an isosurface of 0.2 au^{-3} . This situation is intermediate between the small and large U value cases. The laplacian at the VSCC are -8.9 and -12.5 au^{-5} , comparable to the case of $U(\text{Ti}) > 2 \text{ eV}$.

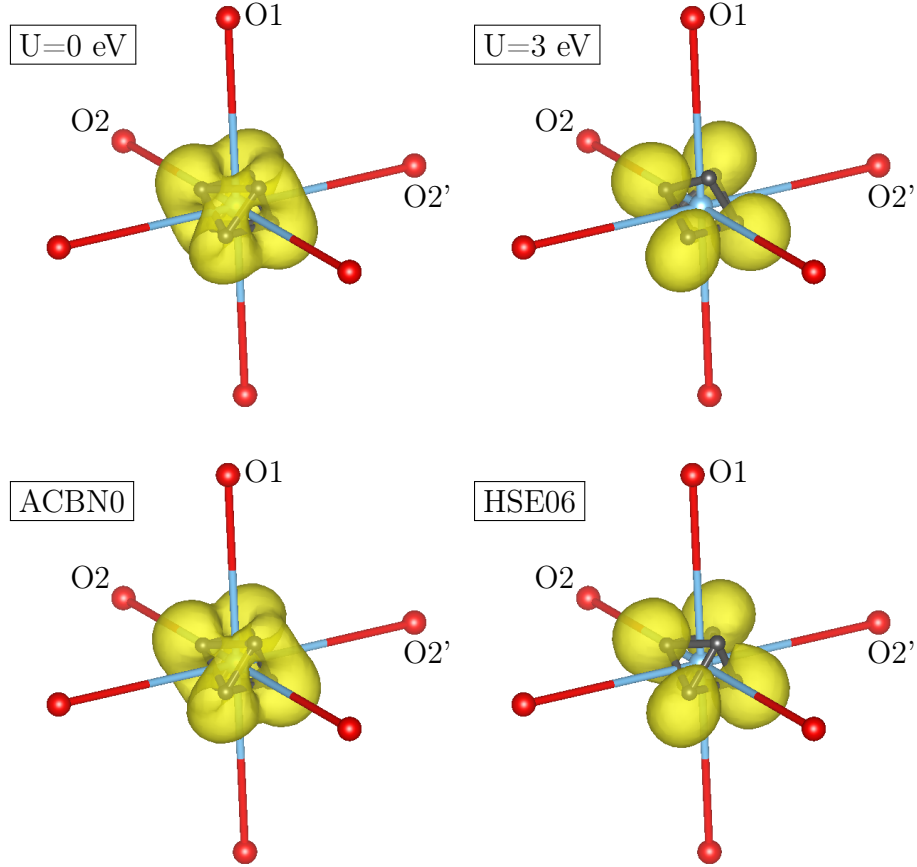


Figure A.5: Spin density and VSCC of YTiO_3 . The spin density isosurface is $0.3/\text{au}^3$. O1 is the apical oxygen, O2 and O2' are the basal oxygen. Ti-O2' is the largest Ti-O interatomic distance.

A.2.2 SrRuO_3

SrRuO_3 is a weakly interacting ferromagnetic metallic perovskite. SrRuO_3 crystallizes in the Pnma structure but differently from YTiO_3 the octahedra in SrRuO_3 are less tilted and less distorted. The Sr-O distances are $1.986 \text{ \AA}$ (Sr-O1 apical), $1.986 \text{ \AA}$ and $1.987 \text{ \AA}$ (Sr-O2 basal). The Sr-O-Sr angle is $\sim 161^\circ$ [111].

Fig. A.6 shows the spin density isolines on the ac plane passing through the Ru ions. The plane containing the Sr and O atoms is almost parallel to the (010) plane. The atomic charges and spin densities integrated in the Bader basins of the charge density are reported in Tab. A.4. Similarly to YTiO_3 , the ACBN0 method yielded a relatively small value of U on the transition metal and a large value of U on the oxygen ions: $U(\text{Ru-4d})=2.06 \text{ eV}$, $U(\text{O-2p})=5.08 \text{ eV}$.

The calculated atomic charges are far from the formal valence charges (Sr:+2, Ru:+4, O:-2). The sum of the partial charges, integrated on a real space mesh, differs by 10^{-4} electrons from the total number of electrons per unit formula. The atomic charges of oxygen are smaller than that of YTiO_3 . The ACBN0 and HSE06

functional tend to concentrate both the charge and the spin on the Ru ion, making the system slightly more ionic in character. The total magnetization is close to $2 \mu_B$ and is compatible with a Ru^{+4} ion in the $t_{2g}^4 e_g^0$ configuration. The atomic magnetic moments on the oxygen atoms are about $0.2 \mu_B$, one order of magnitude larger than those of YTiO_3 . With respect to YTiO_3 , the smaller Bader charge and the larger magnetic moment on oxygen can be explained by the larger overlap between the O-2p orbitals and the Ru-4d which has a larger spatial extent than the Ti-3d orbital.

Differently from YTiO_3 the spin density map, the atomic charges and spin populations are nearly insensitive to the value of U on the Ru ion. The spin density map shows only regions of positive spin density.

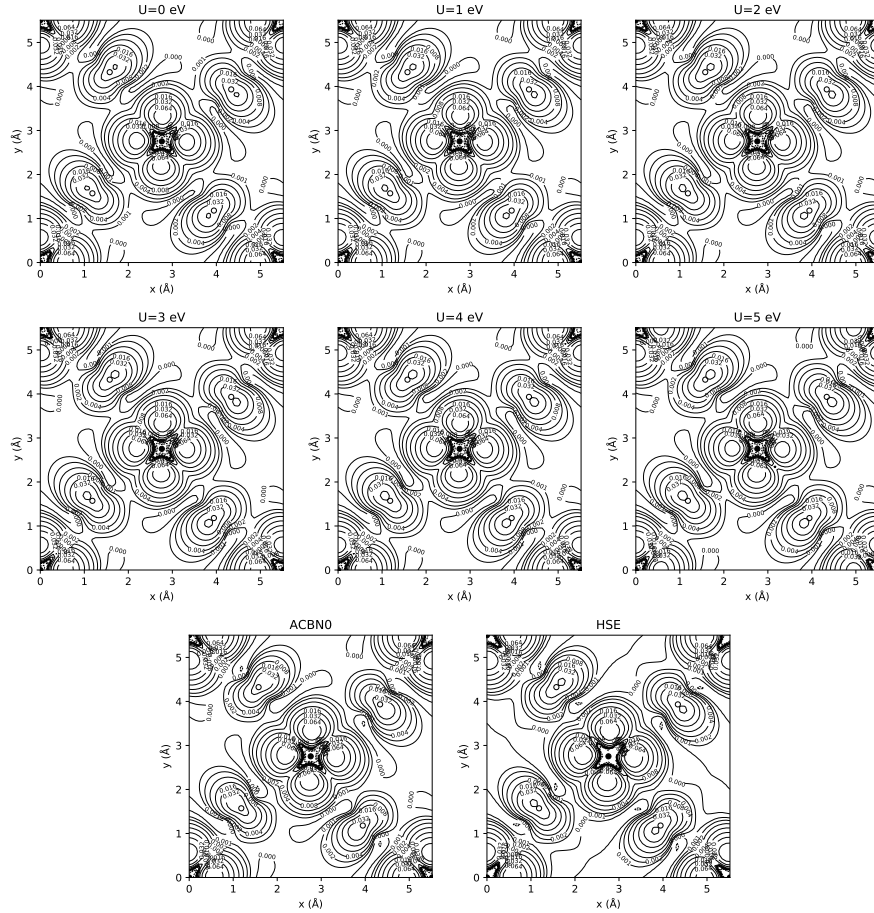


Figure A.6: Isodensity contour of the spin density of SrRuO_3 plotted on the ac plane. The Ti ion is in the center of the cell. The projection of the O2 ions are indicated by open circles. The isovalues are $\pm 0.001 \cdot 2^n$ with $n = 0 \dots 7$.

Method	q(Sr)	q(Ru)	q(O1)	q(O2)	m(Sr)	m(Ru)	m(O1)	m(O2)	Tot. magn.
U = 0 eV	1.5745	1.6715	-1.0795	-1.0872	0.0136	1.3898	0.1942	0.1853	1.9772
U = 1 eV	1.5754	1.6576	-1.0750	-1.0832	0.0136	1.3967	0.1988	0.1909	1.9989
U = 2 eV	1.5763	1.6423	-1.0703	-1.0784	0.0134	1.3869	0.2025	0.1946	2.0000
U = 3 eV	1.5773	1.6263	-1.0653	-1.0733	0.0134	1.3740	0.2068	0.1990	2.0000
U = 4 eV	1.5783	1.6098	-1.0601	-1.0682	0.0134	1.3597	0.2115	0.2040	2.0000
U = 5 eV	1.5793	1.5927	-1.0555	-1.0612	0.0136	1.3436	0.2163	0.2102	2.0000
ACBN0	1.6214	1.8594	-1.1581	-1.1649	0.0086	1.5103	0.1623	0.1565	2.0000
HSE06	1.6608	2.1080	-1.2576	-1.2539	-0.0023	1.4989	0.1801	0.1432	2.0000
expt. 2 K S+L	N/A	N/A	N/A	N/A	N/A	1.35	0.20	0.20	1.95
expt. 2 K S	N/A	N/A	N/A	N/A	N/A	1.42	0.20	0.20	2.02
other DFT (PBE)	N/A	N/A	N/A	N/A	N/A	1.34	0.16	0.13	1.79

Table A.4: QTAIM charges and spin densities of YTiO_3 . O1 is the apical oxygen, while O2 are the basal oxygens. Experimental results and “other DFT” are from Ref. [110]. Two experimental refinements are reported: including the orbital angular momentum (S+L) and without angular momentum (S). “other DFT” magnetic moments are integrated inside atomic spheres of radius 1.25 Å (Ru) and 0.73 Å (O).

The spin density and the VSCC are reported in Fig. A.7. The analysis of the laplacian of the charge density shows that there are eight VSCC points, located ~ 0.44 Å from the Ru ion. The VSCC are arranged as a cube whose vertexes point in the directions of center of the faces of the SrO_6 octahedron. As already shown in Tab. A.4 the spin density depends weakly on the U values and on the choice of the functional. The value of the laplacian at the VSCC goes from -8.18 au^{-5} at $U=0$ to -8.30 au^{-5} at $U=5 \text{ eV}$, -8.26 au^{-5} for ACBN0 and -8.61 au^{-5} for HSE. Thus the charge and spin concentration around the Ru ion depends rather weakly on the DFT methods we have used.

A.2.3 Discussion

The comparison of DFT results to experimental polarized neutron/X-ray diffraction [110,112] and magnetic Compton scattering [116] data has to be carried out with some caution. Diffraction experiments provide, after removing the instrumental and thermal effects, the structure factors which are related to the charge/spin density by a Fourier transform. The atomic and orbital contributions to the experimental charge/spin density is obtained from the multipolar model [117] or from the maximum entropy method [118]. However it is possible to perform a detailed QTAIM analysis on the experimental charge and spin density after a multipolar refinement [119,120]. The other possibility is to calculate the theoretical structure factors directly from DFT and perform multipolar refinement on them.

From our results on two magnetic perovskite, we can draw the partial conclusion that hybrid functionals are the best choice to describe accurately both the spin density and the electronic structure of these materials. The ACBN0 method ranks in

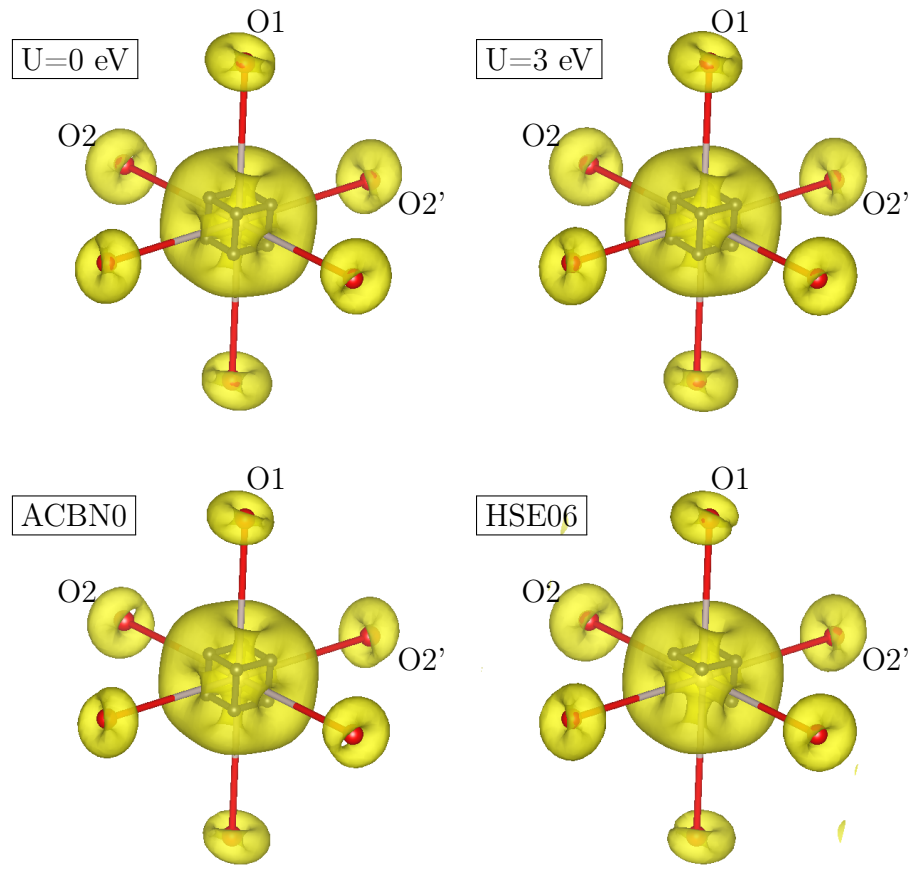


Figure A.7: Spin density and VSCC of SrRuO_3 . The spin density isosurface is $0.3/\text{au}^3$. O1 is the apical oxygen, O2 and O2' are the basal oxygen.

between DFT+U and hybrid functionals. The present DFT+U and ACBN0 implementation acts only on one angular momentum channel per atom. If this limitation will be relaxed in future versions of QE, we expect ACBN0 and DFT+U+V method will be as accurate as hybrid functional, at a fraction of their computational cost.

A.3 Atlas of YN_x structures

In chapter 3 I stated I relaxed with QE all the structures obtained by USPEX and removed those who turned out to be equal by symmetry at 100 GPa. The QE relaxation is more accurate than the SIESTA calculation and many structures turned out to have the same enthalpy, cell parameters and atomic positions. I used `aflow -compare-structures` to eliminate those. In this section I report not only the most stable structures but also the structures with higher enthalpy obtained with USPEX+SIESTA. Note that at 100 GPa the enthalpies are in a energy range smaller than the enthalpies at 50 GPa and 0 GPa. That is, at 100 GPa all the structures are close in enthalpy and this is why USPEX can efficiently explore the enthalpy landscape.

A.3.1 YN_2

This is the `goodStructures` file at the end of the USPEX+SIESTA run at 100 GPa, annotated with a description of the N-N bonding (see fig. A.8). Note that the high energy “layered” structures appear similar in the figure but they have different N_2 arrangement within the planes.

ID	Compositions	Enthalpies (eV/atom)	Volumes ($\text{\AA}^3/\text{atom}$)	fitness ()	SYMM
292	[4 8]	-195.5532	8.7273	-2346.6387	2 N2, layers
325	[4 8]	-195.5525	8.7303	-2346.6295	2 N2, layers
555	[4 8]	-195.5380	8.7579	-2346.4566	2 N2, layers
600	[4 8]	-195.5324	8.7057	-2346.3886	12 N2, layers
307	[4 8]	-195.5317	8.7094	-2346.3803	1 N2, layers
316	[4 8]	-195.5217	8.8783	-2346.2606	2 N2, layers
641	[4 8]	-195.5139	8.8278	-2346.1674	2 N2, no layers
322	[4 8]	-195.5085	8.8840	-2346.1014	14 N4 "cis" chains
524	[4 8]	-195.5061	8.8691	-2346.0728	1 N2, layers
649	[4 8]	-195.4982	8.8500	-2345.9781	2 N2, layers
285	[4 8]	-195.4919	8.8951	-2345.9031	2 N2, layers
661	[4 8]	-195.4918	8.8981	-2345.9013	4 N2, no layers
657	[4 8]	-195.4888	8.8870	-2345.8656	5 N2, layers
169	[4 8]	-195.4826	8.8805	-2345.7909	2 N2, layers
536	[4 8]	-195.4808	8.8469	-2345.7701	2 N2, layers
411	[4 8]	-195.4715	8.9077	-2345.6575	4 N2, no layers
573	[4 8]	-195.4702	8.6968	-2345.6420	2 2*N3 + N2

633	[	4	8	]	-195.4651	8.8937	-2345.5810	12	N2, layers
529	[	4	8	]	-195.4583	8.9203	-2345.4999	140	N2
527	[	4	8	]	-195.4581	8.9042	-2345.4968	140	N2
279	[	4	8	]	-195.4547	8.7986	-2345.4563	15	N2
581	[	4	8	]	-195.4523	8.7251	-2345.4278	2	N4 + 2*N2
639	[	4	8	]	-195.4484	8.6949	-2345.3812	1	N6 chain + 1*N2
201	[	4	8	]	-195.4386	8.9006	-2345.2635	1	N4 "trans" + 2*N2
530	[	4	8	]	-195.4370	8.9506	-2345.2442	140	N2
523	[	4	8	]	-195.4210	8.8672	-2345.0515	1	N2 layers
168	[	4	8	]	-195.4175	8.9358	-2345.0095	1	N2 layers
301	[	4	8	]	-195.4146	8.6873	-2344.9748	2	N4 chains
490	[	4	8	]	-195.4134	8.8529	-2344.9607	1	N2
628	[	4	8	]	-195.3949	8.6646	-2344.7388	1	2*N3 + N2

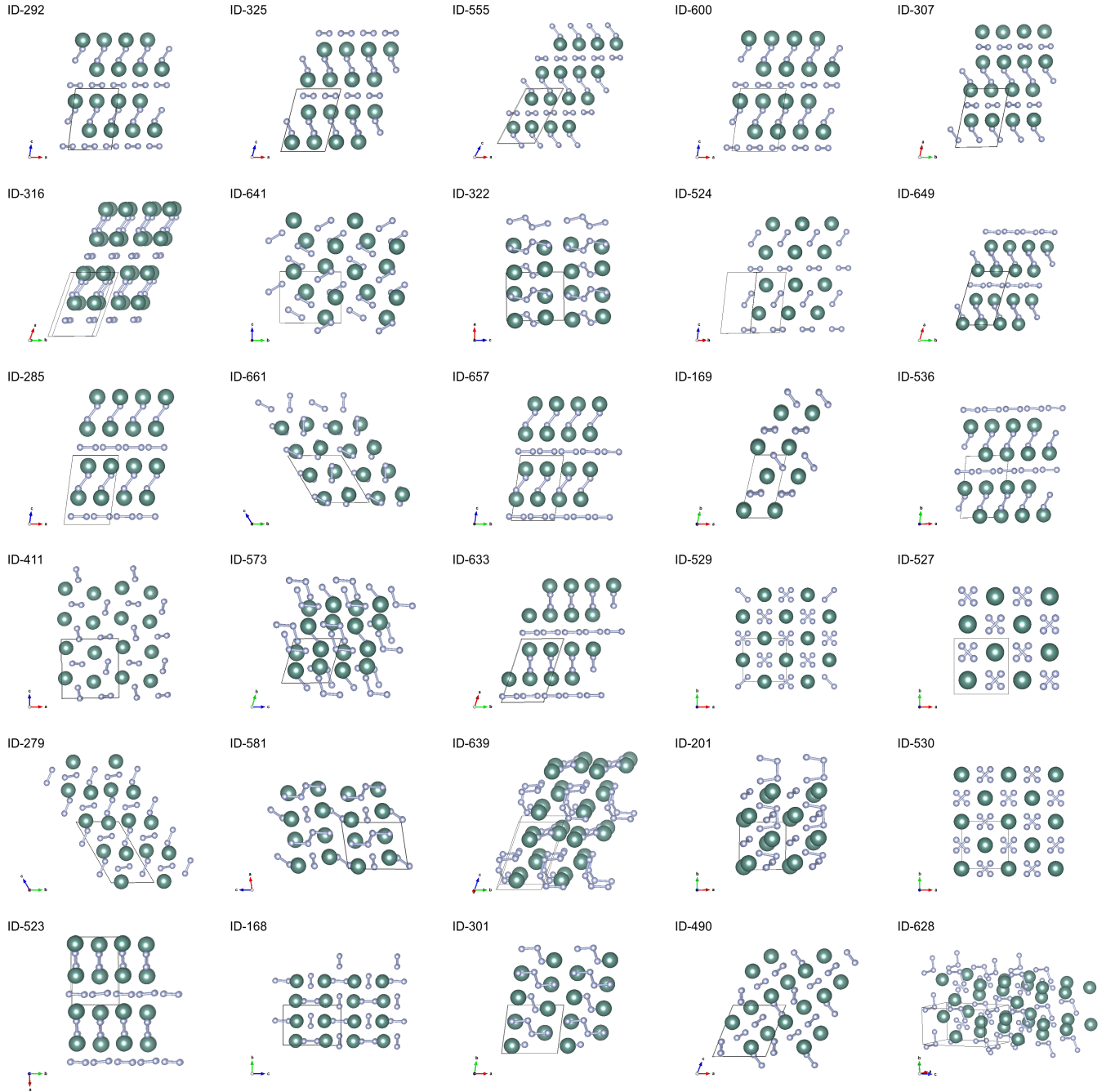


Figure A.8: YN_2 *good structures* from USPEX+SIESTA at 100 GPa. The enthalpy increases from the top-left to the bottom-right structure.

A.3.2 YN_3

This is the `goodStructures` file at the end of the USPEX+SIESTA run at 100 GPa, annotated with a description of the N-N bonding (see fig. A.9). Differently from YN_2 , at 100 GPa YN_3 forms longer chains, and few cyclic molecules. However, as shown in chapter 3, the long nitrogen chain break into shorter chains as soon as the pressure is decreased.

ID	Compositions	Enthalpies (eV/atom)	Volumes ($\text{\AA}^3/\text{atom}$)	fitness ($\circ$)	SYMM	
869	[4 12]	-212.7987	7.9442	-3404.7787	2	infinite chains, layers
625	[4 12]	-212.7983	7.9927	-3404.7726	1	N12 chains
280	[4 12]	-212.7785	8.0167	-3404.4556	4	infinite ch., branched
819	[4 12]	-212.7637	7.9183	-3404.2184	1	infinite ch.
428	[4 12]	-212.7414	8.0662	-3403.8616	1	N12 chains
767	[4 12]	-212.7142	8.0587	-3403.4278	1	infinite chains
672	[4 12]	-212.6950	8.1152	-3403.1192	1	1*N6 + 2*N3
851	[4 12]	-212.6931	8.2769	-3403.0898	40	infinite ch., layers
12	[4 12]	-212.6701	7.9942	-3402.7216	78	infinite ch., spirals
198	[4 12]	-212.6668	8.1862	-3402.6686	1	N10 + N2
635	[4 12]	-212.6583	8.1092	-3402.5328	113	N3 molecules
91	[4 12]	-212.6455	8.0295	-3402.3272	2	N8 + N4
519	[4 12]	-212.6372	8.2545	-3402.1952	1	N4 + 2*N3 + N2
820	[4 12]	-212.6364	8.1694	-3402.1822	1	2*N5 + N2
562	[4 12]	-212.6304	8.2584	-3402.0863	1	N4 + 2*N3 + N2
142	[4 12]	-212.6196	8.0741	-3401.9132	1	N7 + N5
560	[4 12]	-212.6174	8.2403	-3401.8788	1	N4 + 2*N3 + N2
760	[4 12]	-212.6167	8.0624	-3401.8675	1	N12
110	[4 12]	-212.6130	8.0656	-3401.8083	1	N12 with a N5-cycle
623	[4 12]	-212.6094	8.2614	-3401.7505	1	N4 + 2*N3 + N2
222	[4 12]	-212.6023	8.0091	-3401.6362	1	infinite ch., branched
458	[4 12]	-212.5928	8.1266	-3401.4854	12	N12 cyclic molecules
306	[4 12]	-212.5880	8.1219	-3401.4078	1	N12 branched molecules
666	[4 12]	-212.5830	8.1420	-3401.3281	1	N7 + N3 + N2
608	[4 12]	-212.5674	8.2102	-3401.0780	1	N7 + N3 + N2
419	[4 12]	-212.5636	8.1098	-3401.0177	2	2*N4 + 4*N2
339	[4 12]	-212.5621	8.1672	-3400.9935	8	N4 + 2*N3 + N2
654	[4 12]	-212.5602	8.2005	-3400.9630	1	N9 + N3
235	[4 12]	-212.5600	8.0308	-3400.9593	1	infinite ch.
184	[4 12]	-212.5497	8.1604	-3400.7958	1	2*N5 + N2

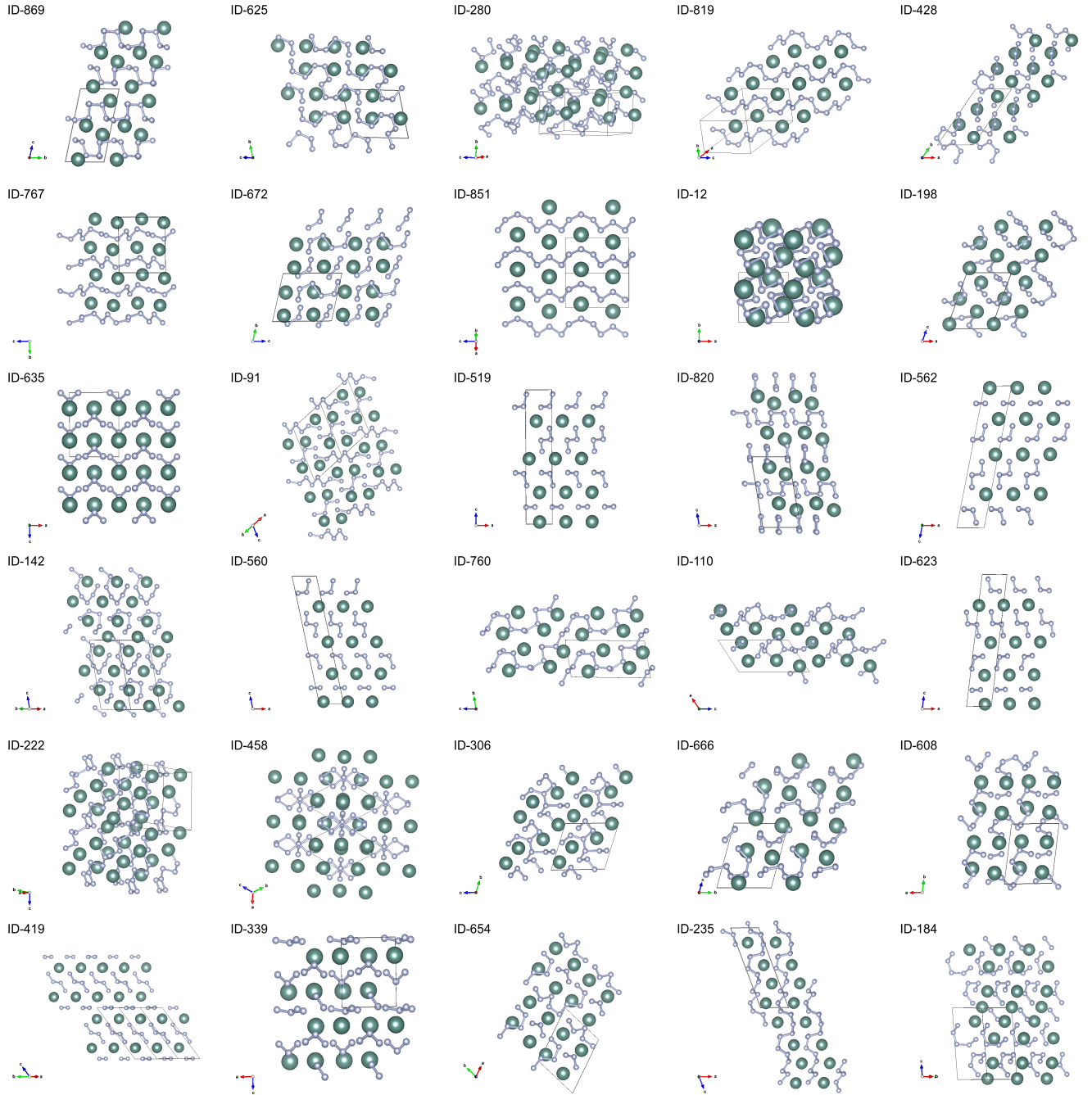


Figure A.9: YN_3 *good structures* from USPEX+SIESTA at 100 GPa. The enthalpy increases from the top-left to the bottom-right structure.

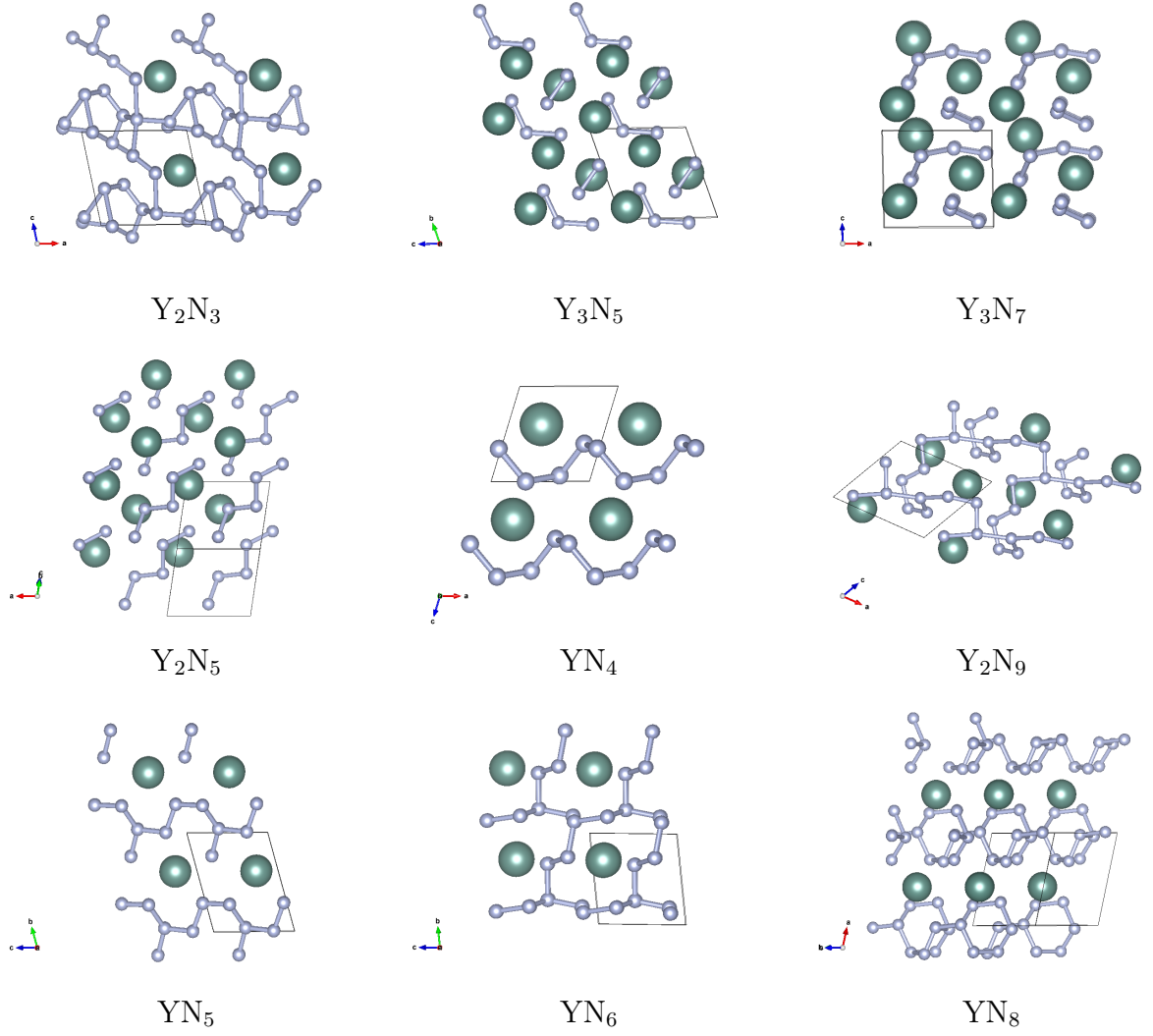


Figure A.10: Selected YN_x structures, close to the convex hull, from the variable composition USPEX run at 100 GPa.

A.3.3 Other compositions

In fig. A.10 I show a selection of the the YN_x close to the convex hull. Not surprisingly, when the N concentration increases, nitrogen tend to form long chains and 3d bulk structures, with interstitial Y ions.

A.4 Exfoliable topological materials

This side project was motivated by a coffee-time discussion in Aarhus with Prof. Bremholm: *Which topological insulator should we synthesize and study?* What is a topological insulator? Do they have any application? You can find the answer in this nice and clear review paper [121].

It turns out that determining if a material has a topological band structure, being a topological insulator (TI) or a Weyl semi-metal (WSM) is relatively easy. It is so easy that it can be done on the ICSD database of inorganic materials and also on organic crystals. Experimentally, it is much more difficult. The most direct technique is angle resolved photoemission spectroscopy (ARPES) which measures the energy/momentum $E(k)$ relation of quasi-particles. This is, in the zeroth approximation, the *band structure*. However, to perform ARPES experiments one needs to synthesize quite large crystals, with no defects, stable in air, stable against oxidation, with well determined surfaces.

Therefore the coffee-time discussion evolved into the question: *Can you make a list of exfoliable topological materials?* It turns out that the “exfoliability” can be defined in many different ways with DFT calculations and that several databases of exfoliable materials exist.

Therefore, together with my supervisor, we wrote few Python scripts to download entire databases (of topological, of exfoliable materials) and to extract the relevant information. We downloaded the database from www.topologicalquantumchemistry.com, and two exfoliable materials database: MaterialsCloud from EPFL (archive.materialscloud.org/2017.0008/v1) and JARVIS-2D from NIST (jarvis.nist.gov/login?next=/jarvisdft/). In order to cross the databases we simply had to convert the chemical formulas into strings of brute formula, with the elements ordered alphabetically (i.e. $\text{NaCoO}_3 \rightarrow \text{Co1 Na1 O3}$, $\text{Mg(OH)}_2 \rightarrow \text{H2 Mg1 O2}$).

Here is what we found:

- MaterialsCloud has 457 exfoliable materials. JARVIS-2D lists 523 materials. Only 182 materials are in both databases! this means that the two databases used a different criterion to classify materials. In addition to the energy require to “exfoliate” the material, MaterialsCloud considers also the difference between the lattice spacing calculated with and without van der Waals terms.
- Therefore we took the union of this two databases: 798 materials.
- Among these 798 exfoliable materials, 82 are classified as topological insulators. Here is the list:

Se4 Ti1 Zr1

Cr1 S2

Cl1 Zr1

Ho1 I1 S1	Ca1 Sn1	Ce1 S1
Ga1 Ge1 Te1	Sb2 Se2 Te1	Te2 Zr1
O2 V1	C2 Cl1 N2 Ni1 Rb1	Cl1 O1 V1
Ca1 Si1	Pt1 Te2	Hf1 S3
Nd1 Te3	Cr1 Se2	Se1 Sn1
Hf1 Si1 Te1	Cr1 Se1	Br1 Zr1
Te3 Zr1	Au1 Cl1 Te2	Bi2 Pb2 Se5
Hf3 Te2	Pd1 Te2	C1 S2 Ta2
Bi4 Se3	Cl1 H1 Lu1	Co1 Nb1 Te2
Bi3 S1 Te2	N1 S1	As2 Te3
Bi4 Ge1 Te7	Bi2 Ge1 Te4	Hf1 Te5
Ni1 Te2	Bi2 Se3	Pb1 S1
Bi2 Pb2 Te5	Sb2 Te1	Sb2 Se1 Te2
I1 N1 Ti1	In1 Nb1 Se2	Sn1 Te1
Ge1 Sb4 Te7	Br1 O1 V1	Ge2 Sb2 Te5
C1 Nb2 S2	Er1 Te3	Bi2 Se2 Te1
Mo1 Te2	Bi2 Te3	I1 O1 Tm1
As1	Cl1 La1	Cl1 O1 Yb1
Bi2 Pb1 Te4	Br1 La1	Br3 Mo1
N3 Na1	Cl1 H1 Sc1	Cl3 V1
Sb2 Sn1 Te4	In1 Se1	Si1 Te1 Zr1
Bi4 Pb1 Te7	Bi4 Sn1 Te7	Te4 Ti1 Zr1
I2 Nd1	S2 Ti1	Cr1 Si1 Te3
Dy1 Te3	C1 Y2	Bi2 Se1 Te2
Bi1 I1	Sb8 Te3	O2 W1
S1 Sn1	S3 U1	Sb2 Te3
H1 Si1		

A large number of these materials are already well studied both experimentally and theoretically. There are chalcogenides, for example, the family of Sb_2Te_3 and hexagonal $\text{Ge}_2\text{Sb}_2\text{Te}_5$ (the cubic polymorphs are used as phase-change materials in DVDs and in flash RAMs), which tend to be defective. The second family is halides especially of Br and I. This is not surprising since a large spin orbit coupling is needed for band inversion in topological insulators. Oxides are nearly absent from this list, or are false-positives, because when they have a large band gap, spin-orbit band inversion is difficult.

The remaining materials are so few that they can be investigated one at the time. There are bulk crystals and materials with 2d or 1d-chain character and they can be further grouped by looking at their structure and space group:

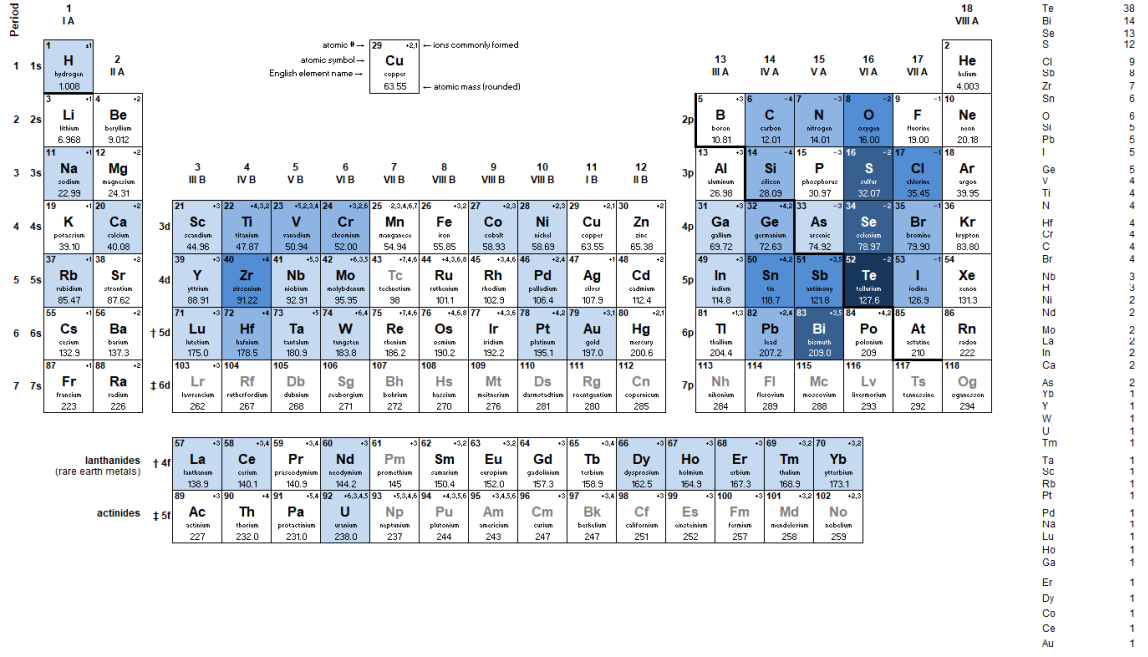


Figure A.11: Element abundance of exfoliable topological insulators.

- As ($Cmcm$)
- BiI ($C2/m$)
- BrLa, BiZr, LuCH, ScCH, ClLa ($R\bar{3}m$), Nb₂CS₂ ($P\bar{3}m1$)
- BrVO, ClVO ($Pnmm$)
- MoBr₃ ($Pnmm$)
- Y₂C ($R\bar{3}m$)
- CaSi, CaSn ($Cmcm$)
- CeS (rocksalt)
- ...

Once the list was obtained, I performed a very simple statistical analysis and I colored the periodic table according to the which element appears more often in this list (fig. A.11). Tellurium is by far the most abundant elements, followed by Bi, the other chalcogenides, by Zr, O, Si, and by the halides. Even if perovskites are not exfoliable, they can be cleaved easily. Therefore we expanded the search and found several perovskites classified as topological insulators. The interesting observation is that they appear to be composed by $4f$ lanthanides and $3d/4d$ transition metals (i.e. PrCoO₃) as shown in fig. A.12. Out of curiosity we looked at the band structures of these perovskites from the topological quantum chemistry database, and the first

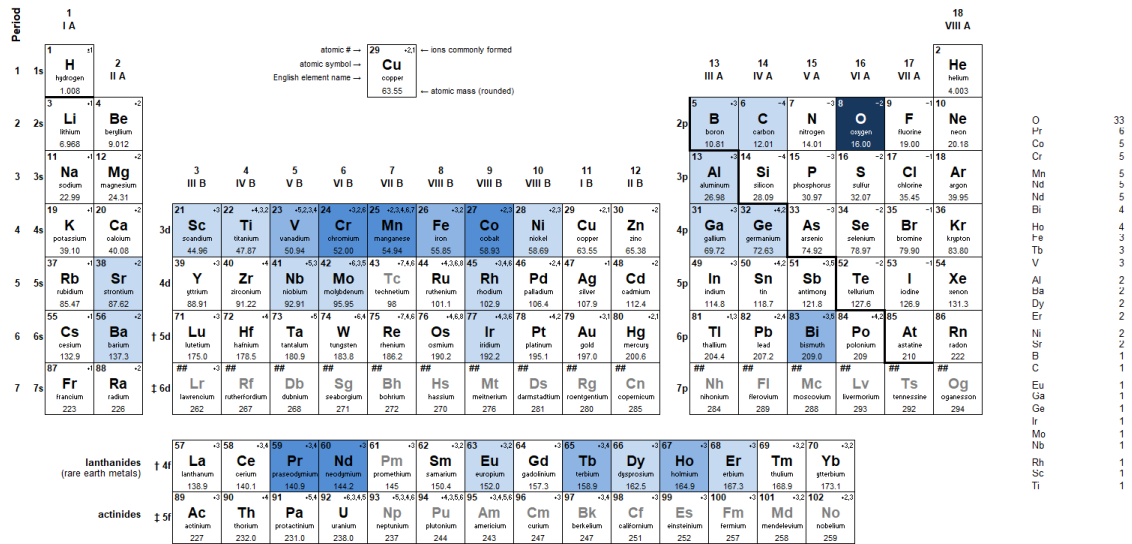


Figure A.12: Element abundance of perovskite topological insulators.

observation is that the lanthanide $4f$ orbital cross the Fermi level. Apparently those DFT calculations did not consider neither magnetism nor the “+U” Hubbard correction on the $4f$ orbitals. In addition to that, it is known that many oxides undergo metal to insulator transitions, and spin crossover (i.e. in cobaltites) as a function of temperature. Therefore, the topological classification of these perovskites has to be examined case by case and not by high-throughput calculations.

Acknowledgements

This work of thesis would never have been possible without the support and the commitment of many people, starting from my tutor Leonardo Lo Presti and my supervisor Davide Ceresoli, whose help and patience were crucial to get to this point. A special thanks also goes to collaborators from Martin Bremholm's group at Aarhus University, especially Camilla Hjort Krombo and Emma Møller Ehrenreich-Petersen, who gave an essential contribution both with their experimental work and the brainstorming sessions they have always been willing to do.

A final thanks goes to my family and friends, especially Veronica, as they never fail to support me and love me every second of my life.

Bibliography

- [1] Maosheng Miao, Yuanhui Sun, Eva Zurek, and Haiqing Lin. Chemistry under high pressure. *Nature Reviews Chemistry*, 4(10):508–527, sep 2020.
- [2] Xiao Dong, Artem R. Oganov, Alexander F. Goncharov, Elissaios Stavrou, Sergey Lobanov, Gabriele Saleh, Guang-Rui Qian, Qiang Zhu, Carlo Gatti, Volker L. Deringer, Richard Dronskowski, Xiang-Feng Zhou, Vitali B. Prakapenka, Zuzana Konôpková, Ivan A. Popov, Alexander I. Boldyrev, and Hui-Tian Wang. A stable compound of helium and sodium at high pressure. *Nature Chemistry*, 9(5):440–445, feb 2017.
- [3] Roman Martoňák, Davide Ceresoli, Tomoko Kagayama, and Erio Tosatti. Ab initio study of properties of BaBiO₃ at high pressure. *APS*, 2017:E2–006, 2017.
- [4] Oto Kohulák and Roman Martoňák. New high-pressure phases of MoSe₂ and MoTe₂. *Physical Review B*, 95(5):054105, 2017.
- [5] Juan A Sans, Rosario Vilaplana, E Lora da Silva, Catalin Popescu, Vanesa P Cuenca-Gotor, Adrián Andrada-Chacón, Javier Sánchez-Benitez, Oscar Gomis, André LJ Pereira, Plácida Rodríguez-Hernández, et al. Characterization and Decomposition of the Natural van der Waals SnSb₂Te₄ under Compression. *Inorganic Chemistry*, 59(14):9900–9918, 2020.
- [6] Demetrio Scelta, Adhara Baldassarre, Manuel Serrano-Ruiz, Alexey Marchuk, Sebastian Vogel, Wolfgang Schnick, Maurizio Peruzzini, Roberto Bini, and Matteo Ceppatelli. High-Pressure Synthesis of Cyclic Phosphazenes by Near-UV Photoinduced Reactivity of NH₃ and Elemental Phosphorus. *The Journal of Physical Chemistry C*, 124(7):4308–4319, 2020.
- [7] Tomasz Poręba, Piero Macchi, and Nicola Casati. On the structural variety of alkali hydrogen maleates at high pressure. *Crystal Growth & Design*, 2020.
- [8] P Hohenberg and WJPR Kohn. Density functional theory (DFT). *Phys. Rev*, 136:B864, 1964.

- [9] Walter Kohn and Lu Jeu Sham. Self-consistent equations including exchange and correlation effects. *Physical review*, 140(4A):A1133, 1965.
- [10] David M Ceperley and Berni J Alder. Ground state of the electron gas by a stochastic method. *Physical Review Letters*, 45(7):566, 1980.
- [11] Warren E Pickett. Pseudopotential methods in condensed matter applications. *Computer Physics Reports*, 9(3):115–197, 1989.
- [12] Frank Herman, John P Van Dyke, and Irene B Ortenburger. Improved statistical exchange approximation for inhomogeneous many-electron systems. *Physical Review Letters*, 22(16):807, 1969.
- [13] Tomoya Naito, Ryosuke Akashi, and Haozhao Liang. Application of a Coulomb energy density functional for atomic nuclei: Case studies of local density approximation and generalized gradient approximation. *Physical Review C*, 97(4), 2018.
- [14] John P. Perdew, Adrienn Ruzsinszky, Gábor I. Csonka, Oleg A. Vydrov, Gustavo E. Scuseria, Lucian A. Constantin, Xiaolan Zhou, and Kieron Burke. Restoring the density-gradient expansion for exchange in solids and surfaces. *Physical Review Letters*, 100(13):1–4, 2008.
- [15] DR Hamann, M Schlüter, and C Chiang. Norm-conserving pseudopotentials. *Physical Review Letters*, 43(20):1494, 1979.
- [16] Paolo Giannozzi, Stefano Baroni, Nicola Bonini, Matteo Calandra, Roberto Car, Carlo Cavazzoni, Davide Ceresoli, Guido L Chiarotti, Matteo Cococcioni, Ismaila Dabo, Andrea Dal Corso, Stefano de Gironcoli, Stefano Fabris, Guido Fratesi, Ralph Gebauer, Uwe Gerstmann, Christos Gougousis, Anton Kokalj, Michele Lazzeri, Layla Martin-Samos, Nicola Marzari, Francesco Mauri, Riccardo Mazzarello, Stefano Paolini, Alfredo Pasquarello, Lorenzo Paulatto, Carlo Sbraccia, Sandro Scandolo, Gabriele Sclauzero, Ari P Seitsonen, Alexander Smogunov, Paolo Umari, and Renata M Wentzcovitch. Quantum ESPRESSO: a modular and open-source software project for quantum simulations of materials. *Journal of Physics: Condensed Matter*, 21(39):395502, September 2009.
- [17] P Giannozzi, O Andreussi, T Brumme, O Bunau, M Buongiorno Nardelli, M Calandra, R Car, C Cavazzoni, D Ceresoli, M Cococcioni, N Colonna, I Carnimeo, A Dal Corso, S de Gironcoli, P Delugas, R A DiStasio, A Ferretti, A Floris, G Fratesi, G Fugallo, R Gebauer, U Gerstmann, F Giustino, T Gorni, J Jia, M Kawamura, H-Y Ko, A Kokalj, E Küçükbenli, M Lazzeri,

- M Marsili, N Marzari, F Mauri, N L Nguyen, H-V Nguyen, A Otero de-la Roza, L Paulatto, S Poncé, D Rocca, R Sabatini, B Santra, M Schlipf, A P Seitsonen, A Smogunov, I Timrov, T Thonhauser, P Umari, N Vast, X Wu, and S Baroni. Advanced capabilities for materials modelling with quantum ESPRESSO. *Journal of Physics: Condensed Matter*, 29(46):465901, October 2017.
- [18] Angelo Gavezzotti. Are crystal structures predictable? *Accounts of chemical research*, 27(10):309–314, 1994.
- [19] Artem R Oganov, Gabriele Saleh, and Alexander G Kvashnin, editors. *Computational Materials Discovery*. The Royal Society of Chemistry, 2019.
- [20] A R Oganov, C W Glass, A O Lyakhov, Q Zhu, G Qian, H T Stokes, P Bushlanov, Z Allahyari, P Graf, V Stevanovic, F Therrien, S Lepeshkin, and Z H Wang. Universal Structure Predictor: Evolutionary Xtallography, 2019.
- [21] Artem R. Oganov, Chris J. Pickard, Qiang Zhu, and Richard J. Needs. Structure prediction drives materials discovery. *Nature Reviews Materials*, 4(5):331–348, apr 2019.
- [22] Colin W Glass, Artem R Oganov, and Nikolaus Hansen. Uspex—evolutionary crystal structure prediction. *Computer physics communications*, 175(11-12):713–720, 2006.
- [23] Chris J Pickard and RJ Needs. High-pressure phases of silane. *Physical Review Letters*, 97(4):045504, 2006.
- [24] Yanchao Wang, Jian Lv, Li Zhu, and Yanming Ma. CALYPSO: A method for crystal structure prediction. *Computer Physics Communications*, 183(10):2063–2070, 2012.
- [25] Will Tipton and Richard Hennig. GASP: The Genetic Algorithm for Structure and Phase Prediction, 2012.
- [26] David C Lonie and Eva Zurek. XtalOpt: An open-source evolutionary algorithm for crystal structure prediction. *Computer Physics Communications*, 182(2):372–387, 2011.
- [27] RFW Bader and TT Nguyen-Dang. Quantum theory of atoms in molecules—dalton revisited. In *Advances in Quantum Chemistry*, volume 14, pages 63–124. Elsevier, 1981.

- [28] R Briggs, D Daisenberger, OT Lord, Ashkan Salamat, E Bailey, MJ Walter, and PF McMillan. High-pressure melting behavior of tin up to 105 GPa. *Physical Review B*, 95(5):054102, 2017.
- [29] Walker-type module description. <https://www.voggenreiter-gmbh.de/en/services/laboratory-equipment/walker-type-modul/>.
- [30] Christopher J Howard and Harold T Stokes. Group-theoretical analysis of octahedral tilting in perovskites. *Acta Crystallographica Section B: Structural Science*, 54(6):782–789, 1998.
- [31] Motohiko Murakami, Kei Hirose, Katsuyuki Kawamura, Nagayoshi Sata, and Yasuo Ohishi. Post-perovskite phase transition in MgSiO_3 . *Science*, 304(5672):855–858, 2004.
- [32] Artem R Oganov and Shigeaki Ono. Theoretical and experimental evidence for a post-perovskite phase of MgSiO_3 in Earth’s D "layer. *Nature*, 430(6998):445–448, 2004.
- [33] Shigehiko Tatenko, Kei Hirose, Nagayoshi Sata, and Yasuo Ohishi. High-pressure behavior of MnGeO_3 and CdGeO_3 perovskites and the post-perovskite phase transition. *Physics and Chemistry of Minerals*, 32(10):721–725, 2006.
- [34] Shigehiko Tatenko, Kei Hirose, Nagayoshi Sata, and Yasuo Ohishi. Structural distortion of CaSnO_3 perovskite under pressure and the quenchable post-perovskite phase as a low-pressure analogue to MgSiO_3 . *Physics of the Earth and Planetary Interiors*, 181(1-2):54–59, 2010.
- [35] Hiroshi Kojitani, Yuichi Shirako, and Masaki Akaogi. Post-perovskite phase transition in CaRuO_3 . *Physics of the Earth and Planetary Interiors*, 165(3-4):127–134, 2007.
- [36] Yuichi Shirako, Hiroshi Kojitani, Masaki Akaogi, Kazunari Yamaura, and Eiji Takayama-Muromachi. High-pressure phase transitions of CaRhO_3 perovskite. *Physics and Chemistry of Minerals*, 36(8):455, 2009.
- [37] S. N. Bushmeleva, V. Yu Pomjakushin, E. V. Pomjakushina, D. V. Sheptyakov, and A. M. Balagurov. Evidence for the band ferromagnetism in SrRuO_3 from neutron diffraction. *Journal of Magnetism and Magnetic Materials*, 305(2):491–496, 2006.
- [38] Alan Callaghan, Carl W. Moeller, and Roland Ward. Magnetic Interactions in Ternary Ruthenium Oxides. *Inorganic Chemistry*, 5(9):1572–1576, 1966.

- [39] Gertjan Koster, Lior Klein, Wolter Siemons, Guus Rijnders, J. Steven Dodge, Chang-Beom Eom, Dave H. A. Blank, and Malcolm R. Beasley. Structure, physical properties, and applications of SrRuO₃ thin films. *Reviews of Modern Physics*, 84(1):253–298, 2012.
- [40] G. H. Zhong, J. L. Wang, Y. L. Li, Z. Liu, and H. Q. Lin. High-pressure and substitution induced effects in SrRuO₃: First-principles insights. *Journal of Applied Physics*, 109(7):107–110, 2011.
- [41] Yongmao Cai, Yingjin Wei, Xing Ming, Fei Du, Xing Meng, Chunzhong Wang, and Gang Chen. Prediction of the phase transition from ferromagnetic perovskite to non-magnetic post-perovskite in SrRuO₃ : A first-principles study. *Solid State Communications*, 151(10):798–801, 2011.
- [42] J. J. Hamlin, S. Deemyad, J. S. Schilling, M. K. Jacobsen, R. S. Kumar, A. L. Cornelius, G. Cao, and J. J. Neumeier. ac susceptibility studies of the weak itinerant ferromagnet SrRuO₃ under high pressure to 34 GPa. *Physical Review B - Condensed Matter and Materials Physics*, 76(1):1–7, 2007.
- [43] M. K. Jacobsen, R. S. Kumar, G. Cao, J. J. Neumeier, and A. L. Cornelius. High pressure structural studies on SrRuO₃. *Journal of Physics and Chemistry of Solids*, 69(9):2237–2239, 2008.
- [44] Mikhail Zhernenkov, Gilberto Fabbri, Omar Chmaissem, J. F. Mitchell, H. Zheng, and Daniel Haskel. Pressure-induced volume collapse and structural phase transitions in SrRuO₃. *Journal of Solid State Chemistry*, 205:177–182, 2013.
- [45] Martin Schlipf and François Gygi. Optimization algorithm for the generation of ONCV pseudopotentials. *Computer Physics Communications*, 196:36–44, 2015.
- [46] DR Hamann. Optimized norm-conserving vanderbilt pseudopotentials. *Physical Review B*, 88(8):085117, 2013.
- [47] Harold T Stokes and Dorian M Hatch. FINDSYM: program for identifying the space-group symmetry of a crystal. *Journal of Applied Crystallography*, 38(1):237–238, 2005.
- [48] Camilla Hjort Kronbo, Louise Ring Jensen, Francesca Menescardi, Davide Ceresoli, and Martin Bremholm. High-pressure, low-temperature studies of phase transitions in SrRuO₃ – Absence of volume collapse. *Journal of Solid State Chemistry*, 287(April):121360, 2020.

- [49] H. Z. Liu, J. Chen, J. Hu, C. D. Martin, D. J. Weidner, D. Häusermann, and H. K. Mao. Octahedral tilting evolution and phase transition in orthorhombic NaMgF_3 perovskite under pressure. *Geophysical Research Letters*, 32(4):1–5, 2005.
- [50] John P. Perdew, Kieron Burke, and Matthias Ernzerhof. Generalized gradient approximation made simple. *Physical Review Letters*, 77(18):3865–3868, 1996.
- [51] Luis A. Agapito, Stefano Curtarolo, and Marco Buongiorno Nardelli. Reformulation of DFT + U as a pseudohybrid Hubbard density functional for accelerated materials discovery. *Physical Review X*, 5(1):1–16, 2015.
- [52] Kevin J. May and Alexie M. Kolpak. Improved Description of Perovskite Oxide Crystal Structure and Electronic Properties using Self-Consistent Hubbard U Corrections from the ACBN0 Functional. *Physical Review B*, 2019.
- [53] K Dornberger-Schiff. The symmetry and structure of strontium germanate, SrGeO_3 , as a structural model for wollastonite, CaSiO_3 . *Soviet Physics-Crystallography*, 6:694–700, 1962.
- [54] Y Shimizu, Y Syono, and S Akimoto. High-pressure transformations in SrGeO_3 , SrSiO_3 , BaGeO_3 , and BaSiO_3 . *High Temperatures-High Pressures*, 2:113–120, 1970.
- [55] Masaki Akaogi, H. Kojitani, H. Yusa, R. Yamamoto, M. Kido, and K. Koyama. High-pressure transitions and thermochemistry of MGeO_3 (M=Mg, Zn and Sr) and Sr-silicates: Systematics in enthalpies of formation of $\text{A}_2\text{B}_4\text{O}_{13}$ perovskites. *Physics and Chemistry of Minerals*, 32(8-9):603–613, 2005.
- [56] Hexiong Yang and Charles T. Prewitt. On the crystal structure of pseudowollastonite (CaSiO_3). *American Mineralogist*, 84(5-6):929–932, 1999.
- [57] Hexiong Yang and Charles T. Prewitt. Crystal structure and compressibility of a two-layer polytype of pseudowollastonite (CaSiO_3). *American Mineralogist*, 84(11-12):1902–1905, 1999.
- [58] Hiroshi Mizoguchi, Toshio Kamiya, Satoru Matsuishi, and Hideo Hosono. A germanate transparent conductive oxide. *Nature Communications*, 2(1):470–475, 2011.
- [59] Qing Qing Ye, Zhao Kui Wang, Igbari Femi, Kai Li Wang, Yue Zhang, Xing Juan Ma, Ming Peng Zhuo, and Liang Sheng Liao. A SrGeO_3 inorganic electron-transporting layer for high-performance perovskite solar cells. *Journal of Materials Chemistry A*, 7(24):14559–14564, 2019.

- [60] Waltraud Hilmer. Zur Strukturbestimmung von Strontiumgermanat SrGeO_3 . *Naturwissenschaften*, 45(10):238–239, 1958.
- [61] W Hilmer. An X-ray investigation of strontium germanate SrGeO_3 . *Soviet Physics-Crystallography*, 7:573–576, 1963.
- [62] Fumito Nishi. Strontium metagermanate, SrGeO_3 . *Acta Crystallographica Section C: Crystal Structure Communications*, 53(4):399–401, 1997.
- [63] Hitoshi Yusa, Masaki Akaogi, Nagayoshi Sata, Hiroshi Kojitani, Yoshitaka Kato, and Yasuo Ohishi. Unquenchable hexagonal perovskite in high-pressure polymorphs of strontium silicates. *American Mineralogist*, 90(5-6):1017–1020, 2005.
- [64] Wansheng Xiao, Dayong Tan, Wei Zhou, Jing Liu, and Jian Xu. Cubic perovskite polymorph of strontium metasilicate at high pressures. *American Mineralogist*, 98(11-12):2096–2104, 2013.
- [65] Madison C. Barkley, Robert T. Downs, and Hexiong Yang. Structure of walstromite, $\text{BaCa}_2\text{Si}_3\text{O}_9$, and its relationship to CaSiO_3 -walstromite and wollastonite-II. *American Mineralogist*, 96(5-6):797–801, 2011.
- [66] Camilla H Kronbo, Francesca Menescardi, Davide Ceresoli, and Martin Bremholm. High pressure structure studies of three SrGeO_3 polymorphs—Amorphization under pressure. *Journal of Alloys and Compounds*, 855:157419, 2020.
- [67] Artem R. Oganov. Crystal structure prediction: reflections on present status and challenges. *Faraday Discussions*, 211:643–660, 2018.
- [68] Emilio Artacho, E Anglada, O Diéguez, J D Gale, A García, J Junquera, R M Martin, P Ordejón, J M Pruneda, D Sánchez-Portal, and J M Soler. The SIESTA method; developments and applicability. *Journal of Physics: Condensed Matter*, 20(6):064208, January 2008.
- [69] David Vanderbilt. Soft self-consistent pseudopotentials in a generalized eigenvalue formalism. *Physical review B*, 41(11):7892, 1990.
- [70] Kevin F. Garrity, Joseph W. Bennett, Karin M. Rabe, and David Vanderbilt. Pseudopotentials for high-throughput DFT calculations. *Computational Materials Science*, 81:446–452, January 2014.
- [71] S A Gramsch, C T Prewitt, and V E Lee. Crystal Chemistry of SrGeO_3 at High Pressure. pages 1–3.

- [72] A. Hachemi, H. Hachemi, A. Ferhat-Hamida, and L. Louail. Elasticity of SrTiO_3 perovskite under high pressure in cubic, tetragonal and orthorhombic phases. *Physica Scripta*, 82(2), 2010.
- [73] Youguo Shi, Yanfeng Guo, Xia Wang, Andrew J. Princep, Dmitry Khalyavin, Pascal Manuel, Yuichi Michiue, Akira Sato, Kenji Tsuda, Shan Yu, Masao Arai, Yuichi Shirako, Masaki Akaogi, Nanlin Wang, Kazunari Yamaura, and Andrew T. Boothroyd. A ferroelectric-like structural transition in a metal. *Nature Materials*, 12(11):1024–1027, 2013.
- [74] T. H. Kim, D. Puggioni, Y. Yuan, L. Xie, H. Zhou, N. Campbell, P. J. Ryan, Y. Choi, J. W. Kim, J. R. Patzner, S. Ryu, J. P. Podkaminer, J. Irwin, Y. Ma, C. J. Fennie, M. S. Rzchowski, X. Q. Pan, V. Gopalan, J. M. Rondinelli, and C. B. Eom. Polar metals by geometric design. *Nature*, 533(7601):68–72, 2016.
- [75] Ronghan Li, Yuanfeng Xu, Jianggang He, Sami Ullah, Jiangxiu Li, Jun-Ming Liu, Dianzhong Li, Cesare Franchini, Hongming Weng, and Xing-Qiu Chen. Weyl Ferroelectric Semimetal. *arXiv*, pages 1–9, 2016.
- [76] Jie Chen, Yoshitaka Matsushita, Taras Kolodiazhnyi, Alexei A. Belik, Yoshihiro Tsujimoto, Yoshio Katsuya, Masahiko Tanaka, Yu Su, Youguo Shi, and Kazunari Yamaura. High-Pressure Synthesis, Crystal Structure, and Semimetallic Properties of HgPbO_3 . *Inorganic Chemistry*, 57(13):7601–7609, 2018.
- [77] A. W. Sleight and C. T. Prewitt. High-pressure HgTiO_3 and HgPbO_3 : Preparation, characterization, and structure. *Journal of Solid State Chemistry*, 6(4):509–512, 1973.
- [78] Alexander I. Lebedev. First-principles study of ferroelectricity and pressure-induced phase transitions in HgTiO_3 . *Phase Transitions*, 86(5):442–453, 2013.
- [79] Hugh O Pierson. *Handbook of Refractory Carbides & Nitrides: Properties, Characteristics, Processing and Apps*. William Andrew, 1996.
- [80] Xiao-Jia Chen, Viktor V Struzhkin, Zhigang Wu, Maddury Somayazulu, Jiang Qian, Simon Kung, Axel Nørhlund Christensen, Yusheng Zhao, Ronald E Cohen, Ho-kwang Mao, et al. Hard superconducting nitrides. *Proceedings of the National Academy of Sciences*, 102(9):3198–3201, 2005.
- [81] Wei-Fu Chen, James T Muckerman, and Etsuko Fujita. Recent developments in transition metal carbides and nitrides as hydrogen evolution electrocatalysts. *Chemical communications*, 49(79):8896–8909, 2013.

- [82] Qinghong Zhang and Lian Gao. Ta₃N₅ nanoparticles with enhanced photocatalytic efficiency under visible light irradiation. *Langmuir*, 20(22):9821–9827, 2004.
- [83] Ashkan Salamat, Andrew L Hector, Peter Kroll, and Paul F McMillan. Nitrogen-rich transition metal nitrides. *Coordination Chemistry Reviews*, 257(13-14):2063–2072, 2013.
- [84] Gudrun Auffermann, Yurii Prots, and Rüdiger Kniep. SrN and SrN₂: Diazenides by synthesis under high N₂-pressure. *Angewandte Chemie - International Edition*, 40(3):547–549, 2001.
- [85] Grigori V Vajenine, Gudrun Auffermann, Yurii Prots, Walter Schnelle, Reinhard K Kremer, Arndt Simon, and Rüdiger Kniep. Preparation, crystal structure, and properties of barium pernitride, BaN₂. *Inorganic chemistry*, 40(19):4866–4870, 2001.
- [86] Jörg von Appen, Marck-Willem Lumey, and Richard Dronskowski. Mysterious platinum nitride. *Angewandte Chemie International Edition*, 45(26):4365–4368, 2006.
- [87] Jun Yang, Faming Gao, Haiyan Wang, Huiyang Gou, Xianfeng Hao, and Zhiping Li. Elastic properties and hardness calculations of lanthanide nitrides in rocksalt structure. *Materials Chemistry and Physics*, 119(3):499–504, feb 2010.
- [88] Morten B. Nielsen, Davide Ceresoli, Jens-Erik Jørgensen, Clemens Prescher, Vitali B. Prakapenka, and Martin Bremholm. Experimental evidence for pressure-induced first order transition in cerium nitride from B1 to B10 structure type. *Journal of Applied Physics*, 121(2):025903, jan 2017.
- [89] Emma Ehrenreich-Petersen, Morten B. Nielsen, and Martin Bremholm. Experimental equation of state of 11 lanthanide nitrides (ndn to lun) and pressure induced phase transitions in ndn, smn, eun, and gdn. *Journal of Applied Physics*, 128(13):135902, 2020.
- [90] Lü Tie-Yu and Huang Mei-Chun. Electronic structure of ScN and YN: density-functional theory LDA and GW approximation calculations. *Chinese Physics*, 16(1):62–66, dec 2006.
- [91] Michael Wessel and Richard Dronskowski. Nature of N-N bonding within high-pressure noble-metal pernitrides and the prediction of lanthanum pernitride. *Journal of the American Chemical Society*, 132(7):2421–2429, 2010.

- [92] Stefano Baroni, Stefano de Gironcoli, Andrea Dal Corso, and Paolo Giannozzi. Phonons and related crystal properties from density-functional perturbation theory. *Reviews of Modern Physics*, 73(2):515–562, July 2001.
- [93] Yongliang Guo, Cun Yu, Jun Lin, Changying Wang, Cuilan Ren, Baoxing Sun, Ping Huai, Ruobing Xie, Xuezhi Ke, Zhiyuan Zhu, and Hongjie Xu. Pressure-induced structural transformations and polymerization in ThC_2 . *Scientific Reports*, 7(March):2–11, 2017.
- [94] F. R. Wagner, D. Bende, and Yu. Grin. Heteropolar bonding and a position-space representation of the 8 - n rule. *Dalton Trans.*, 45:3236–3243, 2016.
- [95] Carlos Outeiral, Mark A. Vincent, Ángel Martín Pendás, and Paul L. A. Popelier. Revitalizing the concept of bond order through delocalization measures in real space. *Chem. Sci.*, 9:5517–5529, 2018.
- [96] Zhen-Hua Wang, Xiao-Yu Kuang, Ming-Min Zhong, Peng Lu, Ai-Jie Mao, and Xiao-Fen Huang. Pressure-induced structural transition of OsN_2 and effect of metallic bonding on its hardness. *EPL (Europhysics Letters)*, 95(6):66005, sep 2011.
- [97] Javier A. Montoya, Alexander D. Hernandez, Chrystèle Sanloup, Eugene Gregoryanz, and Sandro Scandolo. OsN_2 : Crystal structure and electronic properties. *Applied Physics Letters*, 90(1):011909, jan 2007.
- [98] Francis Birch. Finite elastic strain of cubic crystals. *Phys. Rev.*, 71:809–824, Jun 1947.
- [99] R. Wehrich, V. Eyert, and S. F. Matar. Structure and electronic properties of new model dinitride systems: A density-functional study of CN_2 , SiN_2 , and GeN_2 . *Chemical Physics Letters*, 373(5-6):636–641, 2003.
- [100] Zhi-Jian Wu, Er-Jun Zhao, Hong-Ping Xiang, Xian-Feng Hao, Xiao-Juan Liu, and Jian Meng. Crystal structures and elastic properties of superhard IrN_2 and IrN_3 from first principles. *Phys. Rev. B*, 76:054115, Aug 2007.
- [101] Ross J. Angel, Matteo Alvaro, and Javier Gonzalez-Platas. Eosfit7c and a fortran module (library) for equation of state calculations. *Zeitschrift für Kristallographie - Crystalline Materials*, 229(5):405 – 419, 01 May. 2014.
- [102] Y. M. Shy, L. E. Toth, and R. Somasundaram. Superconducting properties, electrical resistivities, and structure of NbN thin films. *Journal of Applied Physics*, 44(12):5539–5545, dec 1973.

- [103] Shanmin Wang, Daniel Antonio, Xiaohui Yu, Jianzhong Zhang, Andrew L. Cornelius, Duanwei He, and Yusheng Zhao. The hardest superconducting metal nitride. *Scientific Reports*, 5(1), sep 2015.
- [104] Dmitrii V. Semenok, Ivan A. Kruglov, Igor A. Savkin, Alexander G. Kvashnin, and Artem R. Oganov. On distribution of superconductivity in metal hydrides. *Current Opinion in Solid State and Materials Science*, 24(2):100808, apr 2020.
- [105] Antoine Georges, Gabriel Kotliar, Werner Krauth, and Marcelo J. Rozenberg. Dynamical mean-field theory of strongly correlated fermion systems and the limit of infinite dimensions. *Rev. Mod. Phys.*, 68:13–125, Jan 1996.
- [106] Brian Boates and Stanimir A Bonev. Electronic and structural properties of dense liquid and amorphous nitrogen. *Physical Review B*, 83(17):174114, 2011.
- [107] Eduard Matito, Miquel Solà, Pedro Salvador, and Miquel Duran. Electron sharing indexes at the correlated level. application to aromaticity calculations. *Faraday Discuss.*, 135:325–345, 2007.
- [108] Francesca Menescardi, Emma Ehrenreich-Petersen, and Davide Ceresoli. High pressure computational search of trivalent lanthanide di-nitrides. *arXiv preprint arXiv:2012.09576*, 2020.
- [109] Ding Peng and Philip N. H. Nakashima. Measuring density functional parameters from electron diffraction patterns, 2020.
- [110] I. A. Kibalin, Z. Yan, A. B. Voufack, S. Gueddida, B. Gillon, A. Gukasov, F. Porcher, A. M. Bataille, F. Morini, N. Claiser, M. Souhassou, C. Lecomte, J.-M. Gillet, M. Ito, K. Suzuki, H. Sakurai, Y. Sakurai, C. M. Hoffmann, and X. P. Wang. Spin density in YTiO_3 : I. joint refinement of polarized neutron diffraction and magnetic x-ray diffraction data leading to insights into orbital ordering. *Physical Review B*, 96(5), August 2017.
- [111] Masys and V. Jonauskas. On the crystalline structure of orthorhombic SrRuO_3 : A benchmark study of DFT functionals. *Computational Materials Science*, 124:78–86, 2016.
- [112] S. Kunkemöller, K. Jenni, D. Gorkov, A. Stunault, S. Streltsov, and M. Braden. Magnetization density distribution in the metallic ferromagnet SrRuO_3 determined by polarized neutron diffraction. *Phys. Rev. B*, 100:054413, Aug 2019.
- [113] A. Otero de-la Roza, Erin R. Johnson, and Víctor Luaña. Critic2: A program for real-space analysis of quantum chemical interactions in solids. *Computer Physics Communications*, 185(3):1007–1018, mar 2014.

- [114] Luis A. Agapito, Marco Fornari, Davide Ceresoli, Andrea Ferretti, Stefano Curtarolo, and Marco Buongiorno Nardelli. Accurate tight-binding hamiltonians for two-dimensional and layered materials. *Phys. Rev. B*, 93:125137, Mar 2016.
- [115] Marco Buongiorno Nardelli, Frank T. Cerasoli, Marcio Costa, Stefano Curtarolo, Riccardo De Gennaro, Marco Fornari, Laalitha Liyanage, Andrew R. Supka, and Haihang Wang. PAOFLOW: A utility to construct and operate on ab initio hamiltonians from the projections of electronic wavefunctions on atomic orbital bases, including characterization of topological materials. *Computational Materials Science*, 143:462–472, feb 2018.
- [116] Z. Yan, I. A. Kibalin, N. Claiser, S. Gueddida, B. Gillon, A. Gukasov, A. B. Voufack, F. Morini, Y. Sakurai, M. Brancewicz, M. Itou, M. Itoh, N. Tsuji, M. Ito, M. Souhassou, C. Lecomte, P. Cortona, and J.-M. Gillet. Spin density in YTiO_3 : II. momentum-space representation of electron spin density supported by position-space results. *Physical Review B*, 96(5), August 2017.
- [117] N. K. Hansen and P. Coppens. Testing aspherical atom refinements on small-molecule data sets. *Acta Crystallographica Section A*, 34(6):909–921, nov 1978.
- [118] C. J. Gilmore, K. Shankland, and G. Bricogne. Applications of the maximum entropy method to powder diffraction and electron crystallography. *Proceedings: Mathematical and Physical Sciences*, 442(1914):97–111, 1993.
- [119] Anatoliy Volkov, Carlo Gatti, Yuriy Abramov, and Philip Coppens. Evaluation of net atomic charges and atomic and molecular electrostatic moments through topological analysis of the experimental charge density. *Acta Crystallographica Section A Foundations of Crystallography*, 56(3):252–258, may 2000.
- [120] Carlo Gatti, Gabriele Saleh, and Leonardo Lo Presti. Source function applied to experimental densities reveals subtle electron-delocalization effects and appraises their transferability properties in crystals. *Acta Crystallographica Section B Structural Science, Crystal Engineering and Materials*, 72(2):180–193, apr 2016.
- [121] Niccolò Traverso Ziani, Luca Vannucci, and Maura Sasseti. Topological insulators: a beautiful revolution. *Il Nuovo Saggiatore*, 34(1–2):13–30, feb 2018.