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FACULTE DES SCIENCES
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THEME

Etude de propriétés structurale, électronique et mécanique des borures de lanthane LaBx (x=4, 6) par la méthode de la DFT

Soutenu publiquement devant le jury composé de :

Mr. LAGOUN Brahim	M.C.B	*Président*
Mr. HANIFI Mebarki	M.A.A	*Examinateur*
Mr. ARAR.Rabie	M.C.B	*Rapporteur*

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Option : Material physics

by:

- *Daoudi Youcef*

THEME

Study of structural, electronic and mechanical properties of lanthanum borides LaB_X (x = 4, 6) by the DFT method

Sustained before a jury composed of:

Mr. LAGOUN Brahim	M.C.B	*President*
Mr. HANIFI Mebarki	M.A.A	*Examiner*
Mr. ARAR Rabie	M.C.B	*Rapporteur*

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Dedication

Dedicate this work to my precious parents, and my family

Dedicate to all my wonderful teachers and professors

Dedicate to all my friends

Dedicate to …

ACKNOWLEDGEMENTS

First thanks are to Allah, we praise him and to inspire the patients in this research.

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Introduction

Introduction

The metal in pure case, characterized by his huge malleability what makes it easy to erosion, in addition to the ease of oxidation. But the metals have excellent electrical conductivity and this is a very important factor[1] and almost quotidian life fields are based on this property, especially technology field. The Boronizing is one of the main processes used to treat this side which is a thermos-chemical process that will increase the surface hardness of the metal and its resistance to erosion, there are other operations for processing as nitriding and carbonization and others…[2].

Rare-earth metals are chemical elements characterized by large electrical conductivity but also the fragility is an attendant problem[3][4], Lanthanum is one of these elements, it has great importance in the electronic devices such as the microscopes specifically as electrons gun, and strength sensor; that is not in its pure state, but after introducing Boron atoms through it, it become more and more hardness. The LaB_6 crystal was the subject of several studies to determine its physical properties [5] making it one of the most famous and widely used, unlike the LaB_4 crystal.

In this work, we took upon ourselves the investigation of Boriding (Boronizing) effect on rare earth metal which is the Lanthanum (La), which is the principle objective of this work. this investigation based on the first principal calculations (Density Functional Theory (DFT) and the density functional perturbation theory) implemented into ABINIT code which uses plane waves and pseudopotentials (PW-PP) to describe the wavefunctions.

The secondary objective is to have control even partially the DFT theory, in addition, to master ABINIT calculation code.

This thesis is organized as follows:

The first chapter: is dedicated to show the importance of Boronizing in industry field, rare earth metals and their properties especially pure Lanthanum and his borides.

The second chapter: we collect the most important demarches and basics going on the Density Functional Theory (DFT) and the density functional perturbation theory (DFPT).

The third chapter: is devoted to our calculation results, starting from the convergence study, the structural optimization, to get to the end to calculate, discuss and compare the electronic and mechanical properties with other works.

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Chapter I

Lanthanum borides

I. Lanthanum borides

I.1. Introduction:

Metallic materials are the oldest materials man has synthesized and used. They are characterized by metallic bonds where the valence electrons are virtually free to flow through the metal. These mobile electrons are responsible for the good properties of thermal and electrical conductivity and their shiny appearance.

The melting temperature of these materials is relatively high. They are mostly relatively ductile and tough. The combination of their toughness (tenacity) and ductility is a major asset for their formatting. Against, they are often sensitive to corrosion. Moreover, because of their plasticity, their fatigue resistance can cause problems. Finally, metals are generally heavy and dense materials, which can be a handicap.[1]

Several studies have been conducted to improve the properties of these surfaces alloys mechanically, physicochemical and tribological. Therefore, the Surface treatments such as Boriding, nitriding, carburizing and carbonitriding are applied to meet these requirements on an industrial scale.[2]

I.2. Lanthanum:

Lanthanum is a soft, ductile, silvery-white metallic chemical element with symbol La and atomic number 57. It tarnishes rapidly when exposed to air and is soft enough to be cut with a knife. It gave its name to the lanthanide series, a group of 15 similar elements between lanthanum and lutetium in the periodic table: it is also sometimes considered the first element of the 6th-period transition metals. Lanthanum is usually found in combination with cerium and other rare earth elements.

Lanthanum has a hexagonal crystal structure at room temperature. At 310 °C, lanthanum changes to a face-centered cubic structure. At 865 °C, it changes to a body-centered cubic structure.[3] Lanthanum is easily oxidized.

I.3. Boriding (Boronizing):

Boriding, also called Boronizing is a thermochemical surface treatment which boron is introduced to a metal or alloy. It is a type of surface hardening. In this process boron atoms are diffused into the surface of a metal component[4]. Like other treatments involving diffusion, the substrate to be treated must be in contact with a boronaceous substance in the form of a solid powder, paste, liquid, or gas and held at high temperatures (700–1,200°C)[5], The resulting surface contains metal borides which have interesting physicochemical properties, mechanical and tribological[2].

I.4. Rare earth borides:

Borides are one of the most important types of refractory compounds widely used in various engineering fields. They are interstitial phase compounds which are characterized by the fact that boron atoms can form direct B-B bonds in the lattice because of their size.

The maximum number of boride phases with various boron contents is formed by the rare earth metals and by the transition metals of the III-VIII groups which can occupy various valence states associated with the overlap of d, f, p and s orbitals. When borides are formed, at the moment of atomic interaction the state of the valence electrons changes. The atomic electrons of simple substances undergo a transition from the s, d and f states to the p states of boron; with the formation of s^xp^y configurations which have a high degree of stability. It is possible that both because of one electron s-p transitions ($s^2p \rightarrow sp^2$) and because of electron interchange between boron atoms ($sp^2 + sp^2 \rightarrow sp^3 + sp$), redistribution of the valence electrons occurs with the formation of sp^2 and sp^3 electron configurations which are typical of rigid covalent states.[6]

During the last three decades, a large interest has developed in the field of rare earth borides. Six different families have been discovered: REB_2, REB, REB_4, REB_6, and REB_{12}, REB_{66}(where 'RE' represents a rare earth metal). Their extension is discussed, and it is shown on the base of both geometrical and electronic considerations how the RE atoms contribute to the stabilization of the electron-deficient boron framework [7]. A wide range of the fascinating physical properties of the rare-earth borides is considered, including insulator-metal transitions, superconductivity, mixed valence behavior, magnetic phase transitions and thermoelectric properties [7]. Our study was based on this end of study memory on MB_x (x:4,6, M: La).

investigation of the basic physical properties of a series of lanthanide hexaborides such as structural, elastic, and electronic properties is necessary and offers credible references for their various applications.

I.5. Previous works on borides Lanthanum:

The band structure of metal hexaborides Arko et al in 1975 mentioned in [8] were the first to carry out a quantitative calculation of the band structure of LaB6, By means of the discrete variational method, concluding that the La-B atomic bonding was covalent and more significant to overall bonding than La-La interactions. in 1976, An explanation of conflicting conclusions drawn by Tanaka et *al* [9] concerning the ionic nature of the charge transfer between La and B atoms. After LaB6 and YB6 were studied by ab initio in 1977[10]. In later work, Hasegawa and Yanase [8] use a non-relativistic, symmetrized augmented plane wave (APW) method to calculate the band structure of LaB6. An interesting point mentioned by Hasegawa and Yanase, is that the six s states of the B atoms in an octahedron, as well as the six p states of these B atoms, form together d-like orbitals retaining some of the symmetry about the B6 octahedral center. These d-like orbitals and the La d state have nearly equal energies in LaB6, and therefore, strong hybridization occurs. The actual bonding of LaB6 could at best be described as uncertain, in 2005 M. Hossain and *al* [11] calculated result revealed the coexistence of covalent, ionic, and metallic bonding in the LaB6 system and partially explains its high efficiency as a thermionic emitter.

in 1977, Measurements have been made of the transit times of pulses of longitudinal and transverse ultrasonic waves propagating in single crystal LaB6 at room temperature by T Tanaka and *al* [12], which aim to calculate the elastic constants of this crystal. a high pressure x-ray power diffraction technique is used to do a compressibility studies of LaB6 by Torsten Lundstrom, Bertil Lonnberg and Bert Torma in 1982 [13]. T. Gürel1 and R. Eryiğit in 2010 [14] have performed an ab initio study of structural, elastic, lattice dynamical, and thermodynamical properties of LaB6 crystal, their calculations have been carried out within the density functional theory and linear response function using pseudo potentials and a plane-wave basis.

Tetraborides of rare earth elements, REB_4 present unusual magnetic, electronic and lattice properties. The metallic type of conductivity is characteristic to rare earth tetraborides.

These properties of heavy rare earth element tetraborides have been the subject of numerous studies [15] [16], However, fewer studies exist of the properties of light RE-tetraborides (beginning with LaB_4) was focused on magnetic, and thermodynamic properties, tetraborides of RE elements are hard and high melting compounds .

Lanthanum tetraborides were obtained from the mixture of its hexaboride and metallic lanthanum by melting it in an electric arc surrounded by argon: 2LaB6 + La = 3LaB4.

I.6. Crystalline structure:

I.6.1. Lanthanum hexaboride LaB_6:

Lanthanum hexaboride crystallizes in a simple cubic structure exactly in space group number: 221: Pm-3m), The lattice parameters of Lanthanum hexaborides crystal are $a = b = c = 4.1572\,A°$, with angles $\alpha = \beta = \gamma = \pi / 2$.[17]

with six Boron atoms forms octahedron in body-centered position, and Lanthanum ions located at the corners of the unit cell as showing next figureII-2, like we see every boron atom surrounding by 8 atoms, the nearest 4 atoms are boron elements who interatomic distance B-B is about $d_{B\text{-}B}$ =1.767 °A which forms short distance bond, it has covalent bond character; the other 4 atoms present in the surroundings boron atom are Lanthanum atoms who separate by distance $d_{B\text{-}La}$=3.051°A.

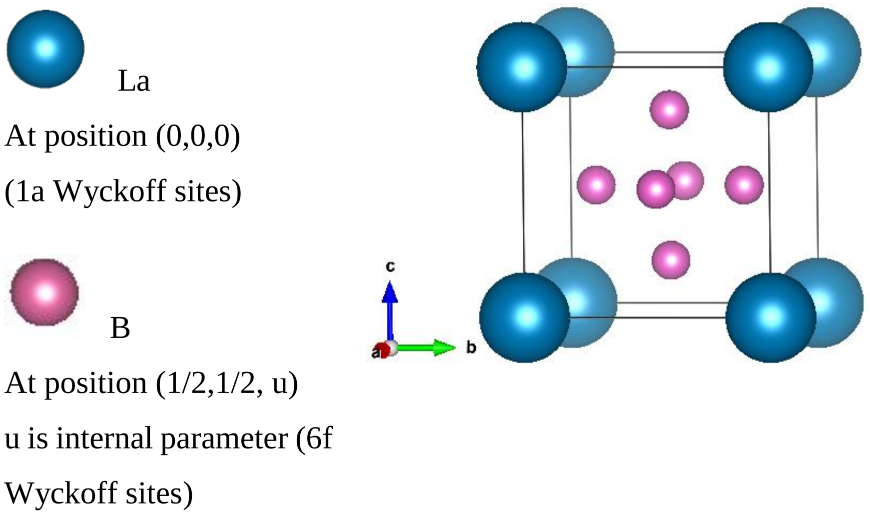


Figure I- 1: Lanthanum hexaboride crystal structure

an important consequence when we see the super cell **Figure I-2**, that the interatomic distance B-B is smaller between adjacent cells (is about 1.65° A) comparing with the others inside the cell, who are positioned in **a**, **b**, **c**, this make us await a big stiffness on those axes.

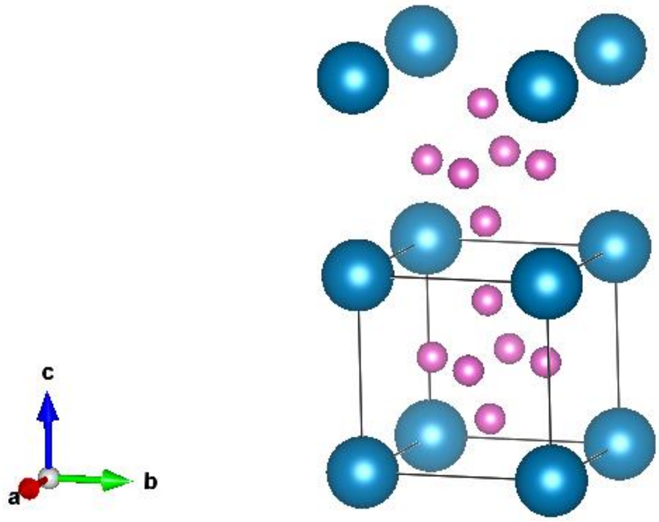


***Figure I- 2** super cell of LaB6 crystal.*

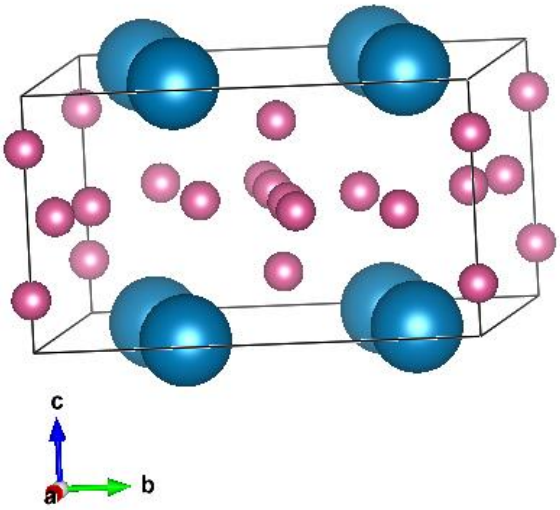
I.6.2. Lanthanum tetraborides LaB_4:

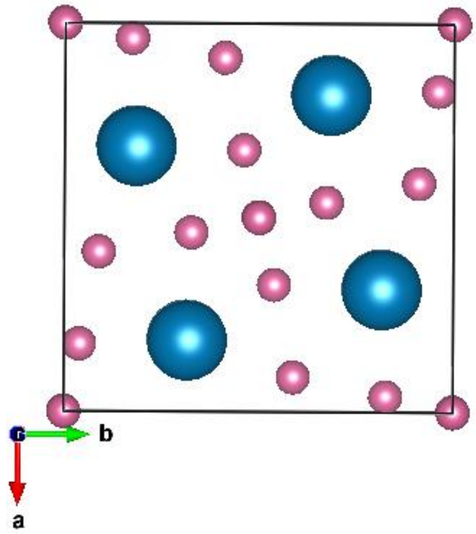
Lanthanum tetraborides are more complicated than Lanthanum hexaboride, LaB4 crystalizes in tetragonal system in group space number :127 (P 4/m b m). The lattice parameters of Lanthanum tetraborides crystal are $a = b = 7.324\,A°$, $c = 4.181\,A°$, with angles $\alpha = \beta = \gamma = \pi / 2$.[18]

There are twenty atoms in a conventional cell, four Lanthanum atoms sixteen Boron atoms in the positions shown in the table. it exists 4 different distances B-B. Two atoms in the lateral rib of cell Separated by distance d_1=2.4608 °A, nearest one is a boron atom at distance d_2=1.902 ° A, this last situated at d_3=1.7748°A to other which participate in making a small octahedron in the center of cell, the interatomic distances B-B forms octahedron are d_4=1.839°A and La-B interatomtic distances are in the average d=2.956 °A, B-B bonds ih this compound between short distance, and long distnace , we remark also the big number of Boron atoms in the plane in the plane XY.

Figure I- 3: Lanthanum tetraborides crystal structure

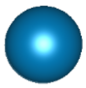
(a) Full 3D view to Lanthanum tetraborides crystal structure.





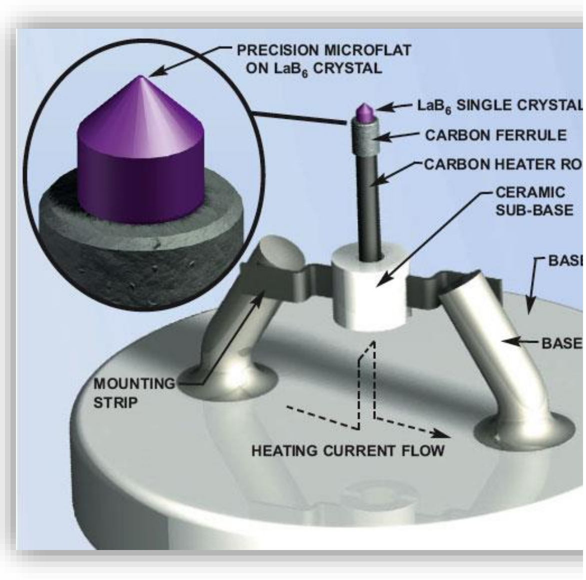
(a) **(b)**

(b) XY plane view to Lanthanum tetraborides crystal structure.

 La	 B	 B
At positions:	At positions:	At positions:
(0.3166 0.8166 0.0000)	(0.0000 0.0000 0.2088)	(0.1743 0.0394 0.5000)
(0.8166 0.6834 0.0000)	(0.5000 0.5000 0.7912)	(0.6743 0.4606 0.5000)
(0.6834 0.1834 0.0000)	(0.0000 0.0000 0.7912)	(0.8257 0.9606 0.5000)
(0.1834 0.3166 0,0000)	(0.5000 0.5000 0.2088)	(0.3257 0.5394 0.5000)
	(0.0884 0.5884 0.5000)	(0.5394 0.6743 0.5000)
	(0.5884 0.9116 0.5000)	(0.0394 0.8257 0.5000)
	(0.9116 0.4116 0.5000)	(0.9606 0.1743 0.5000)
	(0.4116 0.0884 0.5000)	(0.4606 0.3257 0.5000)

I.7. Application:

Several powder diffraction reference materials have been developed by the National Institute of Standards and Technology NIST, including lanthanum hexaboride (LaB6 NIST SRM–660a), it is widely used as a standard reference material for calibrating the line position and line shape parameters of powder diffraction instruments [11]. Amongst other work, precise measurement of the LaB6 lattice spacing using synchrotron radiation [19] usage of these materials includes areas such as field electron emitters, electrical coatings for resistors, transition metal catalysts, high energy optical systems, and sensors for high-resolution detectors[20-22].



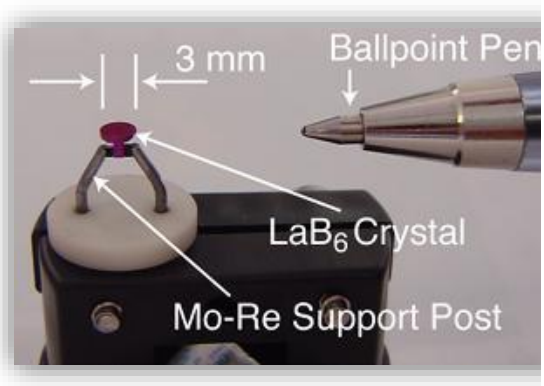


Figure I- 4: Single crystal lanthanum hexaboride (LaB6) cathodes of microscopes

Additional favorable hexaboride properties include durability, extreme hardness,[12] and resistance to corrosive solutions and to moderately high temperatures in oxidizing atmosphere[10].

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Chapter II

Ab-initio methods

II. Ab-initio methods

II.1. Introduction:

The physical properties of a solid system, illustrated by the image of light electrons moving around heavy nuclei depend on the behavior of its electronic structure. Quantum mechanics provides the ideal setting for this study, in practice, the potential suffered by each electron is imposed by the movement not only of the closest neighbors but also by all other electrons of the real system. This would require the solution of a Schrödinger equation with equations ~ 10^{23} simultaneous differential. In general, it is not possible to solve this equation and the use of approximations is required. In the following chapter, we will strive to follow the path with the drive of the various approaches ultimately leading to the formulation and implementation of the density of functional theory (DFT) [1].

II.2. Schrodinger equation of a solid system:

A full description of a quantum system with N electrons requires calculation of the corresponding wave function Ψ. In principle, this can be obtained from the equation independent Schrödinger of the time (when the spin is omitted here for calculus simplicity).

$$H\,\Psi = E\,\Psi \qquad \text{II-(1)}$$

Where H is Hamiltonian operator given by equation n°:

$$H = T_N + T_e + U_{ee} + U_{Ne} + U_{NN} \qquad \text{II-(2)}$$

With:

T_N : the kinetic energy of the nuclei.

T_e : the kinetic energy of the electrons.

U_{ee} : potential energy of electron-electron repulsion.

U_{Ne} : potential energy of attraction between nuclei and electrons.

U_{NN} : potential energy of repulsion nucleus-nucleus.

And:

E: Hamiltonian eigenvalue, it stands for system total energy.

Ψ : Hamiltonian proper function, its which depends on the spatial coordinates of nuclei and electrons. $\Psi : \Psi\left(\{\vec{R}_i\},\{\vec{r}_i\}\right)$

We used for the equations of quantum mechanics atomic units which are summarized in the following table, and this will not create problems.

Table II- 1: The atomic units and IS units for quantities used in calculation

Quantity	Symbol	IS unit	Atomic unit
Electron mass	m_e	$9.10938 \times 10^{-31} kg$	$1\ au$
Electron charge	e	$1.60218 \times 10^{-19} C$	$1\ au$
Reduced Plank constant	$\hbar$	$1.05457 \times 10^{-34}\ j.s$	$1\ au$
length	$a_0 = \frac{h^2 \varepsilon_0}{\pi m_e e^2}$	$0.52918 \times 10^{-10} A^{\circ}$	$1\ au = 1\ Bohr$
energy	$E_0 = \frac{\hbar^2}{m_e . a_0^2}$	$4.35974 \times 10^{-18}\ j$	$1\ au = 1\ Hartree$

.

Well in atomic units, the Hamiltonian of system writing as fellow:

$$H = -\frac{1}{2}\sum_{j=1}^{N}\frac{1}{M_j}\nabla_j^2 - \frac{1}{2}\sum_{i=1}^{Ne}\frac{1}{M_i}\nabla_i^2 - \sum_{j=1}^{N}\sum_{i=1}^{Ne}\frac{Z_j}{\left|\vec{R}_j - \vec{r}_i\right|} + \sum_{i=1}^{Ne}\sum_{k>i}^{Ne}\frac{1}{\left|\vec{r}_k - \vec{r}_i\right|} + \sum_{j=1}^{N}\sum_{l>j}^{N}\frac{Z_j}{\left|\vec{R}_l - \vec{R}_j\right|} \qquad \text{II-(3)}$$

With:

M_j : j^th^ nucleus mass.

Z_j : j^th^ nucleus charge.

$\vec{R}_j$: j^th^ nucleus vector position.

$\vec{r}_i$: i^th^ electron vector position.

II.3. Born – Oppenheimer approximation:

The resolution of equation II-(1) required approximations, in 1927 the two scientists Born and Oppenheimer made this first approximation, which is also called adiabatic approximation when they supposed that the motion of atomic nuclei and electrons in a molecule can be separated[2], mathematically it allows the wave function:

$$\Psi\ (\vec{R},\vec{r}) = \Phi_N(\vec{R}) \times \Psi_e(\vec{r}) \qquad \text{II-(4)}$$

The fact that the nuclei are much heavier than electrons (the mass of a proton or neutron is approximately 1836 times as large as the electron mass), therefore, it is evident that the nuclei move is much slower than that of electrons. In other words, the nuclei appear motionless to electrons. If the nuclei are motionless, their kinetic energies are neglected and the interaction between the nuclei becomes constant, so electrons moving in a rigid lattice of nuclear constant potential; then solve system of equations following:

$$H_e \Psi_e(\vec{r}, \vec{R}) = E_{elec} \Psi_e(\vec{r}, \vec{R}) \quad \text{II-(5)}$$

$$H_N \Phi_N(\vec{R}) = E_{nucl} \Phi_N(\vec{R}) \quad \text{II-(6)}$$

Where H_e and H_N are respectively the electronic Hamiltonian and the nuclei Hamiltonian given as:

$$\begin{aligned} H_e &= T_e + U_{ee} + U_{Ne} \\ H_N &= T_N + E(\vec{R}) \end{aligned} \quad \text{II-(7)}$$

E(R) is the functional electronic energy which defines the potential energy surface of the cores.

When the total energy is:

$$E_{tot} = E_{elec} + E_{nucl} \quad \text{II-(8)}$$

And:

$$E_{elec} = \sum_{i=1}^{Ne} \varepsilon_i \quad \text{II-(9)}$$

ε_i it is the energy of the ith electron.

II.4. Hartree approximation:

In 1928 Hartree[3] proposed the second approximation which is the ground-state wave function of the many-body system is expressed as simple product of orthonormalized one electron spin-orbitals in the form:

$$\Psi_e(\{\vec{r}_i\}, \{\vec{R}_j\}) = \prod_{i=1}^{Ne} \Psi_e(\vec{r}_i) \quad \text{II-(10)}$$

Some consequences of this hypothesis:

- Obviously that the simple Hartree product (10) does not have the correct antisymmetric character for the interchange of space and spin coordinates of any two electrons.

- the Pauli principle is not respected, avoiding multiple occupancies of any given spin-orbital.
- Colombian repulsion is overestimated because the electron interacts with himself.
- Furthermore, a simple product of type (10) completely neglects any correlation in the position of the electrons.

The Schrödinger equation is writing:

$$H_H \Psi_e(\vec{r}_i) = \varepsilon_i \Psi_e(\vec{r}_i) \qquad \text{II-(11)}$$

The electronic charge density n(r) corresponding to the Hartree wave function (8) is given by:

$$n(\vec{r}) = \sum_{i=1}^{Ne} \left|\Psi_e(\vec{r}_i)\right|^2 \qquad \text{II-(12)}$$

When repulsion electron-electron potential (Colombian term) become:

$$U_{ee}(\vec{r}_i) = \int \frac{n(\vec{r}_j)}{\left|\vec{r}_i - \vec{r}_j\right|} d\vec{r}_j \qquad \text{II-(13)}$$

Or using Poisson equation:

$$\Delta U_{ee} = -\frac{n(\vec{r})}{\varepsilon_0} \qquad \text{II-(14)}$$

Different functions can be used to developed the wave function $\Psi(\vec{r}_i)$ as:

- LCAO method: $\Psi(\vec{r}_i) = \sum_{i=1}^{Ne} C_i . \phi_i$.
- Slater development: $\Psi(\vec{r}_i) \propto e^{-\zeta r_i}$.
- Gaussian function: $\Psi(\vec{r}_i) \propto e^{-\gamma . r_i^2}$.

II.5. Hartree-Fock approximation :

One of the missing interactions in Hartree approximation is the exchange. This is the effect which expresses the wave function of the antisymmetry with respect to the exchange of the coordinates of any two electrons, a better approach, that correctly takes into account the antisymmetric character of the wave functions is the Hartree-Fock approach [4], they expressed the multi-electronic wave function in following form of slater determinant:

$$\Psi_e(1,2,..,\mathrm{Ne}) = \Psi_{SD}(1,2,..,\mathrm{Ne}) = \frac{1}{\sqrt{N!}}\begin{vmatrix} \Psi_1(1) & \Psi_2(1) & \dots & \Psi_{Ne}(1) \\ \Psi_1(2) & \Psi_2(2) & .. & \Psi_{Ne}(2) \\ . & . & .. & . \\ . & . & .. & . \\ \Psi_1(Ne) & \Psi_2(Ne) & .. & \Psi_{Ne}(Ne) \end{vmatrix} \qquad \text{II-(15)}$$

Where ψ_i is the spin-orbital is just the product of a spatial orbital and either the α or β spin function (α spin up ↑ or β spin down ↓) . and they are orthonormal wave functions.

$$\psi_i(1) = \varphi_i(r_i) \times \sigma_i(s) \qquad \sigma = \alpha \text{ or } \sigma = \beta$$

ψ_i (j) is the wave function of an ith electron with coordinates of the jth electron.

$(N_e!)^{-1/2}$ factor Guarantee the normalization of the electronic wave function.

The good side of this approach, if we try to put two electrons in the same orbital at the same time Wavefunction becomes null, so all ψ_i must be different. This demonstrates Pauli's exclusion principle.

We need to know all wave functions to know the wave functions! Yes, because we see that the Hamiltonian contain electronic repulsion potential part who we have to know the wave functions to determine it. we got to need to know what we want to need to know, we can solve this iteratively that's essentially the essence of **self-consistent field** approach SCF. When we choose the wave function then we have to use the variational principle in order to find the best functions in order to get the best Slater[1], This is what gives us minimal energy.

To simplify the Hamiltonian to make it simple as possible,

we define one-electron operator:

$$h(i) = -\frac{1}{2}\nabla_i^2 - \sum_k \frac{Z_k}{\left|\vec{r}_i - \vec{R}_k\right|} \qquad \text{II-(16)}$$

Last part represents electron-nuclei attraction its external potential called Hartree energy. we can write the Hartree-Fock energy E_{el} in terms of integrals of the one and two-electron operators as following:

[1] In order to get a smaller amount of energy we use variational principle, in other words, we set wave functions with variational parameters to optimize energy with respect to him.

$$E_{HF} = \langle \psi_{SD} | H | \psi_{SD} \rangle \qquad \text{II-(17)}$$

$$E_{HF} = \sum_{i=1}^{Ne} \langle \psi_i \mid h \mid \psi_i \rangle + \sum_{i=1}^{Ne} \sum_{j>i}^{Ne} \iint |\psi_i(\vec{r}_i)|^2 \frac{|\psi_j(\vec{r}_j)|^2}{|\vec{r}_i - \vec{r}_j|} d\vec{r}_i . d\vec{r}_j$$
$$- \sum_{i=1}^{Ne} \sum_{j>i}^{Ne} \iint \psi_i(\vec{r}_i).\psi_j^*(\vec{r}_i) \frac{1}{|\vec{r}_i - \vec{r}_j|} \psi_j(\vec{r}_j).\psi_i^*(\vec{r}_j) d\vec{r}_i . d\vec{r}_j$$

We can write like following:

$$E_{HF} = \sum_{i=1}^{Ne} \langle \psi_i | \hat{h} | \psi_i \rangle + \frac{1}{2} [\hat{J}_j(\vec{r}_i) - \hat{K}_j(\vec{r}_i)] \qquad \text{II-(18)}$$

$\hat{J}_j$ called Colombian integral which gives the average local potential at the position $\vec{r}_i$ due to the charge distribution from the electron in all other positions $\vec{r}_j$. So is a local entity. $\hat{K}_j$ does not have a simple classical meaning, is a quantum term, called exchange operator it like Colombian term but exchanging spin orbitals ψ_i and ψ_j (in some books or theses imagine the electron in parallel spin distribution has surrounded fermi holes equivalent to one electron charge, this vacuum space surrounding the electron one-half of electron (1/2 é) charge excluded) what mean that it owing to the fact that two of the same electrons spin cannot approach indefinitely.

This Hartree-Fock approximation led to good performances, in particular in molecular physics, but the treatment of the systems extended like the solids remain difficult, is not taken account the correlations between electrons.

the contribution of the correlation in total energy defined as the difference between the exact total energy of the electronic system and that of Hartree-Fock energy.

$$E_{corr} = E_{Exact} - E_{HF} \qquad \text{II-(19)}$$

E_{corr} is a negative energy because of the Hartree-Fock energy E_{HF} is always higher than exact energy like we imagine the electrons with the same spin are surrounded by exchange holes of fermi whose contribute with exchange term in total energy, will do the same thing with opposites spin electrons, electron surrounded by holes called correlations holes.

Intuitively the hole of correlation must be smaller than that of exchange since the rule of exclusion of Pauli is already obeyed, but one we will speak about the same hole of exchange-correlation from which one will exclude the other of the same electrons spin as well as opposite spin.

since Hartree does not take into consideration neither of exchange nor of correlation we can stipulating assemble those two terms in one energy term called exchange-correlation energy E_{XC} .the exact total energy is done as follow:

$$E_{exact} = E_H + E_{XC} \quad \text{II-(20)}$$

II.6. Density of functional theory:

The theory of Thomas and Fermi (1927,1928)[5] is a true theory of DFT (Density of Functional Theory) Thomas and Fermi have proposed an alternative method of resolution of the equation of Schrödinger based on the only electronic density, it consists in subdividing the inhomogeneous system in small boxes of elementary volumes dr^3 where the electrons have a homogeneous gas reaction of constant density electronic, called "jellium"; it is an idealized gas of electrons free for its energy kinetic is easily calculated to them, say that the electrons not undergoing have the potential had by the cores and same for the potential had by the electrons, also being unaware of any.

II.6.1. Kohn-Hohenberg theory:

In 1964, Kohn and Hohenberg [6] showed the following theorems on which the D.F.T is based on them:

H K 1: "they established the bi-univocal correspondence between the electronic density n(r) and the external potential, so we can write the ground state energy of a system of many electrons set in external potential as a unique universal functional of electronic density.

$$E_{GS} = E\left[n(\vec{r})\right] \quad \text{II-(21)}$$

We can demonstrate the previous theorem by absurd like following; either n(r) the electronic density of the system in its ground state has an external potential V_1(r). The function is associated to him of wave function ϕ_1 and energy E_1:

$$E_1 = \langle \phi_1 | H_1 | \phi_1 \rangle = \int V_1(\vec{r}) n(\vec{r}) d\vec{r} + \langle \phi_1 | T_e + V_{ee} | \phi_1 \rangle \quad \text{II-(22)}$$

Supposing that exist another potential $V_2 \neq V_1 + Cste$ associated to ground state ϕ_2 which gives the same electronic density n(r), and related to energy E_2:

$$E_2 = \langle \phi_2 | H_1 | \phi_2 \rangle = \int V_2(\vec{r})\ n(\vec{r}) d\vec{r} + \langle \phi_2 | T_e + V_{ee} | \phi_2 \rangle \qquad \text{II-(23)}$$

the minimization principle of the energy of Rayleigh-Ritz leads to:

$$E_1 < \langle \phi_2 | H_1 | \phi_2 \rangle = E_2 + \int (V_1(\vec{r}) - V_2(\vec{r})) n(\vec{r}) d\vec{r} \qquad \text{II-(24)}$$

With the same procedure:

$$E_2 < E_1 + \int (V_2(\vec{r}) - V_1(\vec{r})) n(\vec{r}) d\vec{r} \qquad \text{II-(25)}$$

The assembling equations (24) and (25) will give:

$$E_2 + E_1 < E_1 + E_2 \qquad \text{II-(26)}$$

And this is a contradiction, so the consequence is “the bi-univocal correspondence between the electronic density n(r) and the external potential”.

H K 2: “the minimal value of this functional is the exact energy of the ground state, and that the density which leads to this energy is the exact density of the ground state. The other ground state properties are also functional of this density”, in other words, the functional E [n(r)] reached its minimum according to the variations of n(r) when the density reaches its value in a ground state (variational principal):

$$E_{HK}\left[n(\vec{r})\right] = \int V_{ext}(\vec{r}) n(\vec{r})\ d\vec{r}\ + F_{HK}\left[n(\vec{r})\right]\ \geq\ E_{GS} \qquad \text{II-(27)}$$

Where the first part of the equation is the contribution of external potential due by nuclei, and the second is a universal functional of n(r) where it does not depend on the external potential which acts on the system. This functional is not known in an exact way. This functional contains the kinetic and Coulomb contributions to energy.

$$F_{HK}\left[n(\vec{r})\right] = \min_{\phi \to n(\vec{r})} \langle \phi | T_e + V_{ee} | \phi \rangle \qquad \text{II-(28)}$$

It will be relatively easy to use the variational principle to determine total energy and the electronic density of the fundamental state for a given external potential, but Kohn-Hohenberg theory doesn't give any formulas of this functional of electronic density $F\left[n(\vec{r})\right]$.

II.6.2. Kohn-Sham approach:

In 1965 Kohn and Sham [7] developed an approach based on the DFT in which they replaced the real system with Ne interacting electrons to a **fictional system** with Ne **independent** electrons of the **same electronic density** as the real system, substitute all potentials and interacting potential by an **effective potential** which gives us an identical energy of the ground state.

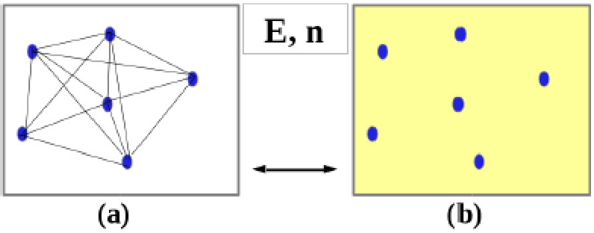

Figure II- 1: (a) Real system consisting of mutual interacting electrons; (b) Fictive system of independent electrons with the same energy and electronic density.

This resulted in solving a system of independent particles like that of Hartree-Fock when his contribution in total energy of system has written as:

$$E_{HF}\left[n(\vec{r})\right]=T\left[n(\vec{r})\right]+U_H\left[n(\vec{r})\right]+U_x\left[n(\vec{r})\right]+U_{ext}\left[n(\vec{r})\right] \quad \text{II-(29)}$$

Where: $T\left[n(\vec{r})\right]$ is kinetic energy in the model Hartree-Fock.

$U_H\left[n(\vec{r})\right]$ is Hartree energy in the same model HF, when:

$$U_H\left[n(\vec{r})\right]=\frac{1}{2}\int\frac{n(\vec{r}).n(\vec{r}\,')}{|\vec{r}-\vec{r}\,'|}d\vec{r}$$

$U_x\left[n(\vec{r})\right]$ is the exchange energy.

For real electronic system, the ground state total energy is:

$$E_{GS}\left[n(\vec{r})\right]=T_0\left[n(\vec{r})\right]+U_0\left[n(\vec{r})\right] \quad \text{II-(30)}$$

Where $T_0\left[n(\vec{r})\right]$ represent the kinetic energy of the real system.

$U_0\left[n(\vec{r})\right]$ is potential energy due of electronic repulsion with the external one of the real system, when $U_0=U_{ee}+U_{ext}$ and $U_{ee}=U_H+U_x$

Subtracting equation (25) from (26) given:

$$E_{GS}-E_{HF}=T_0-T \quad \text{II-(31)}$$

Since we early defined this difference between ground state energy and Hartree-Fock energy as the correlations energy, so:

$$U_c=E_{GS}-E_{HF}=T_0-T \quad \text{II-(32)}$$

Also the exchange energy writing:

$$U_x = U_{ee} - U_H \qquad \text{II-(33)}$$

Hence, the exchange and correlation energy write as following:

$$U_{xc} = U_x + U_c \qquad \text{II-(34)}$$

So can resume Kohn-Sham equations as following:

$$V_{eff}\left[n(\vec{r})\right] = V_H\left[n(\vec{r})\right] + V_{xc}\left[n(\vec{r})\right] + V_{exc}(\vec{r}) \qquad \text{II-(35)}$$

And the electronic density is:

$$n(\vec{r}) = \sum_i |\phi_i|^2 \qquad \text{II-(36)}$$

Schrodinger equation is:

$$\left[-\frac{1}{2}\nabla^2 + V_{eff}\right]\phi_i = \varepsilon_i \phi_i \qquad \text{II-(37)}$$

Where ϕ_i is one particle wave function.

$V_H\left[n(\vec{r})\right] = \frac{1}{2}\int \frac{n(\vec{r}\,')}{|\vec{r} - \vec{r}\,'|} d\vec{r}\,'$ is Hartree potential.

$V_{xc}\left[n(\vec{r})\right]$ is an unknown exchange and correlation potential.

we can write ground state energy of the interactive system as following:

$$E_{KS}\left[n(\vec{r})\right] = T\left[n(\vec{r})\right] + U_H\left[n(\vec{r})\right] + U_{xc}\left[n(\vec{r})\right] + \int V_{ext}\, n(\vec{r}) d\vec{r} \qquad \text{II-(38)}$$

Where $T\left[n(\vec{r})\right]$ is the kinetic energy of electrons system without interactions, and $E_H\left[n(\vec{r})\right]$ is Hartree term (where is purely a classical term), $E_{xc}\left[n(\vec{r})\right]$ is a term for exchange-correlation (where is purely a quantum term), the last one is external potential term including nuclei interactions (nuclei-nuclei, and electron-nuclei).

The three equations II- (35-37) must be solved in a self-coherent way, we beginning from an initial electronic density $n_{input}(r)$, this density gives us an initial effective potential then solving equation II-(37) which gives us new electronic density $n_1(r)$, which gives us a new effective potential then solving equation II-(37), that form a self-consistent cycle repeat until convergence it reached (what mean that it stop when a new and previous densities are equal or very near), it is very hard to obtain two successively densities equal we have to use a convergence criteria to stop this self-consistent cycle .

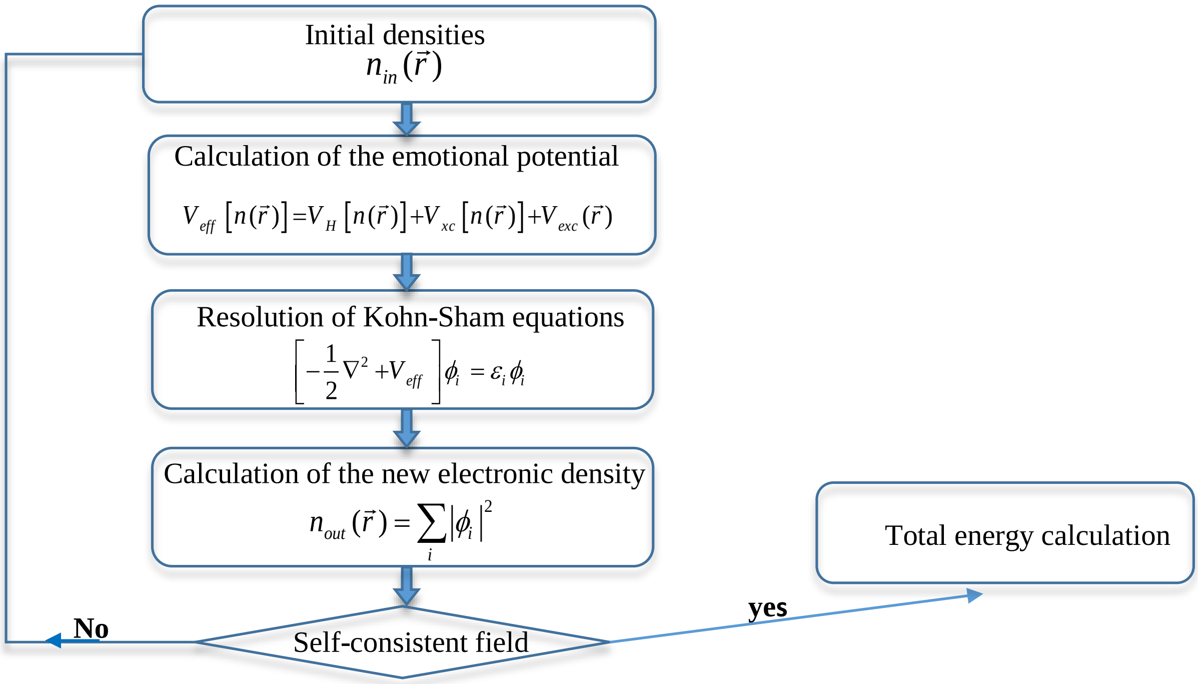

Figure II- 3 schematic representation of the self-consistent cycle within the framework of the DFT.

the electronic density is a fundamental quantity which governed iterative procedure.

Finally, the only **unknown factor** of our problem then becomes the term of exchange and correlation $\mathbf{E_{xc}[n(r)]}$ who is not easier to calculate than F [n(r)], but the advantage of being much smaller. It is especially much smaller than the external potential and Hartree potential and kinetic energy contributions. three terms which determine in a general way the properties of the system. That don't mean we'll neglect it until now many scientists work on this part, Local Density Approximation, and Generalized Gradient Approximation is two approximations mostly used in DFT.

II.6.3. Local Density Approximation (LDA):

The Simplest and one of most popular approximation are the Local Density Approximation. In this approximation, a nonhomogeneous electronic system is observed as locally homogeneous, where Kohn and Sham considered that the density varies slowly in space, then they expressed the potential of exchange and correlation using the energy of exchange and correlation given by:

$$V_{xc}\left[n(\vec{r})\right]=\frac{d\left(n(\vec{r}).U_{xc}\left[n(\vec{r})\right]\right)}{dn(\vec{r})} \quad \text{II-(39)}$$

So the exchange and correlation contribution in total energy is given by:

$$U^{LDA}_{xc}\left[n(\vec{r})\right]=\int\varepsilon_{xc}\left[n(\vec{r})\right].n(\vec{r})\ d^3\vec{r} \quad \text{II-(40)}$$

Where:

$$\varepsilon_{xc}^{LDA}\left[n(\vec{r})\right]=\frac{\partial U_{xc}\left[n(\vec{r})\right]}{\partial n(\vec{r})} \qquad \text{II-(41)}$$

II.6.4. The introduction of the spin into the local approach of the density:

In the case of spin polarization taking account in LDA, this generalization his name LSDA (Local Spin Density Approximation), that's introduce two populations, one of the electrons with spin up $n^{\uparrow}(\vec{r})$, the second population of electrons with spin down. The system is described by two functions in a 3D space. The term ε_{xc} is now function of the two spins $\varepsilon_{xc}\left[n^{\uparrow}(\vec{r}),n^{\downarrow}(\vec{r})\right]$.the energy of exchange-correlation in LSDA is given by the following expression:

$$U_{XC}^{LSDA}\left[n^{\uparrow}(\vec{r}),n^{\downarrow}(\vec{r})\right]=\int\varepsilon_{XC}^{LSDA}\left[n^{\uparrow}(\vec{r}),n^{\downarrow}(\vec{r})\right].n(\vec{r})\,d^{3}\vec{r} \qquad \text{II-(42)}$$

An another approximation appeared using LSDA is to introduce terms in gradient into the expression of the energy of exchange-correlation this introducing a not-local correction, this approximation called GEA (gradient expansion approximation) but this approximation the results are even less good.

LDA and LSDA are leads sometimes to a poor description of the properties of certain systems, especially for actinides and lanthanides.

II.6.5. Generalized Gradient Approximation GGA:

In a real system the density is inhomogeneous in space then the density is non-local more, introduction a correction of n(r) is necessary from where the birth of the approximation of gradient generalized GGA. this correction is introducing into the energy of exchange and correlation of the terms depending on the gradient of the density, where the exchange and correlation energy by GGA is:

$$U_{xc}^{GGA}\left[n(\vec{r})\right]=f\left(n^{\uparrow}(\vec{r}),n^{\downarrow}(\vec{r}),\nabla n^{\uparrow}(\vec{r}),\nabla n^{\downarrow}(\vec{r})\right)d^{3}\vec{r}. \qquad \text{II-(43)}$$

f is function must be parameterized in the analytical form in order to facilitate calculations, it exist various forms of ε_{xc}^{LDA} in LDA, the same thing with f , it is a function of local density and of his gradient must be also parametrized in analytical form, it exists several forms of this function. in our study, we will use the functional calculus of Perdew, Burke and

Ernzerhof (PBE)[8].

II.7. Practical implementations of the DFT:

While placing us in the approximation of Born-Oppenheimer, we saw that it was necessary to use an approximate form of the functional calculus of exchange-correlation in order to be able to apply the DFT in practice. The approximation of Born-Oppenheimer and the approximation of the term of exchange-correlation are of fundamental nature while to be able to solve in practice the equations of Kohn and Sham the digital processing introduces additional approximations, which nevertheless are controlled by the user of a computer code ab-initio. In this section, we will give a total sight of the principal choices of implementation of the DFT and to introduce two numerical approximations: the sampling of the zone of Brillouin or grid of k points and the energy of cut, which defines the size of the base of plane waves used in the development in series of the functions of Bloch.

II.8. Crystals description:

Resolution of Kohn and Sham's equations based on a property of symmetry by translation in periodic systems, so the use of the plane waves as bases expansion for the wave function. That what are said Bloch theorem [9] “the wavefunctions of the crystal Hamiltonian can be written as the product of a plane wave of wavevector k within the first Brillouin zone, times an appropriate periodic function”.

Let us consider a periodic crystalline system bases on the repetition of a cell unit of volume Ω and characterize this repetition by Bravais lattice vector $\vec{R}$.

Each electronic wave function of $\phi_i(\vec{r})$ can develops on the basis of plane wave

$$\phi_{i,\vec{k}}(\vec{r}) = \frac{1}{\sqrt{\Omega}} u_i(\vec{k},\vec{r})\, e^{j\,\vec{k}.\vec{r}} \qquad \text{II-(44)}$$

Where $u_n(\vec{k},\vec{r})$ has the same crystal periodicity, which:

$$u_i(\vec{k},\vec{r}) = u_i(\vec{k},\vec{r}+\vec{a}) = u_i(\vec{k},\vec{r}+b.\vec{a}) \qquad \text{II-(45)}$$

The used plan waves basis is orthonormal by:

$$\langle \vec{k} | \vec{k}' \rangle = \frac{1}{\Omega} \int_{\Omega} e^{-j\,\vec{k}.\vec{r}} e^{j\,\vec{k}'.\vec{r}} d\Omega = \delta_{\vec{k},\vec{k}'} \qquad \text{II-(46)}$$

We can write $u_n(\vec{k},\vec{r})$ as the sum of the Fourier components:

$$u_{i,\vec{k}}(\vec{r}) = \sum_{\vec{G}} C_{i,\vec{k}}(\vec{G}).\, e^{j\vec{G}.\vec{r}} \qquad \text{II-(47)}$$

$\vec{G}$ it is a vector in the reciprocal lattice.

Well, we can now write the wave function as Bloch function in Fourier space:

$$\phi_{i,\vec{k}}(\vec{r}) = \frac{1}{\sqrt{\Omega}} \sum_{\vec{G}} C_{i,\vec{k}}(\vec{G}).\, e^{j\,(\vec{k}+\vec{G}).\vec{r}} \qquad \text{II-(48)}$$

the electronic density is:

$$n(r) = \sum_{i,\vec{k}} \sum_{\vec{G},\vec{G}'} C^{*}_{i,\vec{k}}(\vec{G}').\, C_{i,\vec{k}}(\vec{G}).\, e^{j\,(\vec{G}-\vec{G}').\vec{r}} \qquad \text{II-(49)}$$

We inject the preceding function in the equation (39) and integrate into all space gives

$$\sum_{\vec{G}'} \left[\frac{1}{2}\left|\vec{k}+\vec{G}\right|^2 \delta_{\vec{G},\vec{G}'} + U_H(\vec{G}-\vec{G}') + U_{xc}(\vec{G}-\vec{G}') + U_{ext}(\vec{G}-\vec{G}') \right] C_{i,\vec{k}}(\vec{G}') = \varepsilon_i(\vec{k}) C_{i,\vec{k}}(\vec{G}) \qquad \text{II-(50)}$$

$U_H(\vec{G}-\vec{G}')$, $U_{xc}(\vec{G}-\vec{G}')$ and $U_{ext}(\vec{G}-\vec{G}')$ are Fourier transformer of respectively Hartree, exchange, and correlation, external potentials.

and are solved by diagonalizing the Hamiltonian, or use variational principle to finding $C_{i,\vec{k}}(\vec{G})$ who make total energy minimum as possible this using k points.

II.9. The Cut-off energy:

Make a limit for the wave number in Bloch function (because is infinite) is very necessary, if we don't, the calculation impossible to do it, for this reason, we have present correctly the Bloch function, plane wave of strong kinetic energy is negligible in front of those plane wave of weak kinetic energy.so to truncate the Hamiltonian beyond kinetic Cut-Off energy while limiting itself to the numbers of wave verifying:

$$\frac{1}{2}\left|\vec{k}+\vec{G}\right|^2 \le E_{Cut} \qquad \text{II-(51)}$$

The computing time strongly increases the value of E_{cut} , If E_{cut} is too weak, the number of plane waves in the calculation is not sufficient for representing the wave functions and the electronic density, one must thus determine an E_{cut} realistic on the level of the computing time for which total energy converges with the required precision.

II.10. Sampling of the Brillouin zone (BZ):

$\vec{k}$ is a vector reciprocal lattice which is confined in the first Brillouin zone (FBZ), and it is called Bloch vector plays the role of a translation quantum number. the smallest unit of the reciprocal lattice allowing to rebuild completely the system by symmetry.

in theory equation II- (39) must be solved to every k point, and the description of the system will be done in terms of energy band $\varepsilon_i(\vec{k})$, each electronic state corresponds to energy band in the solid, which one can describe by $\vec{k}$,numerically we can't solve the equation II-(39) to infinite k number, we have to choose a finite k points number(sampling) in Brillouin zone.

The more one will increase the number of these k points, more one will refine the grid of reciprocal space and the calculated physical properties will be close to the infinite crystal.

In addition, more one cell will be large, less it will be necessary to consider a big number of k points. Indeed, in the first approaches consist in saying that the electrons are already wide since the big box (usually used in molecule studies). In the second approach, the zone of Brillouin will be smaller and integration will be already partially carried out.

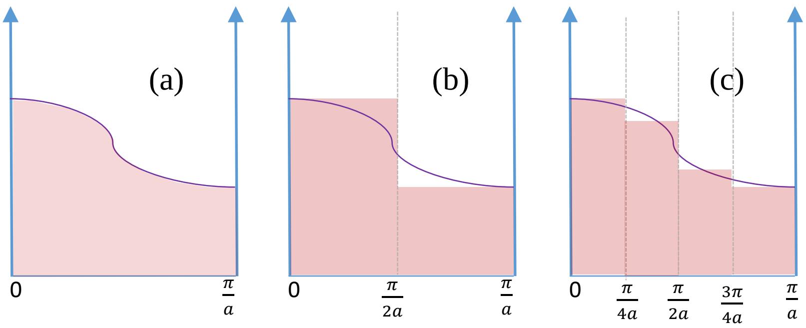

Figure II- 4: (a) Intergation in FBZ , (b) Somation by 2 k points , (c) Somation by 4 k

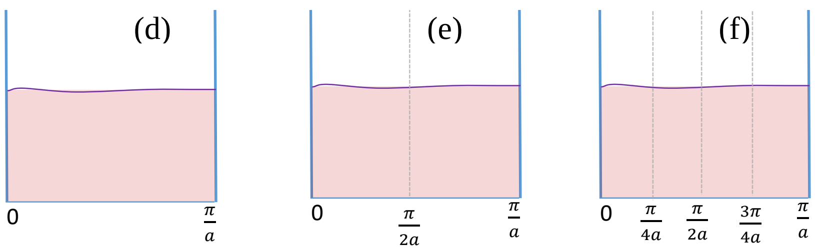

Figure II- 5: (d) Integration in FBZ, (e) Summation by 2 k points, (f) Summation by 4 k points on big box (big unit cell)

The electronic states are allowed only for the collection of k points determined by the boundary conditions. The infinite number of electrons in the solid is taken into account by an infinite number of k points, and only a finished number of electronic states are occupied at each k point. The states occupied at each k point contribute in the calculation of density n(r) and in consequence of the electronic potential and of total energy.

Many procedures of election exist for the sampling of the k points One will quote in particular those of Chadi and Cohen [10], those of Evarestov et Smirnov [11], or those of Monkhorst [12] et Pack which we are used in this work.

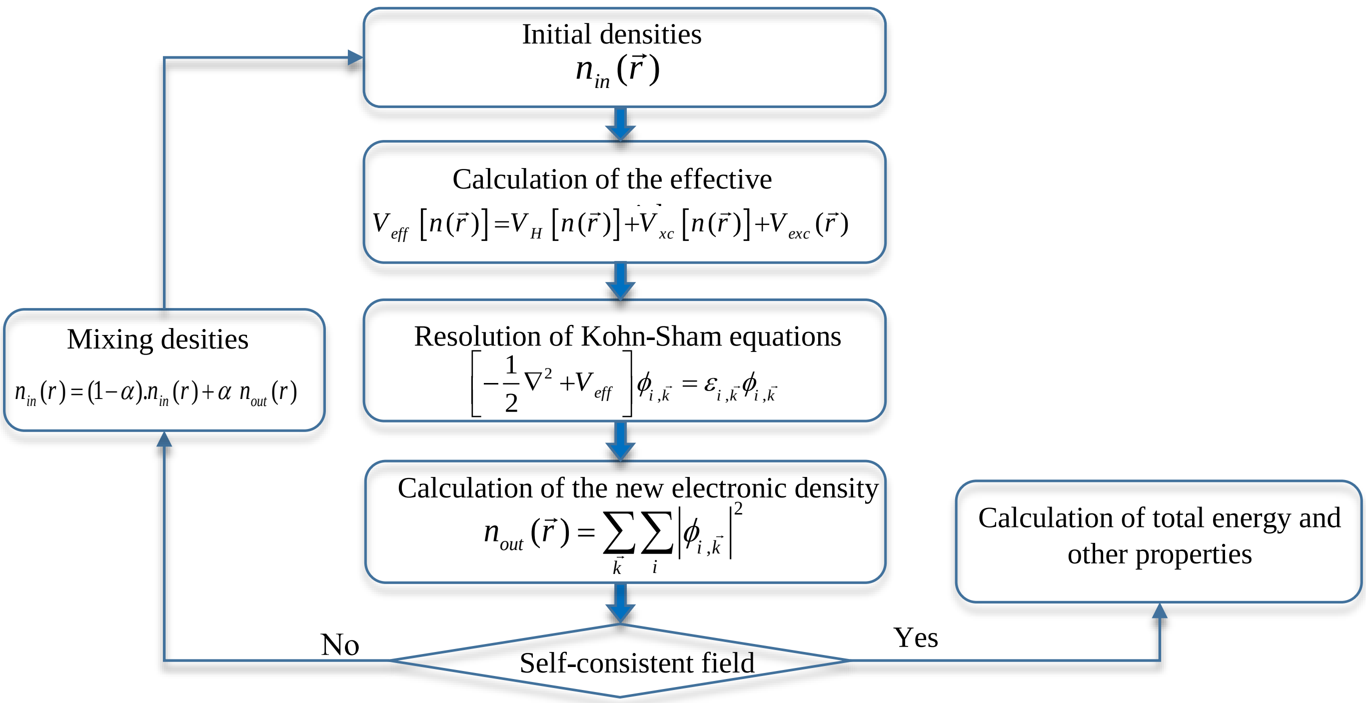

Figure II-6: Flowchart of DFT self-consistent cycle calculation

II.11. Pseudopotentials:

Numerical calculations on the electronic ground state of a system (in the formulation of Kohn-Sham) encounter additional engineering problems. Indeed, they become increasingly expensive as the system to be treated contains a great number of electrons, for example in metals of transition which are characterized by a localization of d orbital.

We will devise the electron on two types; part of core electrons and valence electrons, the core electrons which are localized close to the core, are very strongly related to the core, and they are not very sensitive to the environment, they don’t take part in the chemical bonding. they are difficult to represent on a basis of plane waves because they generally have strong oscillations around the cores. the valence electrons are little located in the neighborhood of the core.

The effect of the core electrons and the nuclei will be replaced by an effective pseudopotential.

Thanks to the use of pseudopotentials calculation will be faster because:

- there is less of electrons to treat, the calculation is less heavy.
- there is less of degrees of freedom (core electrons being "motionless"), therefore the algorithm of convergence is more effective, and faster convergence.
- the cutoff energy is also decreased since the effective electrostatic potential of the core is soft.

We arrived at the equations of Kohn and Sham, of the Schrödinger type to a particle and which are solved in a self-coherent way:

$$\left[T_0\left[n(\vec{r})\right]+V_{eff}(\vec{r})\left[n(\vec{r})\right]\right]\phi_i(\vec{r})=\varepsilon_i\phi_i(\vec{r}) \qquad \text{II-(52)}$$

Where:

$$V_{eff}\left[n(\vec{r})\right]=V_H\left[n(\vec{r})\right]+V_{xc}\left[n(\vec{r})\right]+V_{pseudo}\left[n(\vec{r})\right] \qquad \text{II-(53)}$$

a pseudopotential takes into account the important effects due to the ionic potential (screened potential). In addition, fast variations of the wave functions of valence electrons in the area close to the core defined by a ray of cut-off $R_{cut\text{-}off}$ - "are softened". In this way, the electronic pseudo- wavefunctions can be developed effectively on a basis of plane waves. Program ABINIT rests on it type of approach known as "pseudopotential", next figure summarizes the philosophy of these two approaches.

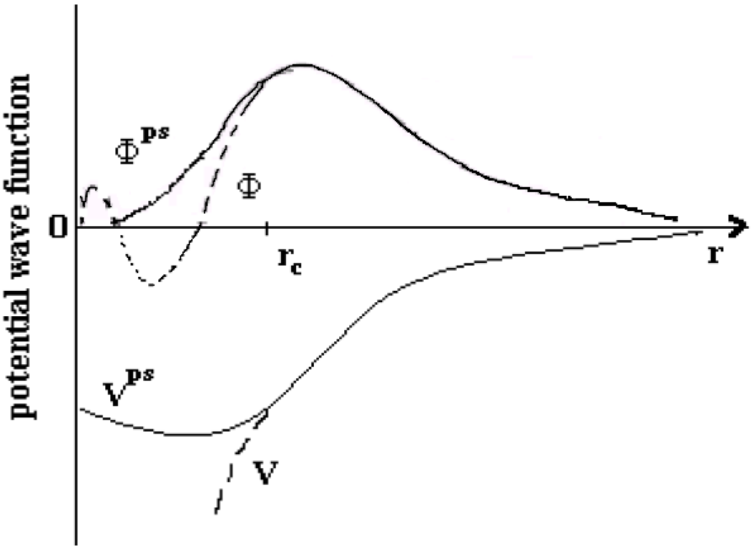

Figure II- 7: Schematic representation of the pseudopotential method

This pseudopotential must be taken into account:

- screened nuclei interaction, electronic repulsion, Pauli principle, the exchange and correlation.
- Make sure from the continuity of wave function and his derives.

It exists many methods for solving Kohn-Sham equations use basis plan waves such as:

all electrons method: which taking account all electrons in considerations (core electrons wave functions complicated taking into account oscillations) that's what make the calculation more complicated and it's take a long time. this needs to very high-performance computers.

Augmented Plan Waves APW: Slater separate electrons on ; core electrons supposing that have behavior of insulator some electrons , and symmetric wave functions and potential , determined by sphere has a radius R_α called MT "Muffin-Tin" radius, the wave function in this zone is radial and spherical parts ; electrons out this R_α radius (interstitial zone) described by plane waves.

Linearized Augmented Plan Waves LAPW: like the previous one but the radial parts of wave functions are developed by Taylor series , wich gives linear combination of basis wave functions with his radial parts and his derives.

II.12. Density functional perturbation theory (DFPT):

Many interesting physical properties (response functions) are the result of the application of an external perturbation to the system under investigation. Response functions are first second, third, or higher order derivatives of the total energy with respect to applied perturbation(s). Typical perturbations can be atomic displacements, homogeneous external electric or magnetic fields, strain, alchemical change, etc... The physical properties related to the derivatives of the total energy are:

- 1st order: forces, stress, dipole moment, ...
- 2nd order: phonon dynamical matrix, elastic constants, dielectric susceptibility, Born effective charges, piezoelectricity, internal strain
- 3rd order: nonlinear dielectric susceptibility, phonon-phonon interaction, Gruneisen parameters, anharmonic elastic constants, ...

if the Hamiltonian H of a system depends on an arbitrary parameter λ. for a normalized wave function, the first derivative of the energy with respect to a parameter is equal to the expectation value of the corresponding first derivative of the Hamiltonian.

$$H(\lambda)\Psi(\lambda) = \Psi(\lambda)E(\lambda) \qquad \text{II-(54)}$$

$$\frac{\partial E(\lambda)}{\partial \lambda} = \left\langle \Psi(\lambda) \right| \frac{\partial H(\lambda)}{\partial \lambda} \left| \Psi(\lambda) \right\rangle \qquad \text{II-(55)}$$

One of its consequences being that in Quantum Mechanics there is a single way of defining a generalized force on eigenstates of the Hamiltonian, associated with the variation of some of its parameters. If we can calculate the ground state total energy of a solid, we can calculate many of properties which linked to derives of the ground state total energy with respect to perturbation.

II.12.1. Hellmann – Feynman Forces and the elastic constants :

We consider three kinds of perturbations applied to such a crystal: (i) displacements λ_n of the atoms away from their equilibrium positions, and (iii) homogeneous electric fields $\mathcal{E}_\alpha$ where (α = x, y, z) are Cartesian directions (ii) homogeneous strains η_j (where j = {1,2...,6} in Voigt notation where:

$$1 \to xx\,,\ 2 \to yy\,;\ 3 \to zz\,;\ yz \to 4;\ zx \to 5;\ xy \to 6 \qquad \text{II-(56)}$$

The corresponding responses that are conjugate to these two perturbations are (i) forces F_m ,(ii) stresses σ_j , and (iii) polarizations P_α .the force F_m called Hellmann-Feynman Forces [13-15], this theorem is a useful tool in solid state physics. obtain by the first derive of total energy with respect to atomic infinitesimal displacement λ_n of atom indexed by n:

$$F_n = \frac{dE}{d\lambda_n} \qquad \text{II-(57)}$$

The forces of Hellmann-Feynman are very sensitive to the errors in the wavefunction. It will thus be necessary that the electronic wave functions are sufficiently well converged so that these errors are negligible.

it exists another theorem more general, called 2n+1 theorem, this theorem stipulates that one can calculate the 2n+1 energy derives of a system from 0,1, 2…., n derives of its function wave.

From perturbation above mentioned, one can construct the response functions of primary interest such the elastic constants Cjk which[16]:

$$C_{jk} = \frac{d\sigma_j}{d\eta_k} \qquad \text{II-(58)}$$

However, in order to define these quantities carefully, it is important to clarify the constraints or boundary conditions that apply to each definition. For example, the elastic constants Cjk may be defined allowing or not allowing internal atomic displacements ("relaxed-ion" or "frozen-ion").

We can write the total energy of a crystal system as function of these deferent perturbations as following[16]:

$$\begin{aligned} E &= E_0 + A_m\lambda_m + A_\alpha\varepsilon_\alpha + A_j\eta_j \\ &+1/2\left(B_{mm}\lambda_m\lambda_m + B_{\alpha\beta}\varepsilon_\alpha\varepsilon_\beta + B_{jk}\eta_j\eta_k \right) \\ &+ B_{m\alpha}\lambda_m\varepsilon_\alpha + B_{mj}\lambda_m\eta_j + B_{\alpha j}\varepsilon_\alpha\eta_j \qquad \text{II-(59)} \\ &+ \text{ terms of third and higher order} \end{aligned}$$

Where A_m encode the forces (F_m=-V_0. A_m), and A_α encode the polarization (P_α= - A_α); and A_j encode the stress (σ_j=A_j); we shall assume that the atomic coordinates and strains are fully relaxed so that A_m=A_j=0.the second order coefficients are: B_{mm} the force constant, $B_{\alpha\beta}$ the susceptibility tensor, B_{jk} the elastic constants, $B_{m\alpha}$ the Born-charge, B_{mj} the internal displacement, $B_{\alpha j}$ the piezoelectric tensor.

the frozen-ion elastic tensor written by following expression:

$$\bar{C}_{jk} = \left.\frac{\partial^2 E}{\partial \eta_j \partial \eta_k}\right|_{\varepsilon,\lambda_m} \quad \text{II-(60)}$$

we can define relaxed one like following:

$$\bar{E} = \min_{\lambda_m}(\lambda_m, \eta, \varepsilon) \quad \text{II-(61)}$$

the relaxed-ion elastic tensor written by the following expression:

$$C_{jk} = \left.\frac{\partial^2 \bar{E}}{\partial \eta_j \partial \eta_k}\right|_{\varepsilon,\lambda_m} \quad \text{II-(62)}$$

Cjk is a matrix of 6×6, each crystal system has tensor distinguish from others, the symmetry of the crystal reduces the number of independent parameters. In cubic systems, there is more than three nonzero independent elements:

Table II- 2: Description Parameters for the elastic constants for some structures.

Parameters describing the elastic properties [17]	
Cubic	C_{11}, C_{12}, C_{44}.
Hexagonal	C_{11}, C_{12}, C_{13}, C_{33}, C_{44}.
Tetragonal	C_{11}, C_{12}, C_{13}, C_{33}, C_{44}, C_{66}
Trigonal	C_{11}, C_{12}, C_{13}, C_{14}, C_{33}, C_{44}.
Orthorhombic	C_{11}, C_{12}, C_{13}, C_{22}, C_{23}, C_{44}, C_{55}, C_{66}

For cubic systems, the tensor C_{ij} is written as following:

$$C_{ij} = \begin{pmatrix} C_{11} & C_{12} & C_{12} & 0 & 0 & 0 \\ C_{12} & C_{11} & C_{12} & 0 & 0 & 0 \\ C_{12} & C_{12} & C_{11} & 0 & 0 & 0 \\ 0 & 0 & 0 & C_{44} & 0 & 0 \\ 0 & 0 & 0 & 0 & C_{44} & 0 \\ 0 & 0 & 0 & 0 & 0 & C_{44} \end{pmatrix} \quad \text{II-(63)}$$

another tensor used to descript this system is compliance constants matrix Sij, is linked to Cij Where $S_{ij}=C_{ij}^{-1}$[18]:

$$S_{ij} = \begin{pmatrix} S_{11} & S_{12} & S_{12} & 0 & 0 & 0 \\ S_{12} & S_{11} & S_{12} & 0 & 0 & 0 \\ S_{12} & S_{12} & S_{11} & 0 & 0 & 0 \\ 0 & 0 & 0 & S_{44} & 0 & 0 \\ 0 & 0 & 0 & 0 & S_{44} & 0 \\ 0 & 0 & 0 & 0 & 0 & S_{44} \end{pmatrix} \qquad \text{II-(64)}$$

For tetragonal crystal elastic constants Cij tensor can take one of these two tensors:

$$C_{ij} = \begin{pmatrix} C_{11} & C_{12} & C_{13} & 0 & 0 & C_{16} \\ C_{12} & C_{11} & C_{13} & 0 & 0 & -C_{16} \\ C_{13} & C_{13} & C_{33} & 0 & 0 & 0 \\ 0 & 0 & 0 & C_{44} & 0 & 0 \\ 0 & 0 & 0 & 0 & C_{44} & 0 \\ C_{16} & -C_{16} & 0 & 0 & 0 & C_{66} \end{pmatrix} ; \; C_{ij} = \begin{pmatrix} C_{11} & C_{12} & C_{13} & 0 & 0 & 0 \\ C_{12} & C_{11} & C_{13} & 0 & 0 & 0 \\ C_{13} & C_{13} & C_{33} & 0 & 0 & 0 \\ 0 & 0 & 0 & C_{44} & 0 & 0 \\ 0 & 0 & 0 & 0 & C_{44} & 0 \\ 0 & 0 & 0 & 0 & 0 & C_{66} \end{pmatrix} \qquad \text{II-(65)}$$

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Chapter III

Results and discussion

III. Results and Discussions

III.1. Introduction

In this chapter, we will have in a first place the computation results by the DFT of the structural and electronic properties of Lanthanum borides: LaB4 and LaB6, the second part of this chapter will be devoted to calculation ab-initio of the elastic constants Cij of our materials like their elastic modules: bulk modulus (rigidity) B, Young E, shearing G and the Poisson's ratio ν. These calculations will be led within the framework of the DFT with PW-PP (Plane Waves -Pseudo Potential) realizing by ABINIT code.

III.2. ABINIT code:

Before calculations beginning in ABINIT code, we must define pseudopotential used, our choice was Trouiller-Martins-type, LDA_CPW (Ceperley, Alder Perdew, Wang) (1992) for Boron atom pseudopotential, OPIUM generated for La pseudopotential using LDA approximation of exchange and correlation, for GGA; Trouiller-Martins-type, GGA_PBE (Perdew, Burke, Ernzerhof) (1996) for boron pseudopotential, OPIUM generated for La pseudopotential, the electrons of valence are fixed by the pseudopotential. For the constituent elements the materials which are subject to this study the valence electrons are presented by:

Lanthanum: Z:57 [Kr] $5s^2\ 5p^6 5d^1\ 6s^2$; Boron: Z:5 [He] $2s^2\ 2p^1$

III.3. Convergence study:

Earlier in ABINITIO methods chapter, we are talking about two parameters very important to limit calculation, and gain of memory and time required to determine system properties. These two parameters should be choosing carefully to don't impact dearly in the precision of the calculation.

The first one is the Cut-off energy is parameter allows us to limit the wave of Bloch function (In theory we should use an infinite number of plane waves and this not practicable) one is obliged to truncate this plane waves number. One restricts plane waves whose kinetic energy is lower than an energy of cut-off Ecut.

$$\frac{1}{2}\left|\vec{k}+\vec{G}\right|^2 \leq E_{Cut} \qquad \text{III-(1)}$$

The second one is k points grid, we have to know that with dense grid, calculation precision is better, and choosing k point grid minimum as possible to calculation speed should not affect the calculation accuracy.

The following table shows results of calculation:

III.3.1. For LaB6 compound:

Convergence with respect to Ecut shows in the next table and the graphical representation in following figure:

Table III- 1: Convergence study: Total energy Vs Ecut for LaB6 crystal

Ecut	Total Energy(Ha)	$\Delta E_T/E_T$
23	-51.95428	-4.94676E-5
29	-51.95562	-2.35753E-5
35	-51.95666	-3.67226E-6
47	-51.95671	-2.70222E-6
50	-51.95672	-2.50342E-6
53	-51.95688	6.628E-7
59	-51.95685	--

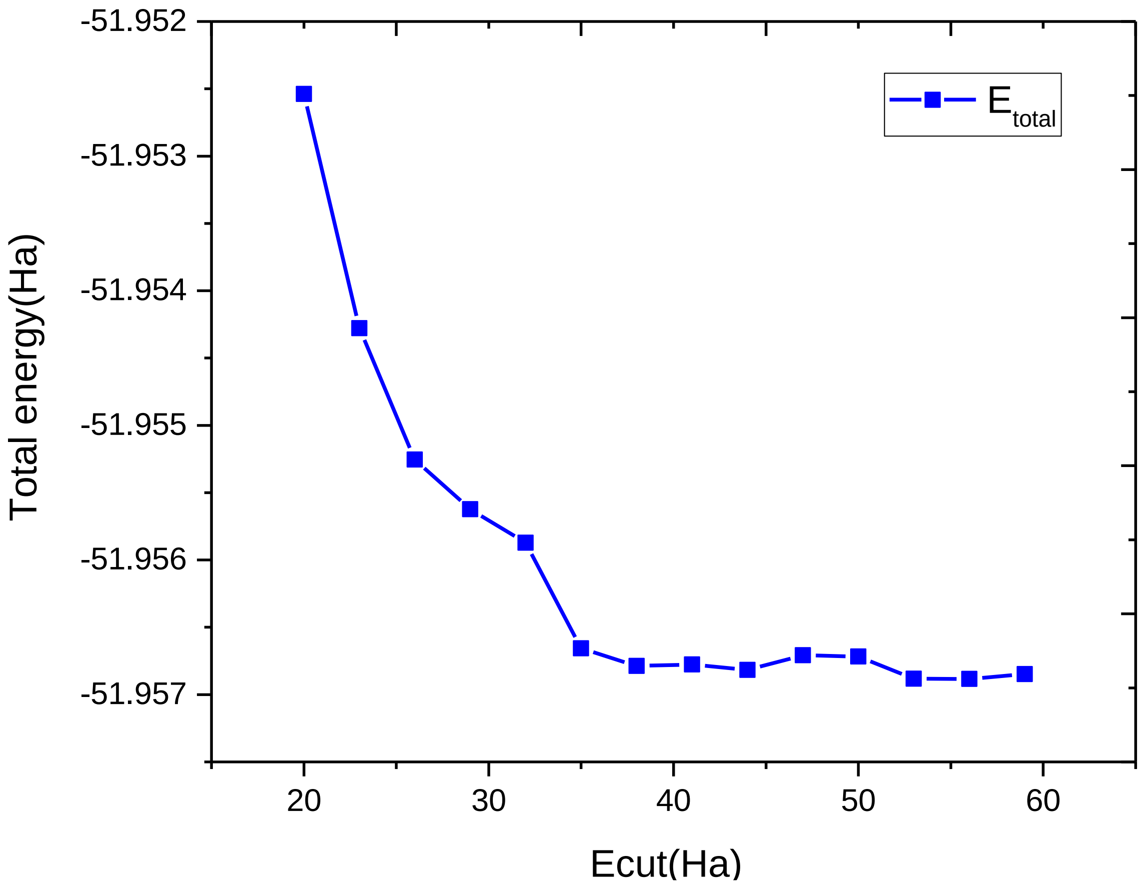


Figure III- 1: Convergence study: Total energy Vs Ecut for LaB6 crystal

Convergence study with respect to nkpt showing in the next table and the graphical representation in following the figure:

Table III- 2: Convergence study: Total energy Vs nkpt for LaB6 crystal

ngkpt	nkpt	Total energy(Ha)	$\Delta E_T/E_T$
4 4 4	4	-51.95135	-7.908E-5
6 6 6	10	-51.95319	-4.37644E-5
8 8 8	20	-51.95483	-1.22052E-5
10 10 10	35	-51.95533	-2.52258E-6
12 12 12	56	-51.95535	-2.0717E-6
14 14 14	84	-51.95546	0

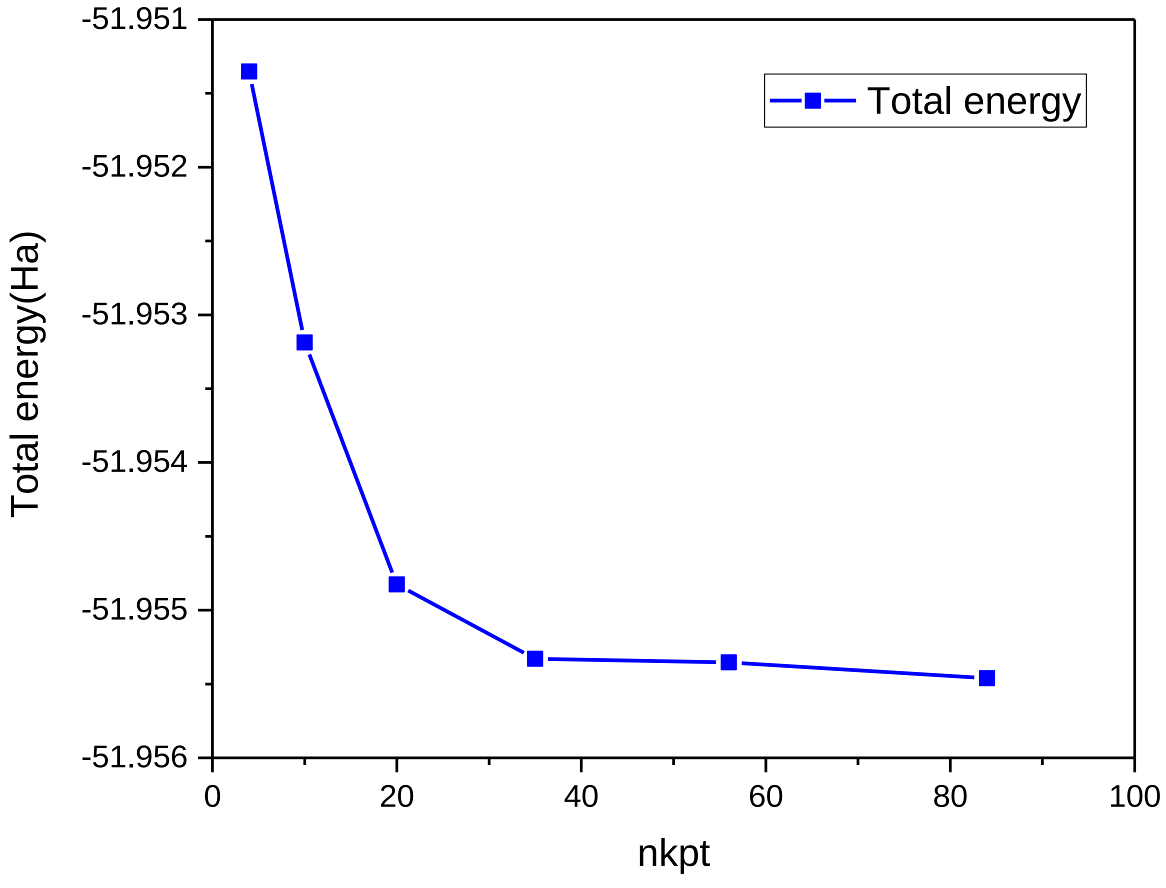


Figure III- 2: Convergence study total energy Vs nkpt for LaB6 crystal.

We chose an energy cutoff Ecut = 55 Ha to ensure convergence the total energy. The calculation was performed in a consistent way with self k-points grid (10x10x10) and bands number as 19 (with precision of 10^{-6} Ha) in the first Brillouin zone.

III.3.2. For LaB4 compound:

Convergence with respect to cut off energy:

Table III- 3:Convergence study: Total energy Vs Ecut for LaB4 crystal

Cut-Off energy(Ha)	Total Energy(Ha)	$\Delta E_T/E_T$
20	-180.9471	-6.83755E-5
25	-180.95596	-1.94378E-5
30	-180.95771	-9.75307E-6
35	-180.95878	-3.87993E-6
45	-180.95917	-1.69425E-6
50	-180.95941	-3.60025E-7
55	-180.95948	0

We can show this values in curve of Total energy=f(Ecut):

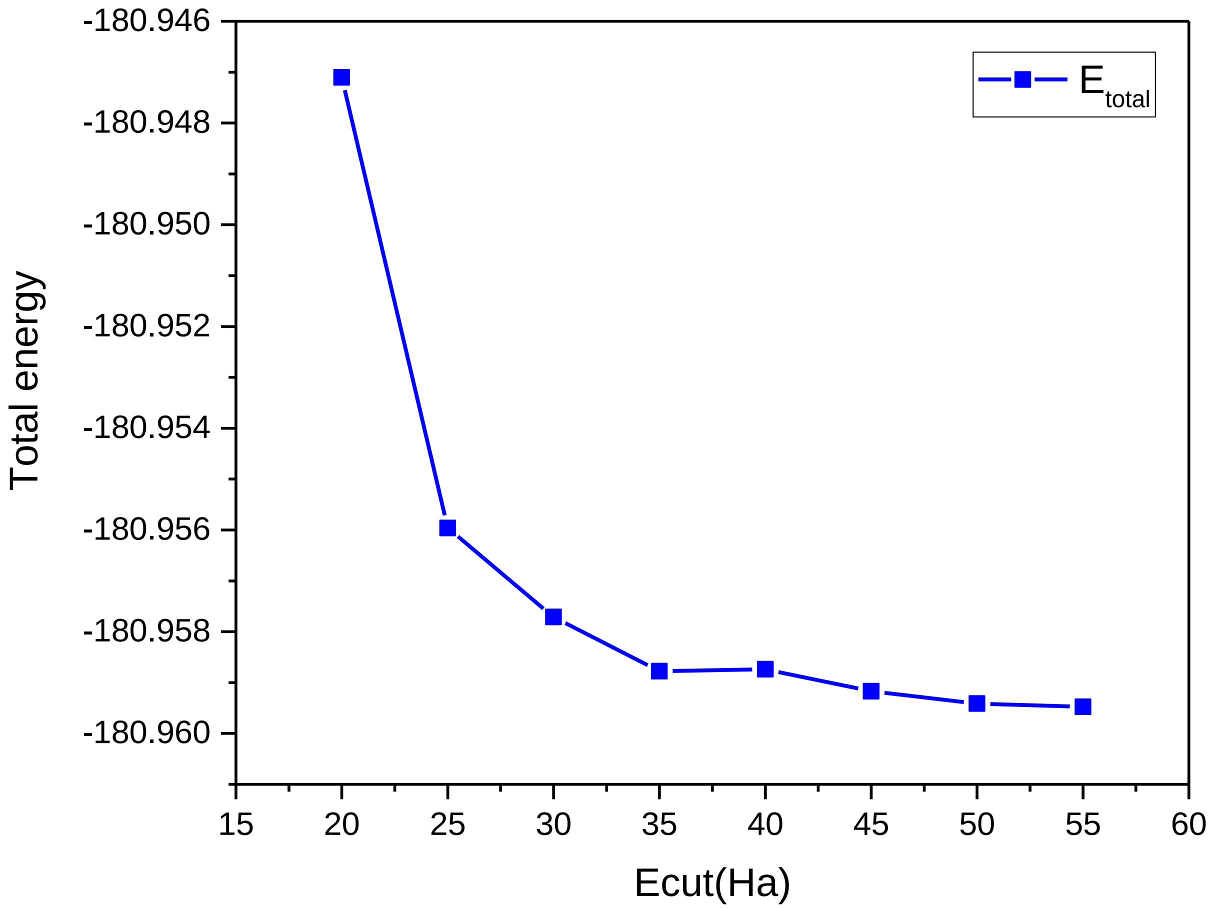


Figure III- 3: Convergence study: Total energy Vs Ecut for LaB4 crystal.

Convergence with respect to nkpt:

Table III- 4: Convergence study: Total energy Vs nkpt for LaB4 crystal

Ngkpt network	nkpt	Total Energy(Ha)	$\Delta E_T/E_T$
3 3 5	9	-180.93733	2.03153E-5
4 4 7	12	-180.93382	9.661E-7
5 5 9	30	-180.93408	2.3649E-6
6 6 11	36	-180.93342	-1.2897E-6
7 7 12	60	-180.93377	6.57589E-7
8 8 14	70	-180.93371	3.17907E-7
9 9 16	120	-180.93371	3.04255E-7
10 10 18	135	-180.93365	0

We can show this values in curve of Total energy=f(nkpt):

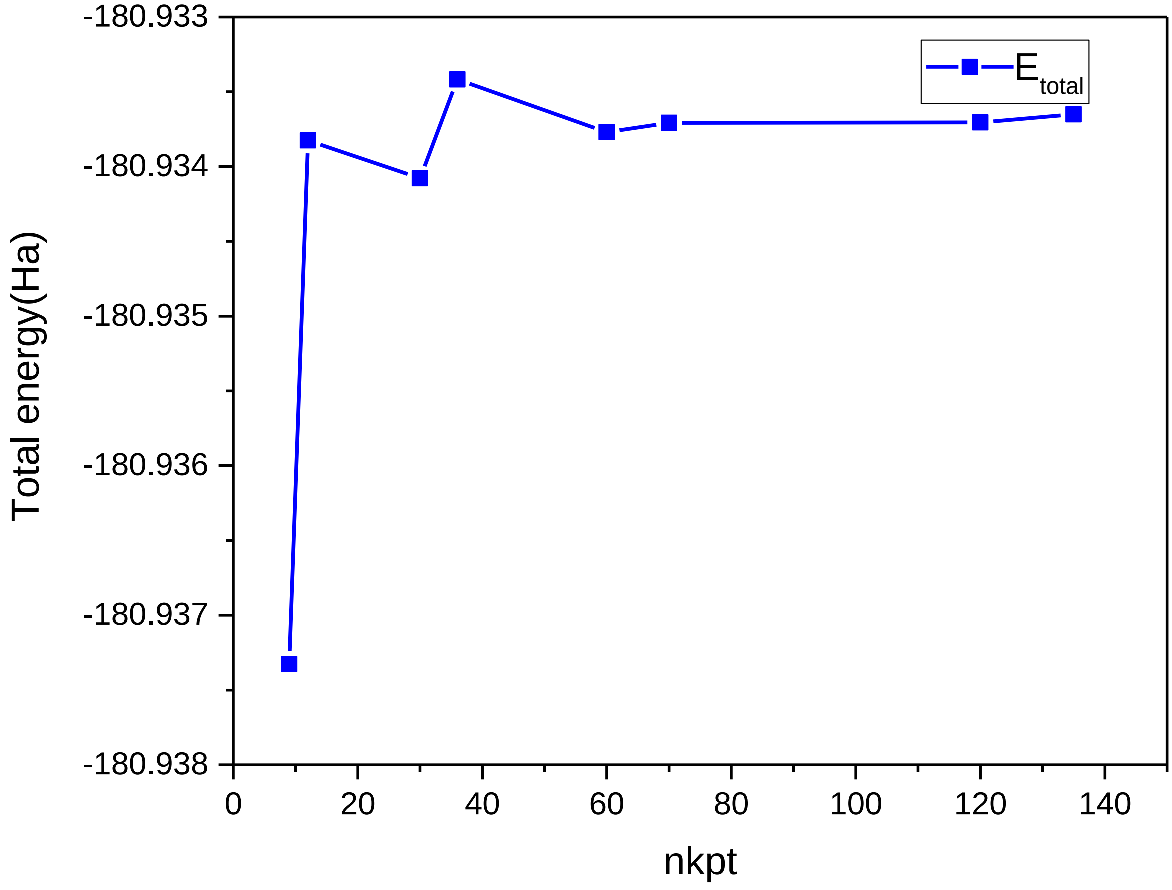


Figure III- 4: Convergence study: Total energy Vs nkpt for LaB4 crystal.

Convergence with respect to bands number (nband):

Table III- 5: Convergence study: Total energy Vs nband for LaB4 crystal.

nband	Total energy(Ha)	$\Delta E_T/E_T$
49	-180.93341682	0
52	-180.93341682	0
55	-180.93341682	0
58	-180.93341682	0
61	-180.93341682	0
64	-180.93341682	0
67	-180.93341682	0
70	-180.93341682	0

The graphical representation:

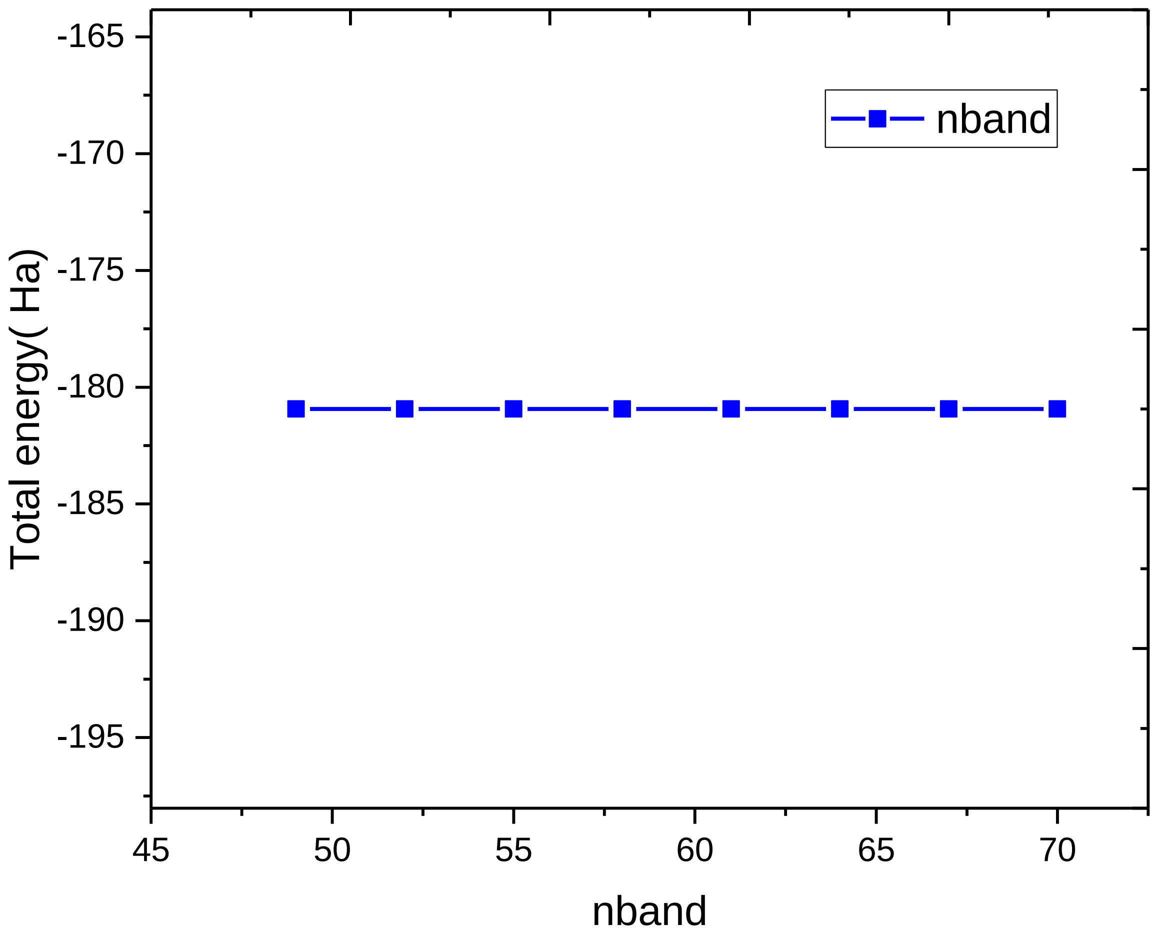


Figure III- 5: Convergence study: Total energy Vs nband for LaB4 crystal.

We chose an energy cutoff Ecut =50 Ha to ensure convergence the total energy. The calculation was performed in a consistent way with self k-points grid (8x8x14) and band number as 65 (with the precision of 10^{-7} Ha) in the first Brillouin zone.

III.4. Geometric optimization:

In order to get better structure (the Most stable as possible), must minimize the total energy of the system with respect to cell parameters (a, b, c, α, β, γ) and atomic positions (x_i,y_i,z_i),this optimization should give us a relaxed structure (Hellmann-Feynman forces applied to each atom tends to zero) , ABINIT offer many algorithms for this (molecular dynamic algorithms, BFGS, BFGS modified ,…),on this work we used BFGS modified to take into account the total energy as well as the gradients .[1][2]

The next figure represents optimization diagram:

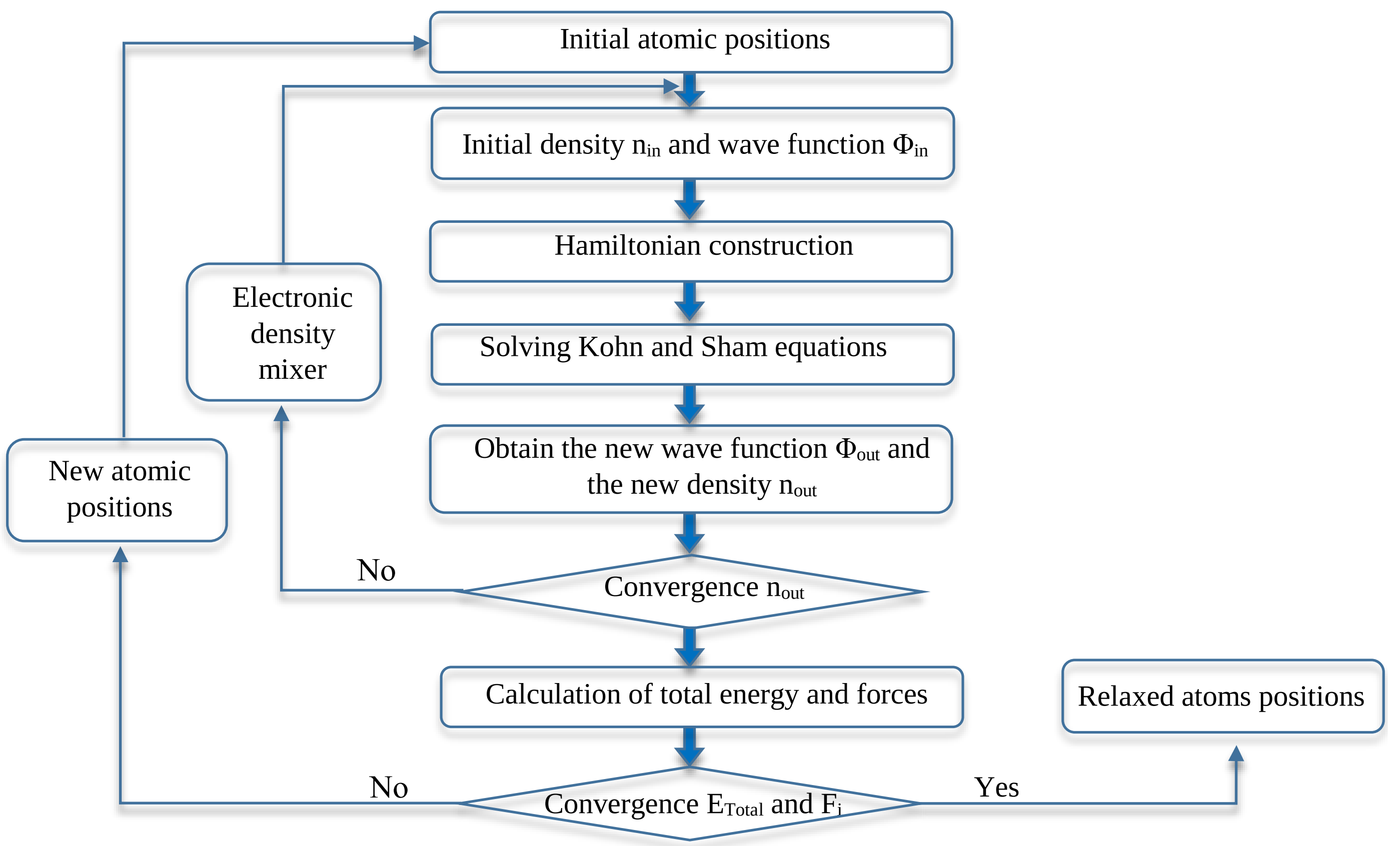


Figure III- 6: Flowchart of geometrical optimization processes

The results of optimization are summarized in table III-6, where xred is the reduced coordinate

Table III- 6: Cell parameters calculated compared with other work, and experimental data

		experimental	Other work	This work	
				LDA xc	GGA xc
LaB6	a (°A)	4.1549[a]	4.1262[b]	4.11994	4.15553
	u (xred)	0.1991[a]	0.201[b]	0.20107	0.20019
LaB4	a (°A)	7.327[c]		7.23409	7.28797
	c (°A)	4.182[c]		4.13531	4.16981

[a]reference [3]

[b]reference [4]

[c]reference [5]

Max force applied on atom for LaB4 using GGA is 1.08093E-07 (Ha/Bohr).

Max force applied on atom for LaB4 using LDA is 2.12276530E-09 (Ha/Bohr).

Max force applied on atom for LaB6 using GGA is 2.4567233892E-08 (Ha/Bohr).

Max force applied on atom for LaB6 using LDA is 2.0975113956E-09 (Ha/Bohr).

We observe that we have great agreement between the results obtained by calculations using the GGA xc and results found by Lihua Xiao and *al* [5] (x-ray diffraction data) with an error of (0.015%) in lattice parameter determination and error of (0.54%) on the internal parameter determination, in addition a comparison between the proposed approach have been taken into an account with recently published letters, we found better result. comparing with results using LDA xc it has an error of (0.84 %) in lattice parameter, and error of (0.54%) on the internal parameter determination. GGA give us good results than LDA xc.

For LaB4 GGA xc give lattice parameters error (0.5%) in **a**, and (0.3%) in **c** parameter, comparing with LDA xc whose give errors (-1.27%) in a lattice parameter, and (-1.12%) in **c** lattice parameter.

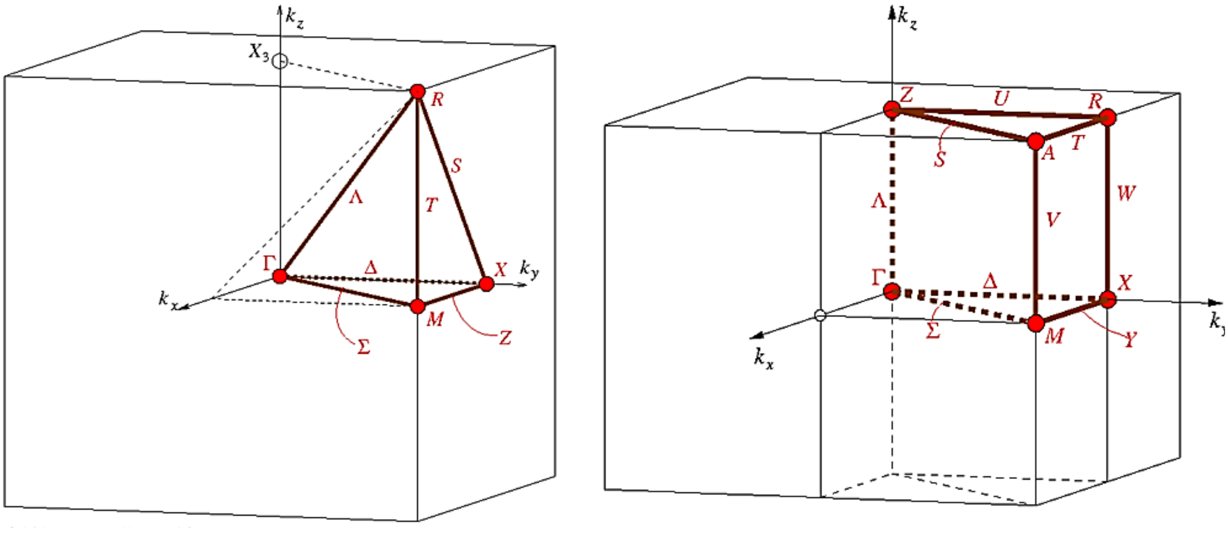
III.5. Electronic properties:

The study of crystal properties will be done in the first zone Brillouin of reciprocal space this first Brillouin zone (FBZ) is showing in **Figure III-7**. This reduced space of the reciprocal lattice is characterized by points of high symmetry.

The First Brillouin zone (FBZ) and high symmetry points:

The form and the volume of the zone of Brillouin only depend on to the geometry of Bravais lattice, without regard to the chemical composition or the number of atoms in the cell unit. The zone of Brillouin is a primitive unit cell of reciprocal lattice have fundamental importance for the study of the electronic properties of the crystals.

The first zone of Brillouin for a simple cubic structure has simple cubic form as showing **figure-III-7**. The calculation of crystal properties does not in the whole First Brillouin Zone, we do it just in this reduced space of the reciprocal lattice is characterized by points of high symmetry.



(a) (b)

Figure III- 7 Brillouin Zone, high symmetry points and high symmetry lines for studied crystals

(a) For simple cubic.

(b) For simple tetragonal.

High-symmetry points:

Γ point: this point is the center of the first zone of Brillouin with the coordinates $k_{\Gamma}(0,0,0)$.

X point: this point is the center of a lateral one face, is located in one of the axes k_x or k_y, we thus have: either $k_x = \pi/a(\pm 1,0,0)$ or $k_y = \pi/a(0,\pm 1,0)$ figure showing X point in $k_y = \pi/a(0,1,0)$.

M point: this point is located in the medium of one lateral segment, figure displaying M point in coordinates $k_M = \pi/a(1,1,0)$.

R point: this point situated in one of the cube corners, the figure showing R point in coordinates $k_R = \pi/a(1,1,1)$ to simple cubic system, for tetragonal, is situated in upper segment medium with coordinates $k_R = (0, \pi/a, \pi/c)$.

Z point: this point is located in the center of the upper face with coordinates $k_z = \pi/a(0,0,\pm 1)$ like shows figure.

A point: this point is located in one of the cube corners of tetragonal system, the figure showing A point in coordinates $k_A = (\pi/a, \pi/a, \pi/c)$.

High symmetry lines:

The high symmetry lines are segments link high symmetry points, the calculation of system properties do in along this segments which divided into equal distances between k points and solving Kohn and sham equation to each k point. The next table show the k point coordinates of high symmetry points in reduced coordinates and reciprocal coordinates, and high symmetry lines where the real space and reciprocal space primitive translation vectors are: $\vec{a}_1 = a\ \hat{x}$; $\vec{a}_2 = a\ \hat{y}$; $\vec{a}_3 = a\ \hat{z}$ and $\vec{b}_1 = \frac{2\pi}{a}\hat{k}_x$; $\vec{b}_2 = \frac{2\pi}{a}\hat{k}_y$; $\vec{b}_3 = \frac{2\pi}{a}\hat{k}_z$;

with: $\vec{k} = u\ \vec{b}_1 + v\ \vec{b}_2 + w\ \vec{b}_3 \quad : (u, v, w)$

Table I- 1: High symmetry points, lines, and his length for simple cubic system

Symmetry points in reduced coordinates (u, v, w)	Symmetry points in reciprocal coordinates (k_x, k_y, k_z)	Symmetry lines	distance
$\Gamma(0,0,0)$	$(0,0,0)$	$\Lambda(v,v,v)\ ;0\leq v\leq 1/2$ $\Gamma\rightarrow R$	$\sqrt{3}\pi / a$
$R(1/2,1/2,1/2)$	$(\pi/a,\pi/a,\pi/a)$	$T(1/2,1/2,w)\ ;1/2\geq w\geq 0$ $R\rightarrow\Gamma$	π / a
$M(1/2,1/2,0)$	$(\pi/a,\pi/a,0)$	$Z(u,1/2,0)\ ;1/2\geq u\geq 0$ $M\rightarrow X$	π / a
$X\ (0,1/2,0)$	$(0,\pi/a,0)$		

Table I- 2: High symmetry points, lines, and his length for tetragonal system

Symmetry points in reduced coordinates (u, v, w)	Symmetry points in reciprocal coordinates (k_x, k_y, k_z)	Symmetry lines	distance
$\Gamma(0,0,0)$	$(0,0,0)$	$\Lambda(0,0,v)\ ;0\leq v\leq 1/2\ \Gamma\rightarrow Z$	π / a
$Z\,(0,0,1/2)$	$(0,0,\pi/c)$	$T(w,w,1/2)\ ;0\leq w\leq 1/2$ $Z\rightarrow M$	$\sqrt{2}\pi / a$
$A(1/2,1/2,1/2)$	$(\pi/a,\pi/a,\pi/c)$	$Z(u+1/2,1/2,1/2);0\leq u\leq 1/2$ $M\rightarrow X$	$\pi\sqrt{\frac{1}{a^2}+\frac{1}{c^2}}$
$R(0,1/2,1/2)$	$(0,\pi/a,\pi/c)$	$Z(0,1/2,u+1/2);0\leq u\leq 1/2$	π / a
$X(0,1/2,0)$	$(0,\pi/a,0)$		

So we can now pass to the electronical properties of our compounds.

III.5.1. For LaB6 compound:

Bands Structure was calculated along high symmetry lines of cubic Brillouin zone (BZ) **Figure III-7- (a)** (X, R, M, G, R: are high symmetry points) and total density of states (TDOS) was also calculated and represented in **Figure III-8** side by side band structure, where the dotted line at zero energy indicates the shifted Fermi level.

We can observe that the bands or the total density **Figure III-8** curve crosses Fermi level (E_F) what indicate that LaB6 is a conductor, what approve his metallic character. The lowest three bands of bands structure (from -11 to -10 eV) are generated by the La 5*p* state. These bands provide a sharp peak in the total density of states. the almost flat band at -8 eV is an isolated part mainly get from the equal contribution of both B 2***s*** and 2*p* states (which make a hybridizing state) and a small contribution of La ***p*** states; this make a very important bond which is a very strong one; it represents covalent band (B-B).

The valence band consist mainly of B ***s*** and B *p* states and very slightly of La *d* state which is a completely occupied state. The valance bandwidth is about 15 eV (from -4 to 10 eV) Penetrated fermi level which allows electronic conductivity. We observe in this valence band, under Fermi level the existence a big contribution of *s* and *p* states related to Boron atom and small contribution of lanthanum atom what make less strong interaction; it participates in the cohesion of this compound.

Another bond present upper Fermi level, present at 8.8 eV consist mainly of La ***d*** state and a little of B *p* state. which very important one is represents a metallic bond. The zoomed zone it just to clarify that our compound has non semi-metallic character.

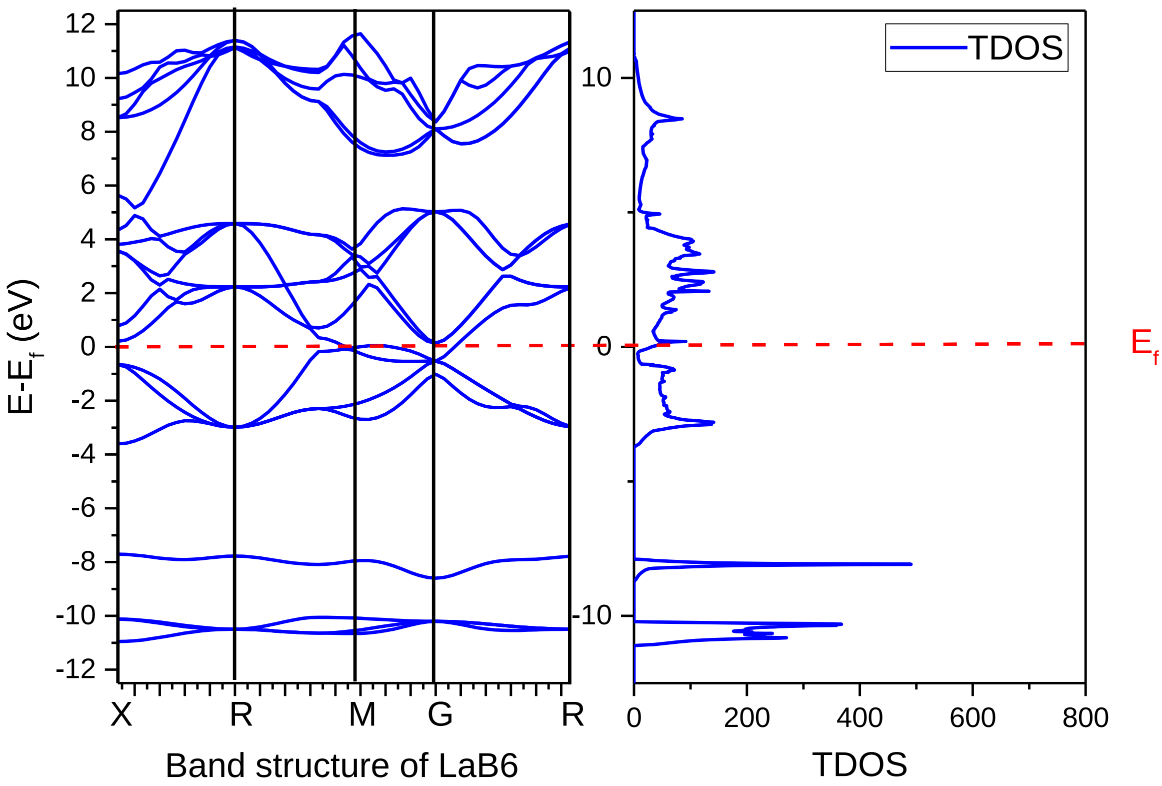


Figure III- 8: Band structure and total density of states TDOS for LaB6

TDOS and PDOS

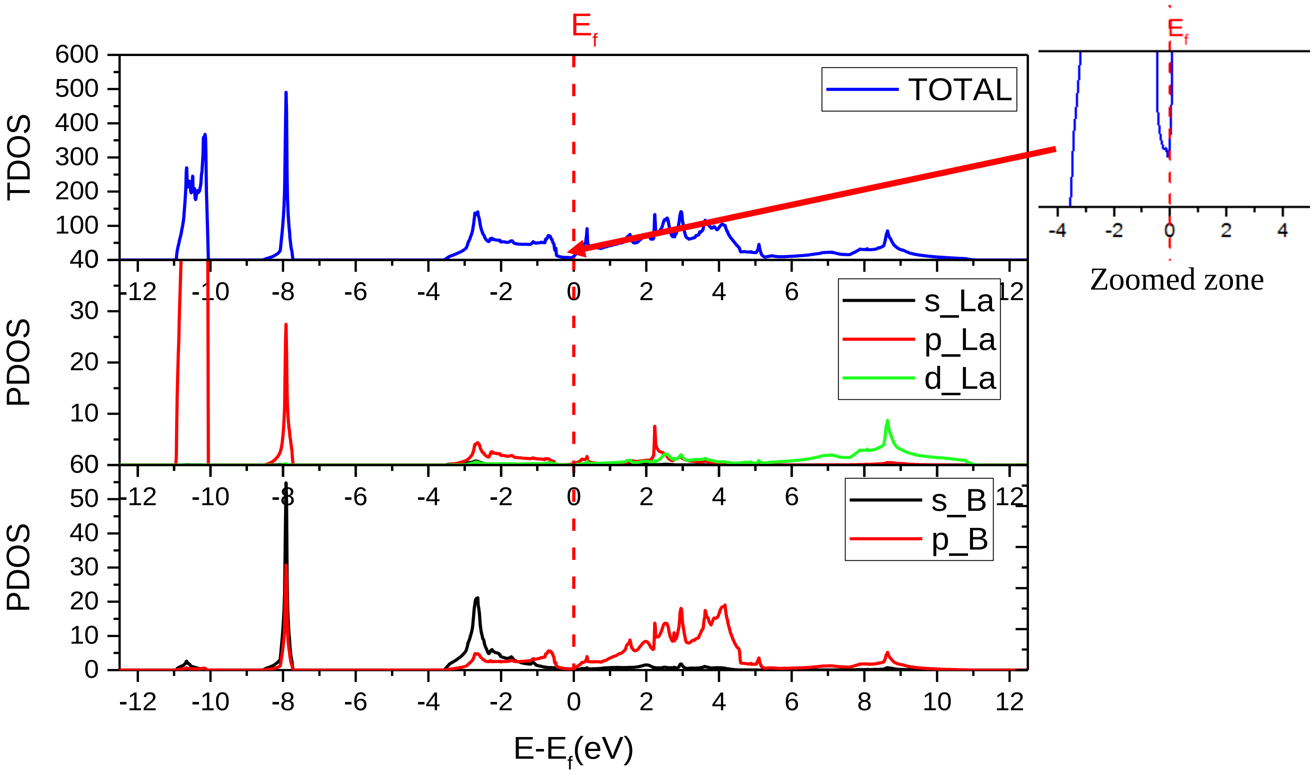


Figure III- 9: Total and partial density of states for LaB6

III.5.2. For LaB4 compound:

Bands Structure was calculated along high symmetry lines of cubic Brillouin zone (BZ) **Figure III-10** (G, Z, A, R, G: are high symmetry points) and total density of states (TDOS) was also calculated and represented in **Figure III-10** side by side band structure, where the dotted line at zero energy indicates the shifted Fermi level.

We can observe that the bands or the total density figure III-3 curve crosses Fermi level (E_F) what indicate that LaB4 is a conductor, what confirm his metallic character. According to Figure III-3 and Figure III-4 The lowest bands (from -9.5 to -11.5 eV) are generated by the La 5*p* state where they have the biggest density showing in a sharp peak in the total density of states. An isolated part in about -7.8 eV is mainly got from the both B 2*s* and 2*p* states (hybridizing state) and a small contribution of La *p* states; what make covalent bond (B-B), but this less strong than exist in LaB6, if we consider the relationship between the type and strength of the bonds (we await that this covalent bond makes the difference in the mechanical properties), so this compound is less stiffness than the previous one. These two regions represent conduction bands.

The valence band consist mainly of B *s* and B *p* states and very slightly of La *d* state which is a completely occupied state. The valance bandwidth is about 14 eV (from - 4 to 10 eV) Penetrated Fermi level which allows electronic conductivity, we observe in this valence band, under Fermi level the existence a big contribution of *s* and ***p*** states related to Boron atom and a small contribution of lanthanum atom what make less strong interaction than contains in LaB6.

Another bond present upper Fermi level, present at 2.7 eV consist mainly of B *p* state and a little of La *p* and *d* states. Another little bit at 5 eV, which very important are represented a metallic bond.

in addition, the conductivity of this compound LaB4 higher than related to LaB6 when we see a high density of states upper Fermi level. this is may be reasonable because of Lanthanum tetraborides was obtained from the mixture of its hexaboride and metallic lanthanum by melting it in an electric arc surrounded by argon: 2LaB6 + La = 3LaB4.

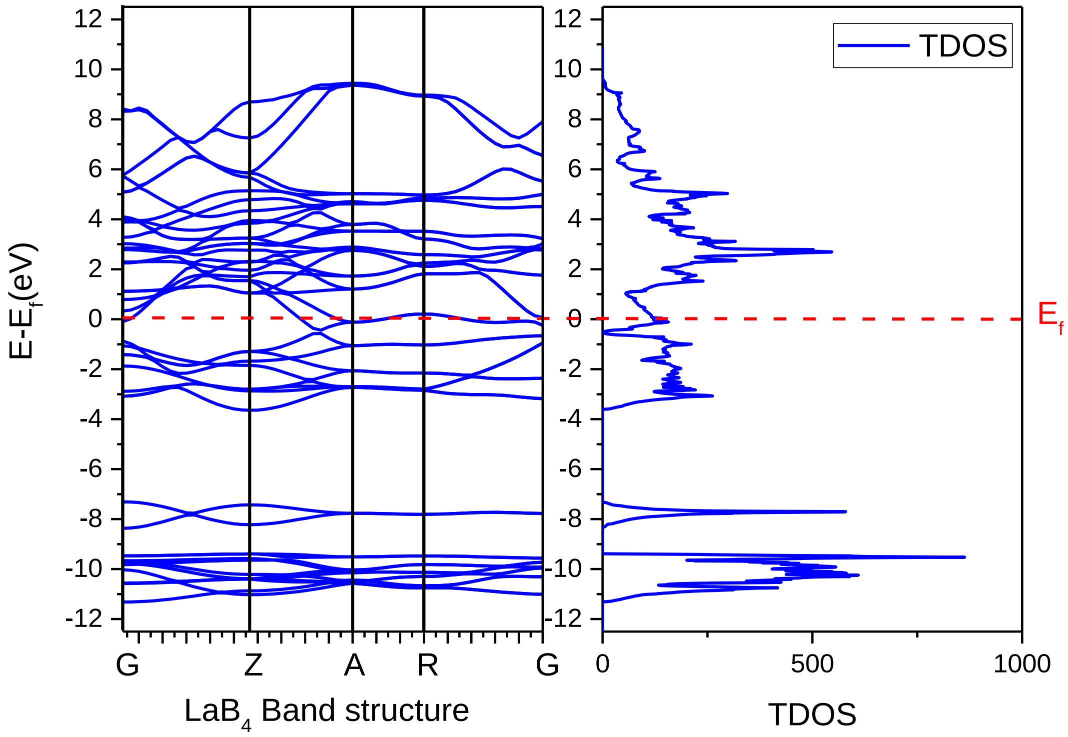


Figure III- 10: Band structure and total density of states TDOS for LaB4

TDOS and PDOS:

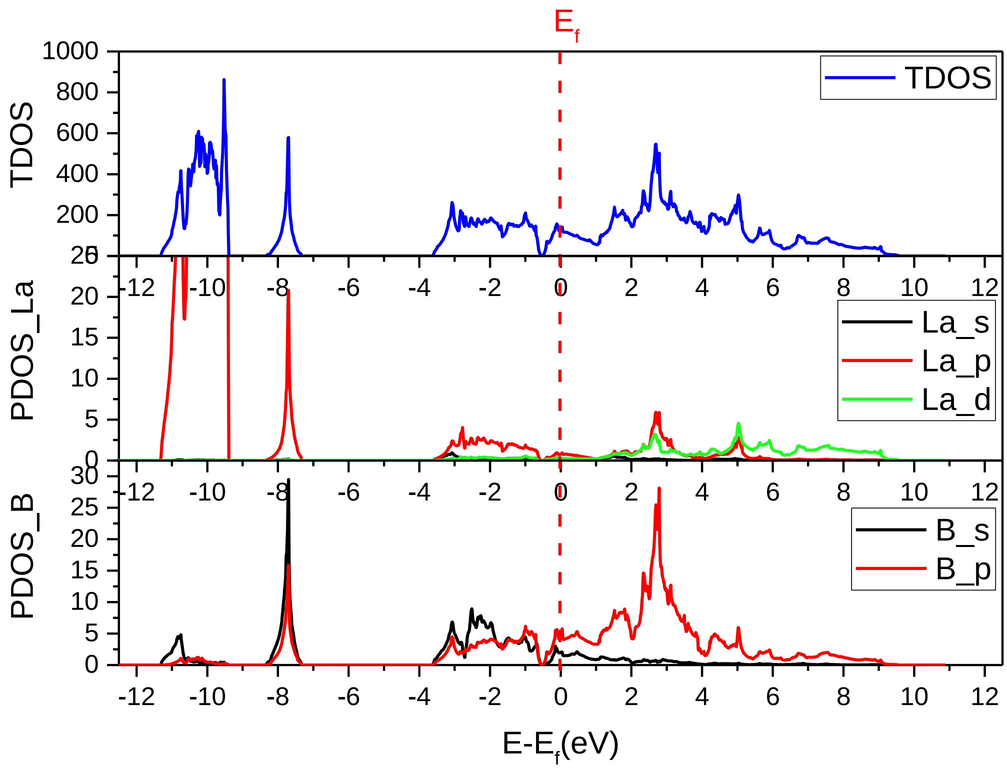


Figure III- 11: Total and partial density of states for LaB4

III.6. Elastic properties:

The elastic constants are related to the macroscopic parameters as the shear modulus (G) and Young (E) and Poisson's ratio (σ). Generally, the elastic properties of a solid are important for the understanding the mechanical behavior of the crystal. For example, Young's modulus (E) which expresses the stiffness of the material (expresses the atomic bonds of strength).

Voigt-Reuss-Hill[6] is approximation useful to determine the elastic properties quantities which better results obtained using elastic constants Cij and compliance constants Sij; calculated by equations of Density of Functional Perturbation Theory (DFPT) {described in chapter-II} , which could be compared with the average of two well-known limitations for single crystals by Voigt and Reuss[7]. It is given by the following expression[8][9]:

$$G^{Hill} = \frac{1}{2}(G^{Voigt} + G^{\mathrm{Reuss}}) \qquad \text{III-(2)}$$
$$B^{Hill} = \frac{1}{2}(B^{Voigt} + B^{\mathrm{Reuss}})$$

For tetragonal system, Reuss and Voigt Bulk modulus is defined as:

$$B_V = \frac{1}{9}\left(2C_{11} + C_{12} + 2C_{33} - C_{13}\right) \qquad \text{III-(3)}$$
$$B_R = \frac{c^2}{M}$$

Where M and c^2 are given by:

$$c^2 = \left(C_{11} + C_{12}\right)C_{33} - 2C_{13}{}^2 \qquad \text{III-(4)}$$
$$M = C_{11} + C_{12} + 2C_{33} - 4C_{13}$$

Reuss shear modulus and Voigt shear modulus are:

$$G_R = 15 \times \left(\frac{18B_v}{c^2} + \frac{6}{(C_{11} - C_{12})} + \frac{6}{C_{44}} + \frac{3}{C_{66}} \right)$$
$$G_V = \frac{1}{30}\left(M + 3C_{11} - 3C_{12} + 12C_{44} + 6C_{66} \right) \quad \text{III-(5)}$$

For cubic system, Reuss shear modulus and Voigt shear modulus are:

$$G_R = \frac{5(C_{11} - C_{12})C_{44}}{4C_{44} + 3(C_{11} - C_{12})}$$
$$G_V = \frac{C_{11} - C_{12} + 3C_{44}}{5} \quad \text{III-(6)}$$

Bulk modulus is:

$$B = \frac{C_{11} + 2C_{12}}{3} \quad \text{III-(7)}$$

To calculate the modulus of rigidity B and shearing G, one takes the average between these two modules: Voigt modulus and Reuss modulus.

$$G^{Hill} = \frac{1}{2}(G^{Voigt} + G^{\mathrm{Reuss}}) \quad \text{III-(8)}$$

$$B^{Hill} = \frac{1}{2}(B^{Voigt} + B^{\mathrm{Reuss}}) \quad \text{III-(9)}$$

The main Poisson characterizes the contraction of the material perpendicular to the direction of the applied force, is defined by:

$$\upsilon = \frac{3B - 2G}{2(3B + G)} \quad \text{III-(10)}$$

Young modulus E characterizes solid resistance to uniaxial deformation for cubic system, it gives by:

$$E = \frac{9BG}{3B + G} \quad \text{III-(11)}$$

Stability condition of cubic crystal and tetragonal crystal gives by: [10]

Table III- 7: Stability conditions for cubic and tetragonal crystals

tetragonal crystal	cubic crystal
$C_{44} > 0 \quad ; \quad C_{66} > 0$ $C_{11} > \lvert C_{12} \rvert$ $2C_{13}^{2} < C_{33}(C_{11} + C_{12})$	$C_{11} - C_{12} > 0$ $C_{11} > 0 \; ; \; C_{44} > 0$ $C_{11} + 2C_{12} > 0$ $C_{11} < B < C_{12}$

III.6.1. For LaB6 compound:

LaB6 elastic constants and modulus calculated in this work carried out within the density of functional perturbation theory DFPT, our results and others experimental and theoretical lists in the table:

Table III- 8: Elastic constants and modulus (Gpa) except ν (without unit)

	method	C11	C12	C44	G	B	E	ν
This work	LDA	479.57	32.38	92.78	133.11	181.44	320.88	0.205
	GGA	455.90	19.52	88.29	128.07	164.98	305.23	0.191
Other works	experimental	453.3 [a]	18.2 [a]	90.1 [a]		163 [a]		
		478 [b]	43 [b]	84 [b]		188 [b]		
	theoretical	466 [c]	37 [c]	88 [c]		180 [c]		

[a]reference [11]

[b]reference [12]

[c]reference [13]

Firstly, we have verified the existence and stability of crystal structure by the criteria imposed (table III-8) by the elastic constants is why these constants were calculated for LaB6.

$C_{44} > 0$ Checked ; $C_{66} > 0$ Checked

$C_{11} > \lvert C_{12} \rvert$ Checked ; $2C_{13}^{2} < C_{33}(C_{11} + C_{12})$ Checked ; $C_{11} < B < C_{12}$ Checked

All stability conditions of LaB6 are respected and for both exchange and correlation approximation used LDA, GGA. what means, that our structure is stable mechanically so it exists.

Comparing with previously published works: Note that the values of C_{11}, C_{12} and C_{44} are very close to the theoretical and experimental results of references [11-13]. Also for compressibility modulus *B*, remark that the GGA give better results than LDA.

Obviously, the compression constant C_{11} is very big than shear constant C_{44}, they are no comparison between them. Also torsion constant C_{12} is less than compressibility and shear constants, we can conclude from this results that the LaB6 compound is easier to torsion or shear than to compressing.

III.6.2. For LaB4 compound:

Also LaB4 elastic constants and modulus calculated in this work, our results and others experimental and theoretical lists in the next table:

Table III- 9: LaB4 Elastic constants and modulus (Gpa) except ν (without unit)

	method	C11	C12	C13	C33	C44	C66	G	B	E	ν
This work	LDA	416.20	70.42	63.63	420.6	155.4	156.9	157.9	220.6	382.5	0.21

Firstly, we have verified the existence and stability of crystal structure by the criteria imposed by the elastic constants (table III-7) is why these constants were calculated for the LaB4 compound.

$C_{11} > 0$ Checked ; $C_{44} > 0$ Checked ; $C_{33} > 0$ Checked ; $(C_{11} + C_{33} - 2C_{13}) > 0$

Checked $C_{66} > 0$ Checked ; $(C_{11} - C_{12}) > 0$ Checked

$2(C_{11} + C_{12}) + C_{33} + 4C_{13} > 0$ Checked

All stability conditions of LaB4 are respected and for both exchange and correlation approximation used LDA. it means that our structure is stable mechanically so it exists.

They are no published letters in this compound in mechanical properties to make comparison with him, this make our work original, return to our results, note that the compression constants C_{11} and C_{33} are more important than the Shear C_{44} and C_{66}.and the C_{11} value near to C_{33} but not equal, is somewhat less, what mean that the compressibility resistance along the ***a*, *b*** axes is equal**,** but in the ***c*** axis is a little bit more.

III.6.3. The elastic anisotropy:

Bulk modulus anisotropy:

Showing an elastic modulus variation in the three dimension can give a better look about his isotropy or anisotropy, the bulk modulus inverse for tetragonal crystal defined as [14]:

$$\frac{1}{B} = (S_{11} + S_{12} + S_{13}) - (S_{11} + S_{12} - S_{13} - S_{33})\ell_3^2 \qquad \text{III-(12)}$$

Where S_{ij} are the elastic compliance constants, and ℓ_1, ℓ_2 and ℓ_3 are the directional cosines to the X, Y and Z axes, respectively.

The 3D representation of bulk modulus is showing in figure III-11.

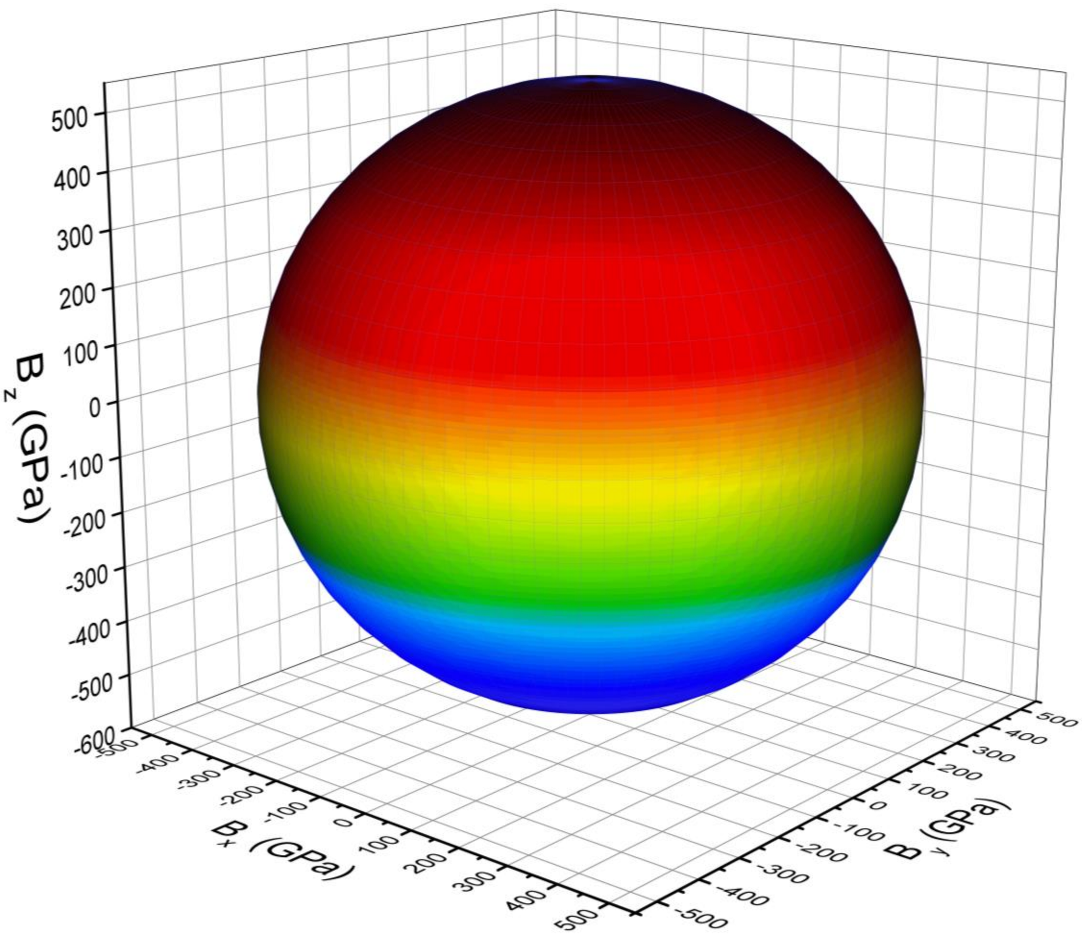


Figure III- 12: Three directions representation of bulk modulus

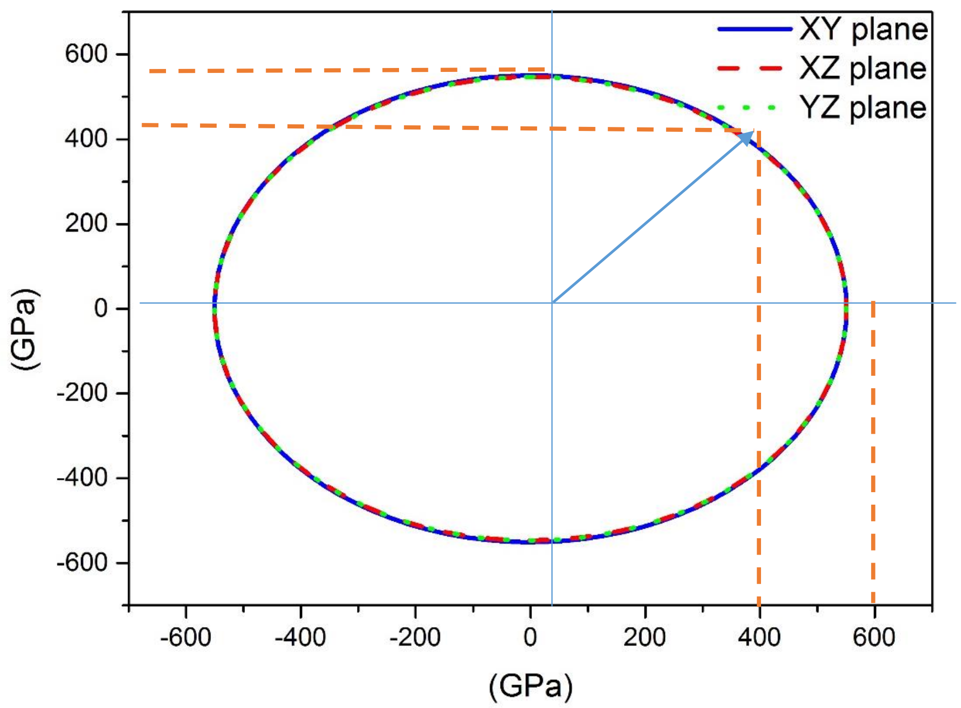


Figure III- 13: Projection of bulk modulus in different planes XY, XZ, YZ

We see in figure III-11 a spherical shape of the directional dependent bulk modulus, also the representation of planes, all are very nearly to perfect circles, in other words, the bulk modulus in the direction (1 0 0) and (0 1 0), but in the direction (0 0 1) is a little bit less, so it is nearly isotropic modulus in LaB4 crystal, that what confirm by the bulk modulus isotropic coefficient, introduced by Chung and Buessem:

$$A_B = \frac{B_V - B_R}{B_V + B_R} \qquad \text{III-(13)}$$

Our calculation hands out A_B = 0.97, our bulk modulus is nearly isotropic

Bulk modulus representation in LaB4 crystal don't give us a good idea on his mechanical properties, because this modulus is no directional; by definition bulk modulus characterize resistance of the material to hydrostatic pressure.

Young's modulus anisotropy:

Despite the coefficient Cij gives a good idea of the most rigid direction, but cannot prejudge the intermediate directions, and what direction is the most rigid, the direction dependent Young's modulus 1/E inverse for tetragonal crystals can be defined as [14]:

$$\frac{1}{E} = (\ell_1^4 + \ell_2^4)S_{11} + \ell_3^4 S_{33} + \ell_1^2 \ell_2^2 (2S_{12} + S_{66}) + \ell_3^2(1-\ell_3^2)(2S_{13} + S_{44}) \quad \text{III-(13)}$$

And

Where S_{ij} are the elastic compliance constants, and ℓ_1, ℓ_2 and ℓ_3 are the directional cosines to the X, Y and Z axes, respectively.

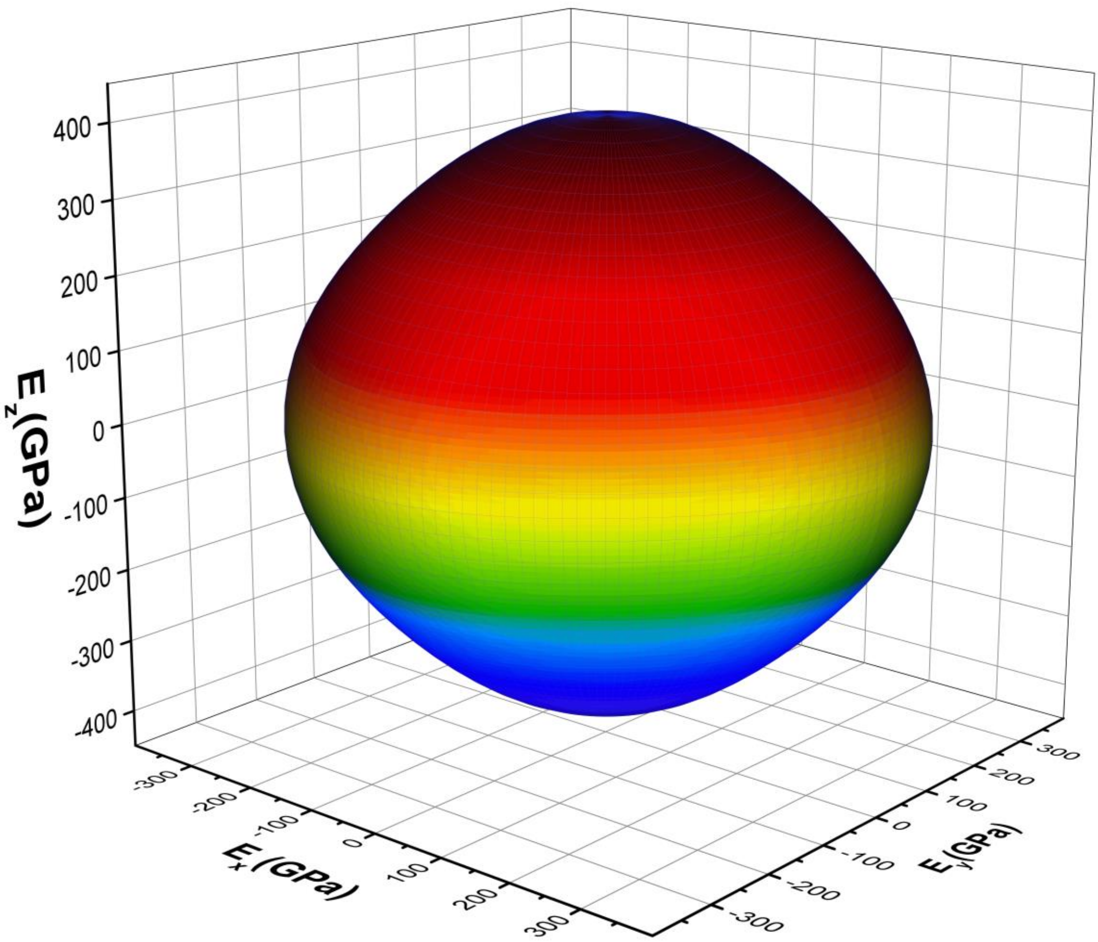


Figure III- 14: Directional young's modulus representation for LaB4

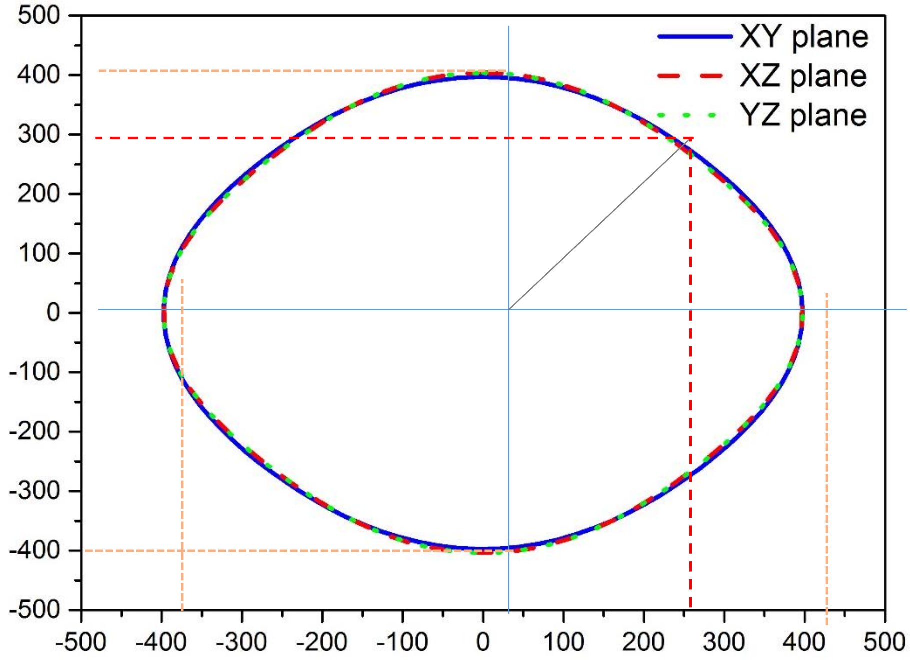


Figure III- 15: Projection of directional young's modulus in different planes XY, XZ, YZ

The 3D curve of young's modulus showing in Figure III-11 display that it is not exactly sphere, so young's modulus in LaB4 is anisotropic.

This figure doesn't make easy to read a values, because that, we take projection in different planes XY, XZ, YZ:

Clearly that the stiffness of this compound is approximatively the same in the two pure directions (1 0 0), (0 1 0) is a little bit more than 400 GPa, where the direction (0 0 1) is few more, which are the most rigid directions, but in the intermediate directions the 2D curves are not a perfect circle, and incline to inside, in other words, the stiffness is a little bit less (about 380 GPa) in the direction (1 1 0), and few less in directions (1 0 1), (0 1 1), with comparison with x, y or z directions. The difference between those directions is remarkable is about 20 GPa, and has an important consequence, Young's modulus in LaB4 compound depend for which direction the forces are applied.

III.6.4. Compounds comparison:

Table III- 10: Elastic constants and modulus of pure Lanthanum, LaB4, LaB6, Carbon diamond

		Elastic constants and modulus (Gpa)										
Material	**Method**	C_{11}	C_{12}	C_{13}	C_{33}	C_{44}	C_{66}	**B**	**G**	**E**	**B/G**	**ν**
La	**Exprt[a]**	**34.5**	**20.4**			**18.0**		**24.8**	**14[c]**	**37[c]**	**1.77**	**0.28[c]**
LaB4	**theor[b]**	**416**	**70.4**	**63.6**	**420**	**155**	**157**	**220**	**157**	**382**	**1.39**	**0.21**
LaB6	**theor[b]**	**479**	**32.4**			**92.8**		**181**	**133**	**320**	**1.36**	**0.20**
C Diamant	**theor[d]**	**1075**	**139**			**567**				**1220**		

[a]reference [15] [c]reference [16]

[b]this work. [d]reference [17]

The mechanical properties of any material related to the following quantities: young's modulus (E), Poisson ratio (ν), and the ratio (B/G), (which depend on elastic constants):

Young's modulus E determine the stiffness of the material, Poisson ratio ν can give us information on bonds type in the material (0.1 for covalent, 0.25 ionic, 0.33 for metallic), it is linked to Young's modulus. It is supposed that for the brittle (fragile) compound, B/G is smaller than 1.75 (for diamond B/G=0.8), ductile compound B/G is greater than 1.75 (for Al B/G=2.74). [18]

We calculated these three quantities values for a number of compounds; the results are shown in the previous table. We discuss now the borazing effect on the metallic compounds, especially Lanthanum.

Lanthanum in the pure phase has smalls values of elastic constants and modulus what can appear in his low stiffness (soft) and ductility which is pure metals characteristics.

The introduction of Boron atoms to the metallic material, in the case of LaB4 compound; has increased considerably his stiffness (Cij and young's modulus are increased), this appears in Poisson ratio ν=0.21 what means that the bonds present in this compound are between ionic and covalent bonds with a dominant ionic character, but this material become brittle (B/G <1.75). In the case of LaB6 compound; this operation increased all elastic constants and modulus compares with the pure Lanthanum, but regarding to LaB4 compound, we remark an important result: LaB6 represent a big stiffness to uniaxial stresses (compressions) than LaB4, this may be due to the strength of covalent bonds discussed above in the electronical properties; where the covalent bond B-B in LaB6 is much stronger comparing to the one in the LaB4 compound. Due to the directional nature of covalent bonds, we ask the following question: Can we be sure that the most important covalent bonds in LaB6 compound are parallel to the three uniaxial axes? In our knowledge, there is no sources to confirm that, so we can just say there is a strong interaction which is due to the short interatomic distances between boron atoms along the three axes mentioned already in the first chapter (Figure I-5)

However, all the rest of elastic constants and modulus in the case of LaB4 compound are higher than those of LaB6 compound. From the relations mentioned in this chapter, the shear is more related to the shear elastic constants C_{44} and C_{66} (equ III-5), and these are much important in LaB4 compound than LaB6 compound which made the calculated modulus much bigger, in addition, Young's modulus which is related to the shear modulus
(equ III-11) become bigger.

In other words, LaB6 compound is more stiffness for uniaxial compressions than LaB4 and pure Lanthanum and less resistant to the shear than LaB4, in addition, this compound become less brittle than the above mentioned compounds.

No comparison between these compounds and diamonds, which contains just covalent bonds what makes it the most stiffness known compound.

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Conclusion

Conclusion

The surface treatments play a critical role in improving the operating performance of mechanical parts. They also contribute to the economy of matter and money, since they allow to design lighter and more resistant parts of phenomena such as corrosion, wear, fatigue ...etc.

Performing ab-initio calculations based on the DFT and DFPT using plane waves pseudopotential method implemented in the ABINIT simulation package to investigate the structural, electronical, mechanical properties of Lanthanum hexaborides LaB6 and Lanthanum tetraborides LaB4, and to show the effect of Boronizing on pure lanthanum.

Our calculations based on (PP-PW) method are very close comparing with number of published letters for LaB6 compound and we predict properties for LaB4 compound which is in our knowledge the first calculations made for this compound.

This work clarifies the importance of metallic bonds and the big contribution of density of states in the electronical conductivity, which is higher in LaB4 compound than LaB6 compound.

The big interaction between ***s*** and ***p*** states of boron atoms, and covalent bonds B-B enhanced the mechanical properties of the intermetallic based La-B. We find that the LaB6 compound represent a big stiffness for uniaxial compressions but the LaB4 compound is more resistant to the torsion or shear than LaB6 compound what establish the big role of Boronizing of intermetallic surfaces.

Perspectives*:*

This work has encouraged us to enter the world of scientific research, from the beginning of the vast amount of problems that can be faced by the researcher during his work, arrive to how do you find solutions, whether on your own or with the help of others, where the big consequence of all master memory projects is “we perform better when we work as a group”.

This work will be a part of a big project aims to investigate the role of Boron atoms in changing the physical properties of intermetallic.

The original work in this memory, it is the LaB4 compound calculated properties, I will Target a publication with these properties.

I will attack other properties to publish it also.

الملخص

عملية البوررة من أهم عمليات المعالجة الكيميوحرارية لسطوح المعادن،و التي تهدف إلى زيادة صلابة هذا المعدن. إن هدف هذا العمل هو التحري في الخواص الإلكترونية و الميكانيكية لبلورات LaB4 و LaB6 ، ومقارنة هاته الخواص مع معدن الـ La النقي ، تمت هاته الدراسة باستعمال نظرية الكثافة الوظيفية (DFT) و نظرية الكثافة الوظيفية للإضطرابات (DFPT) المدمجتين في رمز الحساب ABINIT و الذي يعتمد على طريقة أشباه الكمون و الموجات المستوية لحل معادلة شرودنغر.إنطلاقا من هاته الدراسة لاحظنا الفرق التي تحدثه الروابط التساندية التي تخلقها أساسا ذرات البورB و قوة ارتباطها من أجل تقوية خواص البلورات المدروسة، فبالرغم من الإنزياح الكبير في المقالات العلمية لبلورة LaB6 على حساب LaB4 ، لإبرازه أداءا أحسن ميكانيكيا ضد الضغط الأحادي المحاور بالإضافة الى توحد خواصه في جميع الإتجاهات ، مع مراعات خواصه الإلكترونية الجيدة. إلا أن الـ LaB4 أظهر بعض التميز في الخواص الالكترونية، بالإضافة إلى مقاومته للقص و الفتل.

Abstract

Boronizing is one of important thermo-chemical treatments due to metal surfaces, aim to make it more stiffness. Our objective in this work is investigating on the electronical and mechanical properties of LaB4 and LaB6 crystals, and do a comparison with the pure La metal, this study was done by the density of functional theory (DFT), and density function perturbation theory (DFPT) whose are integrated in calculation code ABINIT. Based on this study we observed that the difference caused by the covalent bonds which generated by Boron atoms and his strength, what have the big role to get better mechanical properties of studies crystals, In spite of the large drift in scientific articles to LaB6 crystal on account of LaB4 ,who highlight a better mechanical performance against the uniaxial compression, in addition to his isotropy and the good electronic properties However, the LaB4 showed some excellence in electronic properties, as well as resistance to shear and torsion.

Résumé

La boruration est une méthode thermochimique de durcissement de surface des intermétalliques, le but de notre travail est faire une enquête sur les propriétés électroniques et mécaniques des cristaux LaB4 et LaB6, et faire une comparaison avec le Lanthane La pur, cette étude basée sur la théorie fonctionnelle de la densité (DFT), et la théorie fonctionnelle de la densité perturbé (DFPT) qui sont intégrés dans le code de calcule ABINIT. On a vu dans cette étude la grande différence de la liaison covalente qui a été fait par les atomes de Bor et leur puissance, ce qui lui donne un rôle important pour améliorer les propriétés mécaniques du cristaux étudiés, En dépit de la grande dérive dans des articles scientifiques à cristal LaB6 en raison de LaB4, qui a apparu une meilleure performance mécanique contre la compression uni-axiale, en plus de son isotropie et les bonnes propriétés électroniques, Cependant, le LaB4 a montré une certaine excellence dans les propriétés électroniques, ainsi que la résistance au cisaillement et à la torsion.