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*Contribution to the study of the physical properties
of the binary compound ScAs*

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Dedication

To our beloved parents, brothers and family

To our dear friends

And to everyone who supported us in this journey

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List of Abbreviations and symbols

e.g. : Exemple

i.e. : That is (Used to specify something mentioned previously)

Ar : Argon

As : Arsenic

Sc : Scandium

ScAs : Scandium Arsenide

NaCl : Sodium chloride (also means a rocksalt structure)

Ag₂S : Silver sulfide

STP : Standard conditions for temperature and pressure

DAC : Diamond anvil cell

DFT : Density functional theory

GGA : Generalized gradient approximations

LDA : Local-density approximation

DFT-LDA : Density functional theory method with local density approximation

FP-LMTO : Full potential linear muffin-tin orbitals

DOS : Density of states

PP : Pseudopotential

PSPW : Pseudopotential plane-wave

PW : Plane-waves

ECP : Effective core potentials

FCC : Face-Centered Cubic lattice

BC : Conduction band

BV : Valence band

BS : Band structure

E_g : Energy gap

E_F : Fermi level

E_{cut} : Cut-off energy

E-V : Energy-volume

\vec{k} : Wave vector

L : Energy-loss function

R : Optical Reflectivity

T : Temperature

V : Potential energy

n_i : The intrinsic concentration

p : Holes concentration

n : Electrons concentration

n and k (Chapters II & III) : Refractive index and extinction coefficient (Respectively)

I : Transmitted intensity

I_0 : Initial intensity

t : The film thickness

$\epsilon(\omega, k)$: Dielectric function

ϵ_{xc} : Exchange-correlation energy

ρ : Electrical resistivity

ρ_{vm} : Volume-Masse density

σ : Electrical conductivity

ψ : Wave function

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ملخص

Abstract

Résumé

General introduction

General introduction

In the year 1833, the first documented observation of a material (silver sulfide Ag_2S) which is now labeled as a semiconductor was by an English chemist and physicist Michael Faraday [1], and this labeling was due to the fact that this material couldn't fit inside the two classical labels (insulators and conductors) because of its properties so it took a place in between due to its behaviors. The conductivity of a semiconductor can become variable under the influence of many factors including pressure, temperature, light, and the presence of impurities (e.g. doping), etc.

Under the semiconductor class we can distinct many families including one of the most important ones in the technological applications i.e. III-V semiconductors, they are binary compounds that contain one element from both of the columns III and V of the Mendeleev table. In the last two decades, the use of III-V semiconductors has known a significant progression because of how advantageous they are in the domains of high-speed electronics and optoelectronics [2, 3].

Amongst the III-V semiconductors family, the Scandium Arsenide was the subject of interest for our studies. To take the advantageous properties of this compound for eventual technological applications, a theoretical investigation of the structural, electronic, and optical properties was necessary. For this purpose, we used the first principle calculations to investigate these properties.

At this end of studies project, our goal was to use the module CASTEP in the Accelrys's Materials Studio software to build a Scandium Arsenide (ScAs) lattice with a rocksalt crystal structure and also to simulate its structural, electronic, and optical properties. The manifestation of the achieved results and graphs was obtained with the help of OriginLab's Origin software.

Our work was built of three main chapters in addition to a general introduction and a general conclusion.

- The first chapter, covered the fundamental notions about semiconductors.
- The second chapter, was an insight into the different properties of semiconductor material, including the atomic, physical, electronic, and optical properties.
- The final chapter, was about the simulation's results and discussions.

Chapter I

Fundamental notions about
semiconductors

I.1 Introduction

The study of semiconductors and their properties requires before everything a basic knowledge about them and also requires having an insight about their fundamental notions and that is our task in this chapter.

I.2 Basic knowledge about semiconductors

Solid materials can be divided to three groups insulators, conductors and semiconductors, while insulators have a low conductivity (*around* $\sigma < 10^{-8} S/cm$) and conductors have a low resistivity (around $\rho < 10^{-3}\Omega$), semiconductors can have both. At $T = 0 K$ semiconductors behave like insulators and the more we increase the temperature the more conductive they get (their conductivity varies between around $10^{-8} S/cm < \sigma < 10^3 S/cm$ or $10^8\Omega > \rho > 10^{-3}\Omega$) [4].

I.2.1 Intrinsic and extrinsic semiconductors

A semiconductor is called intrinsic as long as it doesn't contain any impurities and this will maintain the same free carriers' concentration and keep the electric behaviour independent from the material structure. For a temperature T different than $0K$, electrons with the concentration n can become free and pass from the valence band (BV) to the conduction band (BC), these electrons leave holes behind them in BV with a value p (i.e. is holes concentration). Due to the absence of doping atoms in this kind of semiconductors, in BC the origin of all present electrons is BV, this says that there are holes as much as there are electrons, this will translate the intrinsic concentration ni to this relation [5] :

$$n = p = ni(T) = AT^{3/2} \exp\left(-\frac{E_g}{2kT}\right) \quad (\text{I. 1})$$

Where, A is a specific constant of a material, E_g is the energy of gap (Forbidden band), k is the Boltzmann constant.

A semiconductor is called extrinsic when it is injected with impurities, even with small amounts of doping the electrical properties can very sensitively variate. The introduction of specific impurities gives the semiconductor electrical properties adopted to electronic applications (e.g. diodes, transistors...) and also, optoelectronic applications (transmitters/receivers of light...). According to the nature of the impurity (dopant) extrinsic semiconductor can have two types of conduction, it can have a conduction by electrons and it requires a type N (negative) doping using a dopant like Phosphorus, Arsenic and Lithium..., and also it can have a conduction by holes and it requires a type P (positive) doping using a dopant like Boron, Gallium and Indium... [6].

I.2.2 Binary compounds of semiconductors

The binary semiconductors are a semiconducting compound that are made of two atoms where the sum of valence electrons for both atoms equals eight. The majority of binary semiconductors are a combination of the group III and group V of the periodic table elements (one from each), they have the ability to form very similar crystal structure in comparison with Silicon [7].

The primary advantage of binary semiconductors is that they have a direct band gap, not only that, we can see other advantages like thermal stability, critical electric field strength and also, they are useful in the miniaturisation of components. However, we can still see many disadvantages, the most important one is the high cost of manufacturing [8].

I.2.3 Electrical Conductivity/Resistivity for semiconductors

The electrical conductivity σ ($SI = S/cm$) for semiconductors is between the one of metals and the one of insulators, At $T = 0K$ a semiconductor will behave like an insulator and an ambient temperature $T \approx 300K$ it will behave like a conductor by conducting electricity in a limited manner all the is shown in the figure bellow.

These under various factors influenced electric conductivity variations makes semiconductors the favourite choice as a material for electronics domain and its applications.

The electrical resistivity ρ ($SI = \Omega$) is the reversed value of conductivity, it means [9] :

$$\rho = \frac{1}{\sigma} \quad (I.2)$$

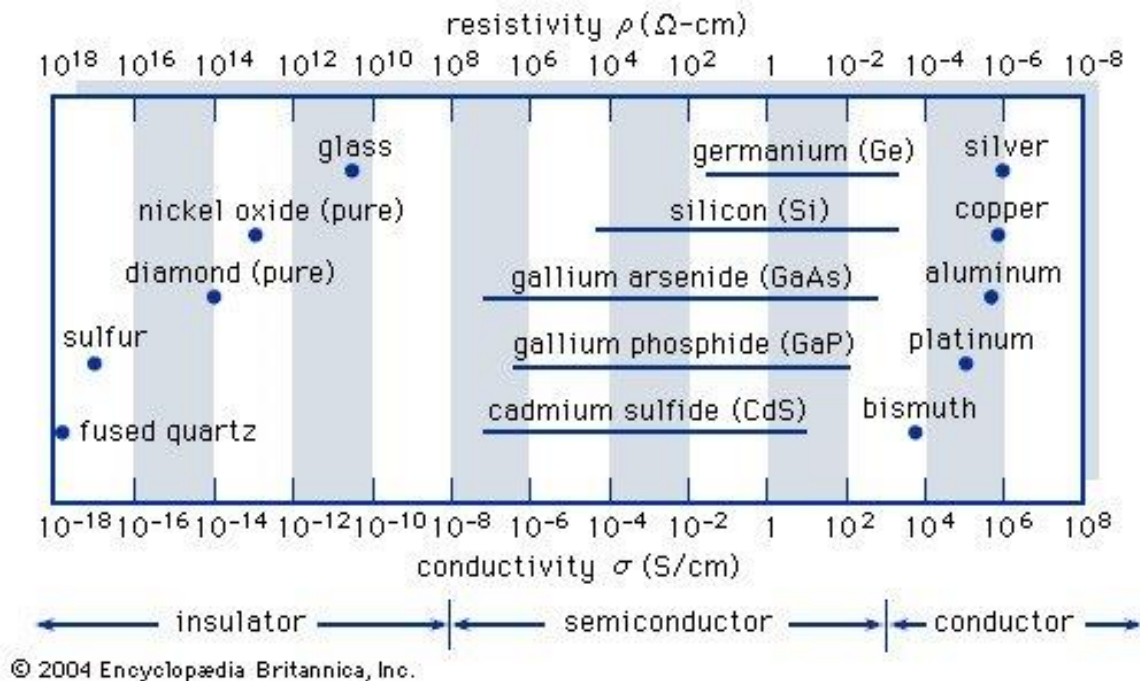


Figure I.1 : Electrical conductivity for different kinds of materials at 300K [10]

I.3 Energy Bands

In the atomic space that surrounds the atom, electrons cannot orbit the atom at a random distance because they only have specific permitted orbits where they can exist and these orbits are specific and discrete levels. The electrons energy can take any value inside an interval that depends on the material structure, this interval is what we call an **energy band**. It can exist many bands where the electron's energy can belong and they're called **allowed bands**. In the opposite, bands where the electron's energy cannot belong are called them **forbidden bands** [4].

I.3.1 Notion of band structure

Band structure is the manifestation of the data about the two categories of energy level's ranges that an electron has (conduction bands and valence bands) and the range(s) that he doesn't have (band gap(s) or forbidden band(s)) [11].

I.3.2 Conduction band and Valence band

At the fundamental state of the matter (0K), two bands have a particular role :

- Full bands with low energy corresponding to electrons participating in the maintenance of crystal structure, these are called **valence bands**.

- Empty bands with high energy, corresponding to electrons participating in electrical conduction, and these are called **conduction bands**.

The energy that separates these two bands is called a gap (or a **band gap**) and it's important to determine electronic and optical properties of semiconductors in order to have an idea about their domain of application. Metals, insulators and semiconductors can be

distinguished one from another by their band structures as It's shown in the figure I.2 bellow [12]. The width of the gap varies according to the temperature function, this variation is generally described by the Varshni equation [13] :

$$E_g(T) = E_g(0) - \frac{\alpha T^2}{T + \beta} \quad (I.3)$$

Where, $E_g(0)$ is the energy of the forbidden band at $T = 0K$,

α and β are the parameters that helps to describe the variation of the forbidden band according to the temperature function.

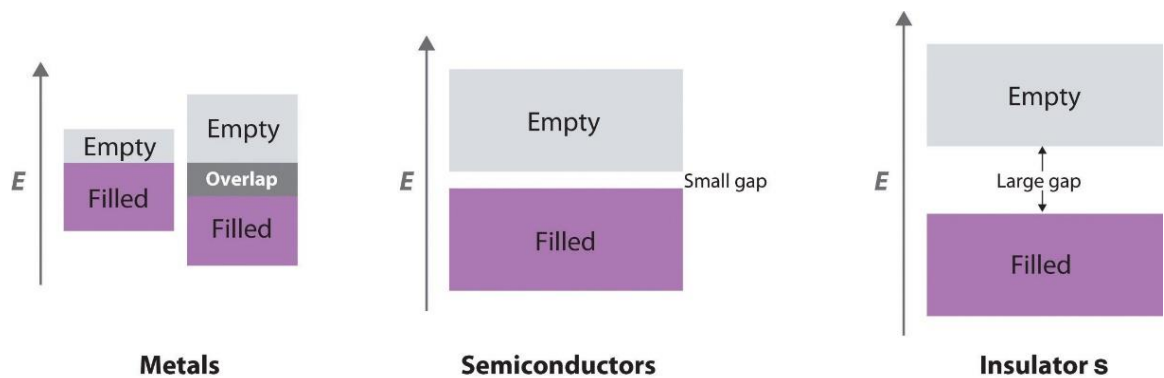


Figure I.2 : Band structure for metals, semiconductors and insulators [14]

I.3.3 Direct and indirect gap

In the band structure of a semiconductor material, the forbidden band is the area between the valence band (BV) and the conduction band (BC) which cannot be occupied by electrons. The gap is the difference of energy between the absolute minimum of the conduction band and the absolute maximum of the valence band. The extremes of the conduction and valence bands are characterized by an energy E and a wave vector \vec{k} .

In reciprocal space, if the minimum of the conduction band and the maximum of the valence band correspond to the same value of \vec{k} we say that the semiconductor has a **direct gap**. On the other hand, if the minimum of the conduction band and the maximum of the valence band correspond to different values of \vec{k} , we say that the semiconductor has an **indirect gap**. This is well explained in the figure I.3 below [12].

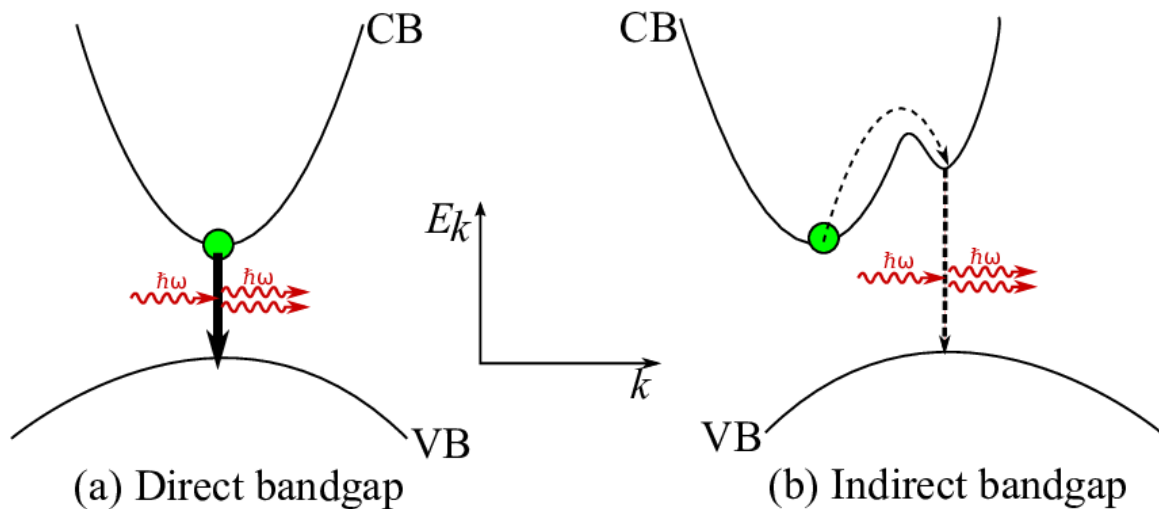


Figure I.3 : Band structure for direct and indirect bandgap [15]

I.4 Schrödinger equation

The Schrödinger equation is a linear partial differential equation that governs the wave function of a quantum-mechanical system [16]. It is a key result in quantum mechanics, and its discovery was a significant landmark in the development of the subject. The equation is named after Erwin Schrödinger, who postulated the equation in 1925, and published it in 1926, forming the basis for the work that resulted in his Nobel Prize in Physics in 1933 [17, 18]. The equation he found is [19] :

$$i\hbar \frac{\partial}{\partial t} \psi(r, t) = -\frac{\hbar^2}{2m} \nabla^2 \psi(r, t) + V(r, t) \psi(r, t) \quad (\text{I.4})$$

Where, i is the imaginary number, $\sqrt{-1}$,

\hbar is the Planck's constant h divided by 2π : 1.05459×10^{-34} *joule · second*,

$\psi(r, t)$ is the wave function, defined over space and time,

m is the mass of the particle,

∇^2 is the Laplacian operator, $\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$,

$V(r, t)$ is the potential energy influencing the particle.

I.5 Density of states

The density of states (DOS) is essentially the number of different states at a particular energy level that electrons are allowed to occupy, i.e. the number of electron states per unit volume per unit energy. Bulk properties such as specific heat, paramagnetic susceptibility, and other transport phenomena of conductive solids depend on this function. DOS calculations allow one to determine the general distribution of states as a function of energy and can also determine the spacing between energy bands in semi-conductors [20].

I.6 Pseudopotential and the plane-waves

The pseudopotential (PP or PSP) (also called effective potential or effective core potentials (ECP)) is concept is based on the natural energetic and spatial separation of core and valence electrons. The concept allows a significant reduction in computational efforts without missing the essential physics of phenomena provided the interaction of core and valence electrons is well described by some effective (model) Hamiltonian [21].

The plane-waves (PW) are a common way to compute energies of crystals. In solid state physics it can be defined as a grid basis in momentum space [22]. As such they extend over

the whole real space and are thus particularly suited for periodic boundary conditions in solid state calculations. The convergence is fast for one-particle methods and for many-body methods truncation schemes can be employed. A drawback of plane waves is the inability to represent sharp features such as interelectronic or electron–nuclear cusps in the wave function but it can be alleviated by the use of sophisticated pseudopotentials [22].

The pseudopotential plane-wave (PSPW) method is a fast and efficient way to calculate molecular properties using density functional theory (DFT). In this approach the fast varying parts of the valence wavefunctions inside the atomic core regions and the atomic core wave functions are removed and replaced by pseudopotentials. The pseudopotentials are chosen such that the resulting pseudoatoms have the same scattering properties as the original atoms. The rationale of this approach is that the changes in the electronic structure associated with making and breaking bonds only occur in the interstitial region outside the atomic core regions (see Figure I.4) [23].

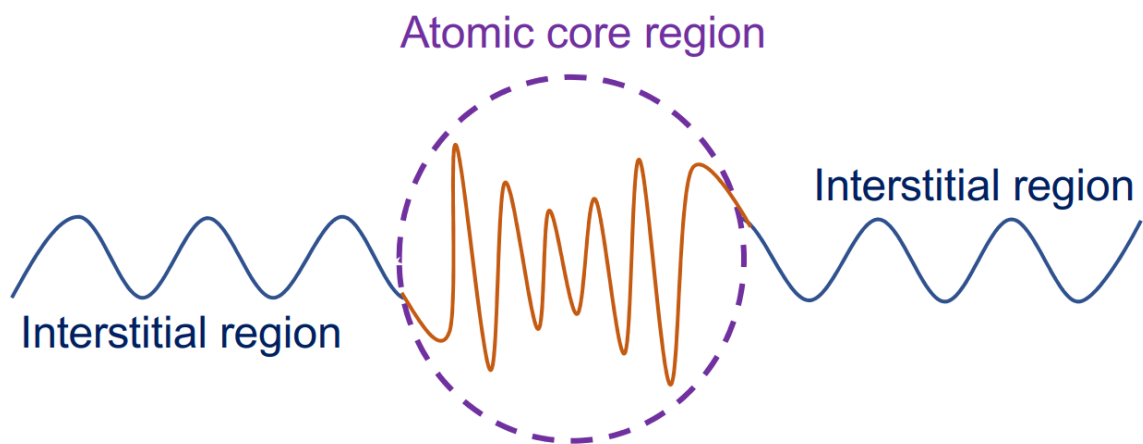


Figure I.4 : Illustration of the atomic core and interstitial regions in a valence wavefunction. Bonding takes place in the interstitial region and the atomic core regions change very little from molecule to molecule [23]

Chapter II

Physical properties of ScAs

II.1 Introduction

The goal of this end of studies project is to study the binary compound ScAs (Scandium Arsenide), but it is desirable and necessary to provide to the reader a scientific literature preview for the compounds that it contains and their properties.

II.2 Atomic properties of ScAs

The Scandium Arsenide is a binary compound made of two kinds of atoms, Scandium which is an element with the atomic number 21 and the symbol Sc, it belongs to the bloc p and the group 3 and it has the electron configuration [Ar] 4s² 3d¹ (1s² 2s² 2p⁶ 3s² 3p⁶ 4s² 3d¹), and Arsenic which is an element with the atomic number 33 and the symbol As, It belongs to the bloc p and the group 15(pnictogen) and it has the electron configuration [Ar] 4s² 3d¹⁰ 4p³ (1s² 2s² 2p⁶ 3s² 3p⁶ 4s² 3d¹⁰ 4p³) [24].

II.3 ScAs Crystal structure

The Scandium Arsenide can have many crystal structures, one of them was the subject of this study. A face-centered cubic system with $a = b = c = 5.47 \text{ \AA}$, $\alpha = \beta = \gamma = 90^\circ$ and a volume of 163.6673 \AA^3 , it has the orientations Sc(0.5, 0.5, 0.5), As(0, 0, 0) with 4 octahedron sites and It represents a rocksalt structure of ScAs [25].

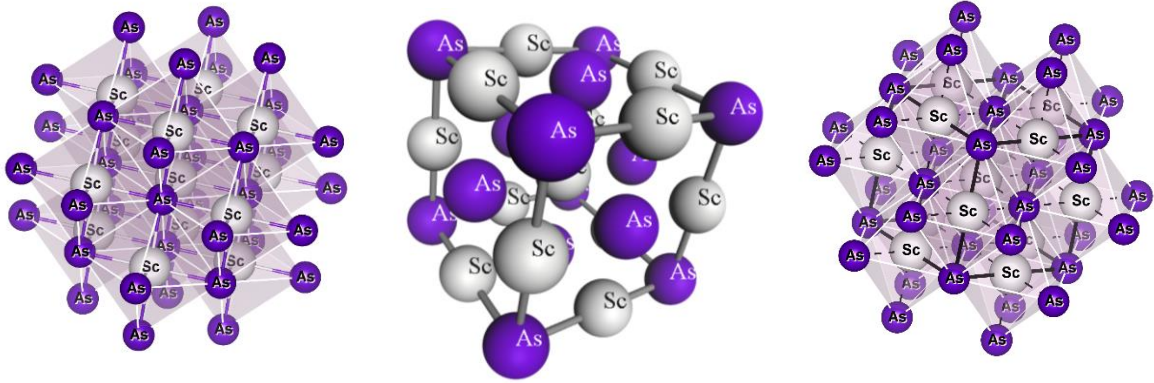


Figure II.1 : ScAs unit cell in rocksalt crystal structure

II.3.1 Crystal parameters of ScAs structure

A crystal structure is a structure that's made of unit cells that has a certain and a unique arrangement, by being stacked in one or two or all three dimensions these unit cells build a crystal structure.

Now, for ScAs we have two crystal structures, the stable one and the unstable one and each one of them has its unique parameters :

The coordination number in a crystal structure is highest number of atoms that have the same and the closest distance to a central atom, we can find this number by looking for cubic, tetrahedron or octahedrons sites where the coordination number will respectfully to the order 8, 4 and 6.

The studied ScAs structure has a unit cell made of 4 octahedron sites, which makes 6 the coordination number in this case.

The multiplicity N is the total number of atoms inside a unit cell in a crystal structure.

The studied ScAs structure contains 4 Sc atoms and 4 As atoms which means $N_{Sc} = 4$ and $N_{As} = 4$ and also means $N_{ScAs} = 8$.

The compactness C is the percentage a volume occupied by the atoms (V_a) from the volume of their unit cell (V_{uc})

$$C = \frac{V_a}{V_{uc}} = \frac{N_{Sc} \times \frac{4}{3}\pi r_{Sc}^3 + N_{As} \times \frac{4}{3}\pi r_{As}^3}{a^3} \quad (\text{II. 1})$$

Where, V_a is the volume of the atoms included the unit cell, V_{uc} is the volume of the unit cell, N_{Sc} and N_{As} are respectively the numbers of Scandium and Arsenic atoms in a unit cell of ScAs, r_{Sc} and r_{As} are respectively the radiuses of Scandium and Arsenic atoms.

Knowing that $r_{Sc} = 1.84 \times 10^{-10} \text{ m}$ [24], $r_{As} = 1.14 \times 10^{-10} \text{ m}$ [24] and $a^3 = 1.64 \times 10^{-28} \text{ m}^3$, the studied ScAs structure has a compactness value of 79%

$$\left(C = \frac{4 \times \frac{4}{3}\pi (1.84 \times 10^{-10})^3 + 4 \times \frac{4}{3}\pi (1.14 \times 10^{-10})^3}{(1.64 \times 10^{-28})^3} \approx 0.79 \right).$$

The volumetric mass ρ_{vm} (or the volumetric mass density or the density) is basically how much weight there is in a unity of volume, its unit is g/cm^3

$$\rho_{vm} = \frac{N \times M}{V \times N_A} = \frac{\frac{N_{ScAs}}{2} (M_{Sc} + M_{As})}{V_{uc} \times N_A} \quad (\text{II. 2})$$

Where, N_{ScAs} is the total number of atoms in a ScAs unit cell,

M_{Sc} and M_{As} are respectively the molar masses of Scandium and Arsenic atoms, and N_A is the Avogadro's number, equal to $6.02214076 \times 10^{23} \text{ mol}^{-1}$.

Knowing that $M_{Sc} \approx 44.96 \text{ g/mol}$ [24], $M_{As} \approx 74.92 \text{ g/mol}$ [24] and $V_{uc} = 1.63 \times 10^{-22} \text{ cm}^3$, the studied ScAs structure has a volumetric mass of $\approx 4.89 \text{ g/cm}^3$

$$\left(\rho_{vm} = \frac{4 \times (44.96 + 74.92)}{1.63 \times 10^{-22} \times 6.02214 \times 10^{23}} \right).$$

II.3.2 Zinc-Blende and Rocksalt structures

In the crystallography domain, we can find many compounds that are different in the elements that they contain but they share the same crystal structure and many of the crystal parameters and that has led to having a very known compound as a standard crystal structures including :

The Zinc-Blende structure (N°216 in the International Tables for Crystallography) is named after the mineral zinblende (also called sphalerite) which is one of the forms of Zinc sulphide (β -ZnS), this structure is based on a Face-Centered Cubic lattice (FCC) it has a tetrahedral coordination (at the vertices of a tetrahedron each cation is coordinated to 4 anions and vice-versa with each anion) with 4 tetrahedral crystallographic sites [26].

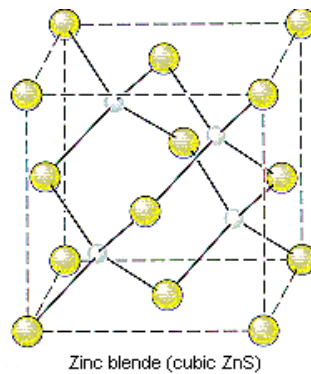


Figure II.2 : Zinc-Blende structure of crystal

The rocksalt structure (N°225 in the International Tables for Crystallography) is named after the metal halide Sodium chloride (NaCl) which is known as rocksalt, this structure is based on a Face-Centered Cubic lattice (FCC) it has an octahedral coordination (at the vertices of an octahedron each cation is coordinated to 6 anions and vice-versa with each anion) with 4 octahedral crystallographic sites for each unit cell [27].

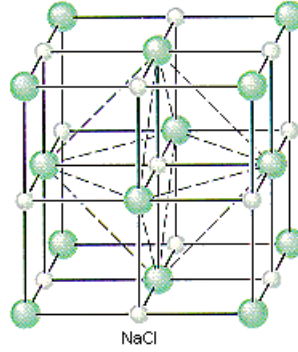


Figure II.3 : Rocksalt structure of crystal

II.3.3 Murnaghan's EOS for $E(V)$

The application of stress on a crystal structure results in a change in its volume and this will lead to a variation in the energy according to Murnaghan's EOS [28] :

$$E(V) - E(V_0) = \frac{B_0 V}{B'_0} \left[\frac{(V_0/V)^{B'_0}}{B'_0 - 1} + 1 \right] - \frac{B_0 V_0}{B'_0 - 1} \quad (\text{II.3})$$

V_0 is the equilibrium lattice volume [\AA^3],

B_0 the bulk modulus [GPa] and B'_0 is its pressure derivative [29].

II.4 Physical properties of ScAs

The ScAs is a binary semi-conducting compound made of two kinds of atoms, The first, Scandium which is a transition metal that has a silvery-white colour, its density at STP is 2.985 g/cm^3 and at a liquid state is 2.8 g/cm^3 , its weight is around 44.95u, it melts at $1,541^\circ\text{C}$ and it boils at $2,830^\circ\text{C}$, and finally its abundance in the universe is $3 \times 10^{-6} \%$ which means it's a rare-earth element.

The second, Arsenic which is a metalloid that has a silver-grey colour, its density at STP is 5.727 g/cm^3 and at a liquid state is 5.220 g/cm^3 , its weight is around 74.92u, it melts

at 816.9°C and it boils at 614°C, and finally its abundance in the universe is 8×10^{-7} % which means it's a rare-earth element too and it is known to be a lethal poison [24].

II.5 Electronic properties of ScAs

Studying and understanding the electronic behaviour of the ScAs compound requires an insight about Energy Bands and Density of States and the relation between them and also requires a knowledge about the density functional theory that gives us ability and methods to calculate these electronic properties.

II.5.1 Band structure and density of states relation

The definitions that we gave previously in chapter one allows us to say that the relation between band structure (BS) and density of states (DOS) is an explanatory relation that let us predict one starting from the other, they both have in common the Y axis which represents the energy levels, and for each level where there's band gaps there's a low DOS value and where there's a high DOS value we find permitted energy levels.

II.5.2 Density functional theory DFT

The density functional theory (DFT) is one of the most used methods to work on quantum calculations of the electronic properties of matter and it has two ways for that, Generalized gradient approximations GGA and Local-density approximation LDA.

II.5.2.1 Local-density approximation LDA

The Local-density approximation (LDA) is based on the idea of locally processing the electronic density as a uniform gas of electrons, It variates slowly in function of the r coordinate, and its equation is [30] :

$$E_{xc}[\rho(r)] = \int \rho(r) \varepsilon_{xc}[\rho(r)] dr \quad (\text{II. 4})$$

$\varepsilon_{xc}[\rho(r)]$ designates the exchange correlation energy for a particle of a homogeneous electron gas, this function can be decomposed into a contribution of exchange $\varepsilon_x[\rho(r)]$ and correlation $\varepsilon_c[\rho(r)]$ [30] :

$$\varepsilon_{xc}[\rho(r)] = \varepsilon_x[\rho(r)] + \varepsilon_c[\rho(r)] \quad (\text{II. 5})$$

II.5.2.3 Generalized gradient approximations GGA

The Generalized gradient approximations (GGA) is an approximation that has more precision than the LDA approximation and the difference is that GGA is based on the idea of processing the electronic density but as a non uniform gas of electrons. In this case, the functional that describes the exchange correlation will not be depending only on the electronic density but also on the derivatives of the density. In another word, It will consist on introducing the gradient of the density [31, 32].

In the GGA methods, the first derivative is introduced as a variable in the functional that describes the exchange correlation. Which means that in the GGA approximation the exchange correlation energy is defined by [33] :

$$E_{xc}^{GGA}[\rho_\alpha, \rho_\beta] = \int \rho(r) \varepsilon_{xc}[\rho_\alpha, \rho_\beta, \nabla\rho_\alpha, \nabla\rho_\beta] d^3r \quad (\text{II. 6})$$

α and β are the bottom and top spins.

II.6 Optical properties

Optical properties are those physical quantities that let us have a good understanding of how materials interact with light.

In physics there's a branch called Optics it includes optical physics where Optical properties of matter are a subject of study.

For our end of studies project, we've studied some of those properties including Reflectivity, Absorption, Refractive Index, Dielectric Function, Conductivity and Loss Function and we will be talking about them with brief details in this section.

II.6.1 Reflectivity

The reflectivity of a surface (e.g. an interface between two optical media) is defined as the ratio of reflected optical power to the incident optical power. Usually, it is applied to cases with specular reflections on exactly flat unstructured surfaces, i.e., not to extended objects and diffuse reflections.

Complex reflection coefficients and reflectivities at optical interfaces can be calculated with Fresnel equations. They depend only on the refractive indexes of both optical materials [34].

II.6.2 Absorption

Absorption of electromagnetic radiation is how matter (typically electrons bound in atoms) takes up a photon's energy — and so transforms electromagnetic energy into internal energy of the absorber (for example, thermal energy) [35].

The optical absorption in crystals is mostly due to interband transitions, that is, to the promotion of electrons from occupied valence bands to empty conduction bands [36].

II.6.3 Refractive Index and extinction coefficient

Refractive Index (also called refraction index or index of refraction) Is a value that describes the light speed of traveling through the studied material, it has no unit and it is defined by the law [37],

$$n = \frac{c}{v} \quad (\text{II. 7})$$

Where, n is the refractive Index,

c is the speed of light in a vacuum, it's a constant value (*around* $2.998 \times 10^8 \text{ m/s}$)

and v is the phase velocity of light in the medium its unit is m/s .

The extinction coefficient (k) (also known as the imaginary part of refractive index) is a measure of light lost due to scattering and absorption per unit volume [38], It is calculated from Swanepoel method [39] using the relation:

$$k = \alpha\lambda/4\pi \quad (\text{II. 8})$$

Where, α is optical absorption coefficient, which is given by [40] :

$$\alpha = \frac{1}{d} \ln\left(\frac{1}{T}\right) \quad (\text{II. 9})$$

T is the transmittance, and d is the average value of thickness of the film obtained from the Swanepoel method [39] using the following expression :

$$d = \frac{\lambda_1 \lambda_2}{2(\lambda_2 n_1 - \lambda_1 n_2)} \quad (\text{II. 10})$$

The complex index of refraction of the medium N is defined as [41] :

$$N = \sqrt{\varepsilon} = n + ik \quad (\text{II. 11})$$

where, n is the usual refractive index and k is the extinction coefficient.

In optical experiments, one does not usually measure n and k directly. The measurable quantities are the reflectivity R and the absorption coefficient α . It can be shown (see textbooks on electromagnetism) that these quantities are related to n and k by the expressions [41] :

$$R = \left| \frac{1 - N}{1 + N} \right|^2 = \frac{(1 - n)^2 + k^2}{(1 + n)^2 + k^2} \quad (\text{II. 12})$$

$$\alpha = \frac{2\omega}{c} k \quad (\text{II. 13})$$

Note that Eq.(II.9) gives the reflectivity at normal incidence. In general, the formula becomes more complicated [41].

II.6.4 Dielectric Function

Dielectric function $\varepsilon(\omega, k)$ describes the dielectric response to the plane-wave electric field [42],

$$\varepsilon(\omega, k) = E(\omega, k)e^{-i(\omega t - kr)} \quad (\text{II. 14})$$

Where, ω is the angular frequency, k is the Wave vector.

It can be in principle realized for arbitrary values of ω, k by using appropriate external electric charges and currents. When one limits to propagating electromagnetic waves in macroscopically homogeneous media, the values ω, k become mutually dependent. For example, for transverse waves $E \perp k$ which propagate along the optical axes [42],

$$k(\omega)^2 = (\omega^2/c^2)\varepsilon(\omega) \quad (\text{II. 15})$$

Such waves, whose propagation is characterized by a complex wave vector, characterize mixed electromagnetic and lattice vibrational (phonon) or electron excitations called polaritons. Knowing the complex dielectric function, polariton dispersion branches are fully determined [42].

The Kramers-Kronig relations establish a fundamental relationship between the dispersions of the real and imaginary parts of the dielectric function. This way refraction of light and energy dissipation appear to be interconnected phenomena. Kramers-Kronig relations are derived for both insulators and electrical conductors making use of the theory of generalized functions. Simple sum rules are derived, too [43].

So, if we take as an example a complex dielectric function [42],

$$\varepsilon(\omega) = \varepsilon_{Re}(\omega) + i\varepsilon_{Im}(\omega) \quad (\text{II. 16})$$

The Kramers-Kronig relations will be given by [44],

$$\varepsilon_{Re}(\omega) = \frac{1}{\pi} \mathcal{P} \int_{-\infty}^{\infty} \frac{\varepsilon_{Im}(\omega')}{\omega' - \omega} d\omega' \quad (\text{II. 17})$$

and

$$\varepsilon_{Im}(\omega) = -\frac{1}{\pi} \mathcal{P} \int_{-\infty}^{\infty} \frac{\varepsilon_{Re}(\omega')}{\omega' - \omega} d\omega' \quad (\text{II. 18})$$

Where \mathcal{P} denotes the Cauchy principal value.

From this we assume that the real and imaginary parts of such a function are not independent, and the full function can be reconstructed given just one of its parts [44].

II.6.5 Conductivity

The optical conductivity is the extension of electrical transport to high frequencies (energies). It is a contact free quantitative measurement, mostly sensitive to charged responses. Current techniques allow us to cover over three orders of magnitude in energy in a range spanning 1meV to 6 eV (or, in the lingo of spectroscopists, 10 to 50000 cm^{-1}). It is a most powerful tool in the study of conducting media.

The complex optical conductivity σ is the extension to high frequencies of dc transport measurements and is related to the dielectric function by [45] :

$$\sigma = 2\pi i(1 - \varepsilon) \frac{\omega}{Z_0} \quad (\text{II. 19})$$

where, $Z_0 = 377 \Omega$ is the vacuum impedance.

II.6.6 Loss Function

Energy-loss function, defined as [46],

$$L = \text{Im}[-1/\varepsilon(q, \omega)] \quad (\text{II. 20})$$

as a function of momentum transfer $\hbar q$ and energy loss $\hbar\omega$ characterizes inelastic scattering process. The dielectric function $\varepsilon(q, \omega)$ in energy-loss function reflects the response of a solid to an external electromagnetic perturbation [46].

Chapter III

Results and discussions

III.1 Introduction

The Theoretical advances and the reduction in the cost of computation have pushed to a considerable normalization of ab initio modelling, several codes have been marketed, their use is growing exponentially, and researchers are becoming increasingly sensitive to their results. As an aid to the analysis and interpretation of experimental data, ab initio modelling has now become an almost essential tool. In addition, its predictive capabilities make it a real "computer experience" capable of unambiguously identifying microscopic mechanisms underlying the phenomena or properties studied [4].

The study of the properties of materials under pressure has become an important research activity. This is due to the development of the diamond anvil cell (DAC) (a device that allows to make a material a subject to a very high pressures and temperatures and to carry out numerous physical measurements under these conditions) and the extension of the static pressure range of optical and X-rays measurements. On the other hand, several calculation techniques for the electronic structure and ab initio calculations made it possible to better understand the fundamental properties of the material under pressure. In fact, the pressure parameter has a big effect on the fundamental properties of semiconducting materials and can lead to new materials with new behavioural properties [4].

Despite the importance of the semiconductor based on ScAs in the rocksalt phase, there has been few works about the fundamental properties of this type of semiconducting compound under pressure. For this, further investigations on the material of interest under pressure are necessary.

In this contribution, the study of the structural, optical and electronic properties of the semiconductor compound ScAs in the rocksalt phase has taken action. Using the

pseudopotential plane wave (PP-PW) method as part of the density functional theory (DFT) implemented in the CASTEP software, the functional that describes exchange-correlation is treated in the local density approximation (LDA) for the ScAs.

The aim of this work is to study the properties of ScAs in the rocksalt structure, we are interested in their dependence on hydrostatic pressure (which is the pressure that any fluid in a confined space exerts). In order to study the structural properties, in particular, the lattice parameter, the volume and the crystal density, and some other parameters, such as: the bulk modulus and its derivative, of the semiconductor compound ScAs in the rocksalt phase.

We also propose to study the optical and electronic properties, namely the energy gap, refractive index, dielectric functions, optical conductivity, reflectivity and band structure (The study was carried out at zero pressure and under the effect of hydrostatic pressure).

III.2 Structural properties of ScAs

Before calculating the various desired properties, we have made convergence tests of the total energy E_{tot} of the ScAs compound as a function of the k-points number in the first Brillouin zone and as a function of the cut-off parameter E_{cut} . The convergence tests carried out on our compound allowed us to fix the value of the cut-off energy at 400 eV for the basic set of the plane wave. The Brillouin zone integrations are performed using 60 k-points in the irreducible part, which corresponded to the set of Monkhorst-Pack points $8 \times 8 \times 8$.

Convergence tolerance for geometry optimization is selected in a way where the minimum energy, the maximum force, the maximum stress and the maximum displacement are less than 2×10^{-5} eV/atom, 0.05 eV/Å, 0.1 GPa, and 2×10^{-3} Å, respectively.

III.2.1 Study of structural properties of ScAs

In the first step, we have run a geometric optimization of the semiconducting compound ScAs in the rocksalt phase zero-pressure and zero-temperature. The figure III.1 shows the structure of the ScAs compound, a prototype of the face-centered cubic ScAs unit cell.

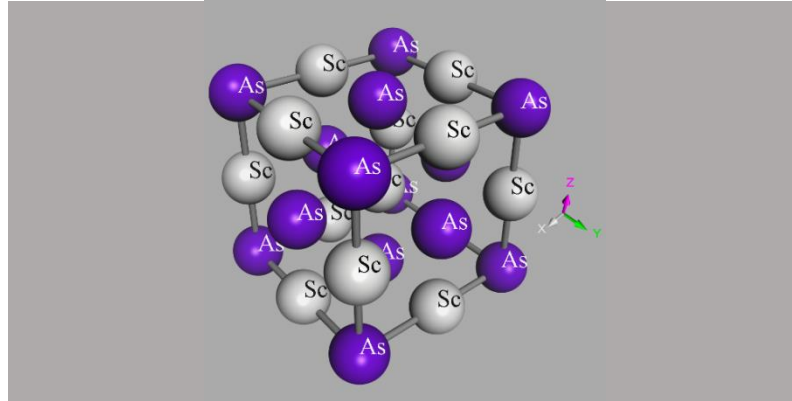


Figure III.1 : ScAs face-centered cubic unit cell (rocksalt)

The unit cell volume (V_0), The calculated relaxed lattice constant (a_0), the bulk modulus (B_0) and its pressure derivative (B'_0) of ScAs in the rocksalt structure are shown in the Table III.1, which also contains the available data that is reported in the scientific literature [29, 47, 48] in order to have the capability of comparing them with our actual results. We take into consideration the difference between our calculated a_0 and the reported a_0 from first-principle full potential linear muffin-tin orbitals (FP-LMTO) method [29] is less than 2.5%, the same conclusion is drawn for V_0 with a difference that's less than 7.3%.

The process of geometry optimization is performed at equilibrium. The figure III.2 shows the resulting total energy-volume (E-V) data. These data are adapted to the Murnaghan equation of states which makes it possible to obtain the bulk modulus noted B_0 and its derivative with respect to the pressure noted B'_0 . The values obtained for B_0 and B'_0 are given

in Table III.1. To the best of our knowledge, our results are a prediction that may contribute to future studies.

Table III.1 : Unit cell volume (V_0), calculated relaxed lattice constant (a_0), bulk modulus (B_0) and its pressure derivative (B'_0) of ScAs.

Parameters	Present calculations	Other calculations
V_0 (\AA^3)	151.96 ^a 153.38 ^b	163.824 (40.956×4) [29]
E_0 (eV)	-5815.749 ^a -5818.865 ^b	--
a_0 (\AA)	5.3363 ^c 5.3529 ^c	5.472 [29], 5.489 [47], 5.476 [48]
B_0 (GPa)	101.61 ^b	102.975 [29], 91.522 [47], 86.0 [48]
B'_0	2.96 ^b	2.945 [29], 3.484 [47], 3.81 [48]

^a Values from the DFT-LDA calculation results using CASTEP module in Material Studio.

^b Values from the Origin software's Non-linear Curve Fit of Murnaghan's equation.

$$^c a_0 = \sqrt[3]{V_0}$$

The structural values calculated by the LDA approximation method agree well with those obtained from the adjustments of the Murnaghan equation (E-V). This serves as a proof of the reliability and accuracy of the theoretical method used and gives confidence in the predicted results for electronic properties reported in the present work.

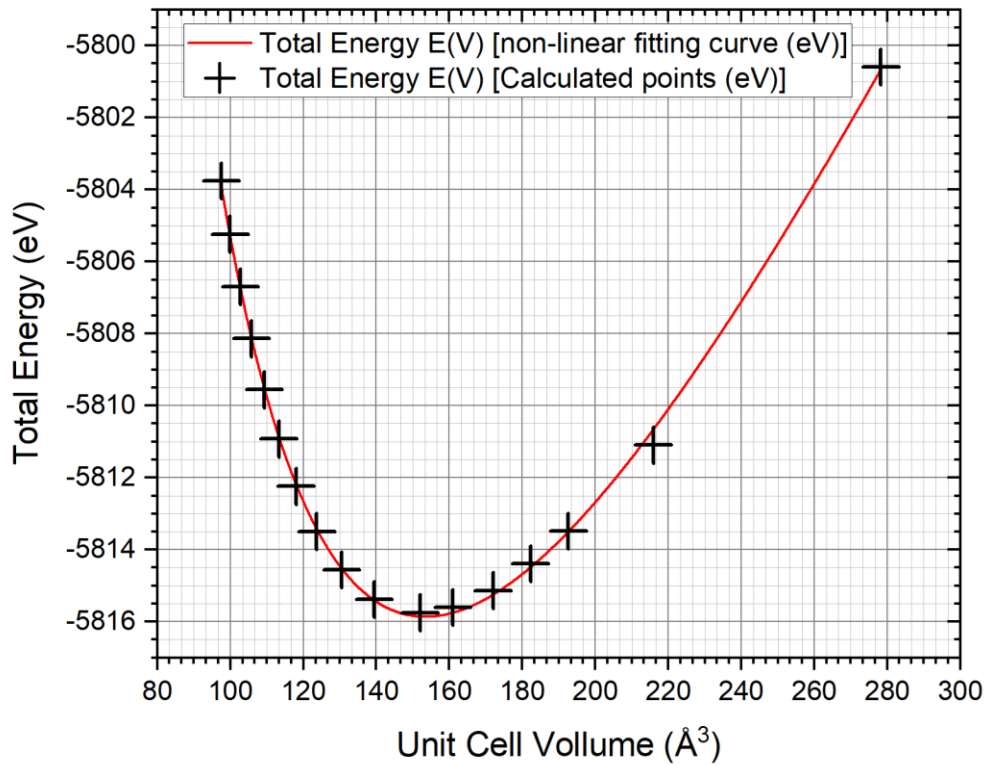


Figure III.2 : Variation of the total energy as a function of volume

III.2.2 Pressure effect on structural properties of ScAs

The response of the semiconductor compound ScAs in rocksalt structure to the applied external pressure was estimated by exploring the dependence of the unit cell volume (V/V_0) at the hydrostatic pressure applied. Our results are presented in figure III.3. The geometry optimization process is performed at various pressures. Note that all normalized structural parameters monotonically decrease with increasing pressure. The values of the volume (V) start with the zero-pressure value $\approx 151.96 \text{ \AA}^3$, and they reach the value $V \approx 97.47 \text{ \AA}^3$, at 100 GPa pressure.

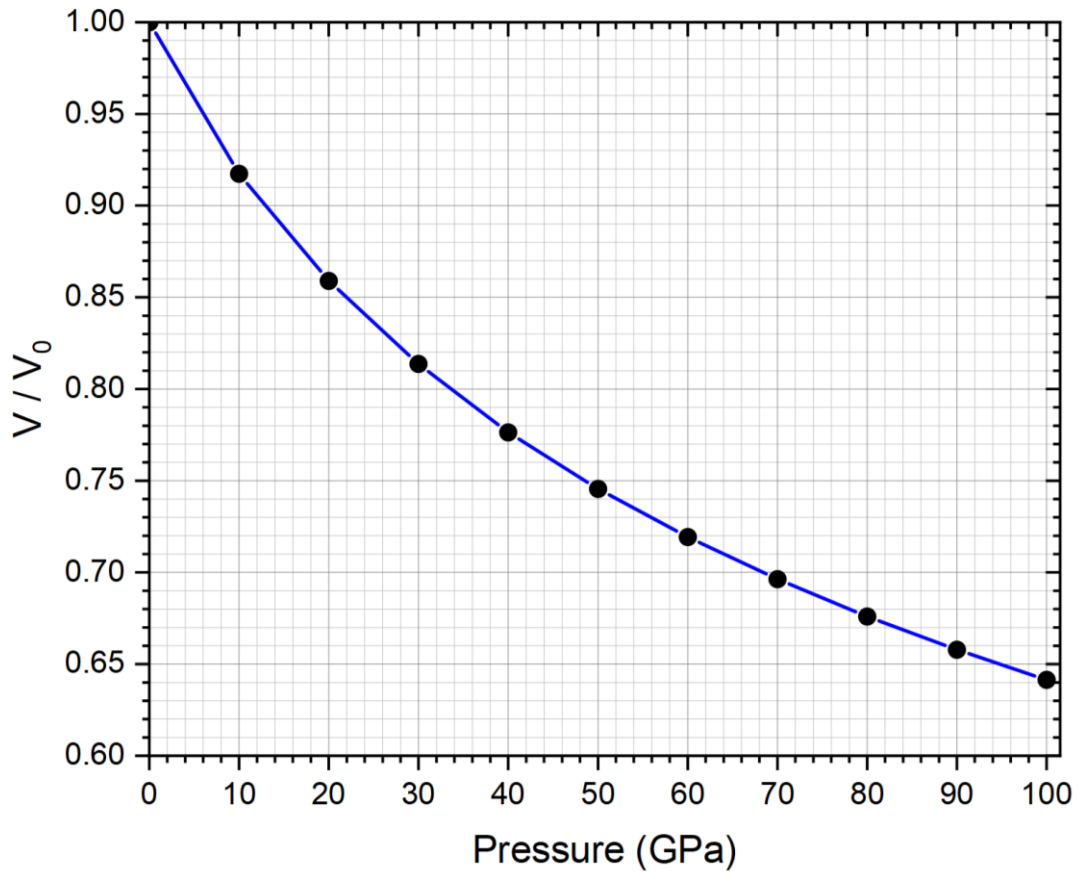


Figure III.3 : Normalized unit cell volume constant (V/V_0) versus hydrostatic pressure applied to ScAs semiconducting compound

The variation of the crystal density as a function of the unit cell volume in this compound can be estimated by the following the formula :

$$\rho_{vm}(V) = 796.26 / V \quad (\text{III. 1})$$

The variation of this parameter as a function of the hydrostatic pressure of this compound is represented in figure III.4, where it was noticed that the crystal density takes a value of approximately 5.24 g/cm^3 at zero pressure, likewise it reaches a value of 8.17 g/cm^3 at $P = 100 \text{ GPa}$.

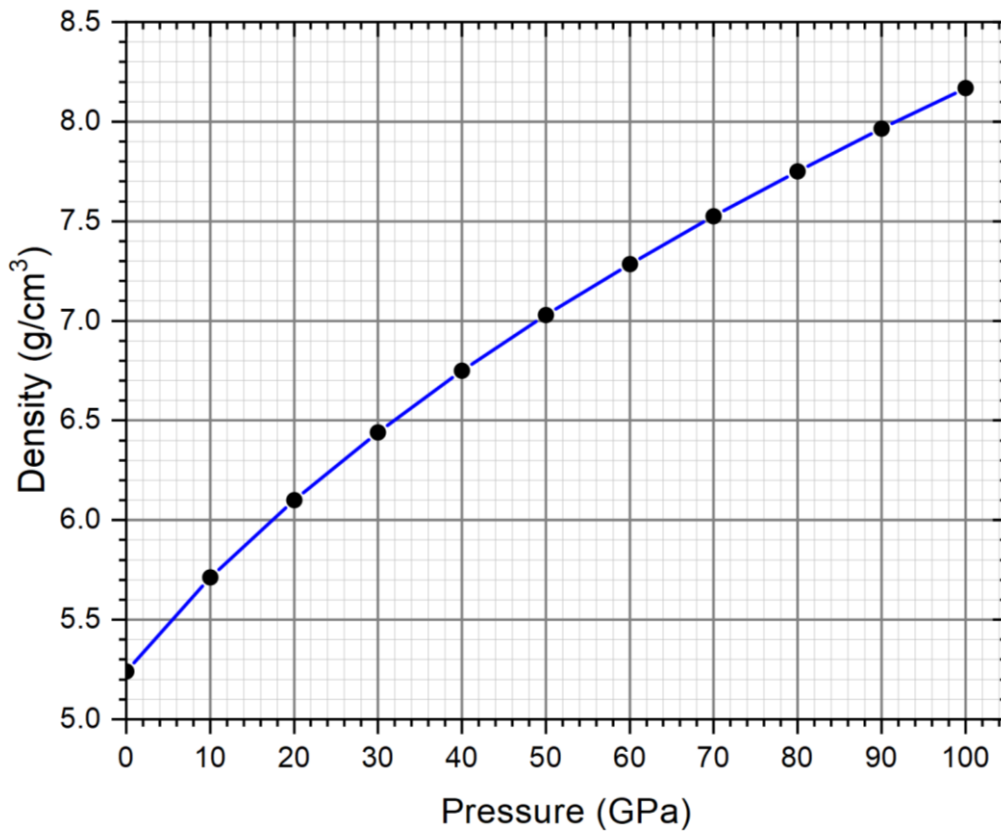


Figure III.4 : Variation of crystal density as a function of the hydrostatic pressure of ScAs

III.3 Electronic properties of ScAs

The energy band structures and the density of states of the ScAs compound in the rocksalt structure were calculated using the plane wave pseudopotential method with the Local-density approximation (LDA). The energy spectra obtained along the directions of high symmetry in the Brillouin zone are shown in figure III.5 and figure III.6 next to their density of states.

In these figures the top of the last valence band of the studied compound is as the origin of the energies. At zero pressure (see figure III.5), we notice that the maximum of the valence band and the minimum of the conduction band are located close to the point of high symmetry

Γ (named G) in the Brillouin zone. While this is the case of the ScAs compound, we can conclude that this compound has a direct bandgap.

However, the conduction band of this compound is more dispersed than the valence band. This is due to the fact that the conduction band is more relocated, which explains the reaching of the highest values of the density of states (DOS) when energy is above 0 eV. For the ScAs compound, the difference noted between the minimum of the conduction band and the maximum of the valence band is ~ 0.14 eV, which is slightly lower than the experimental one 0.7 eV of single-crystal epitaxial thin films reported in the literature [49]. In general, the electronic polarizabilities for III-V group semiconductors decrease with energy gaps.

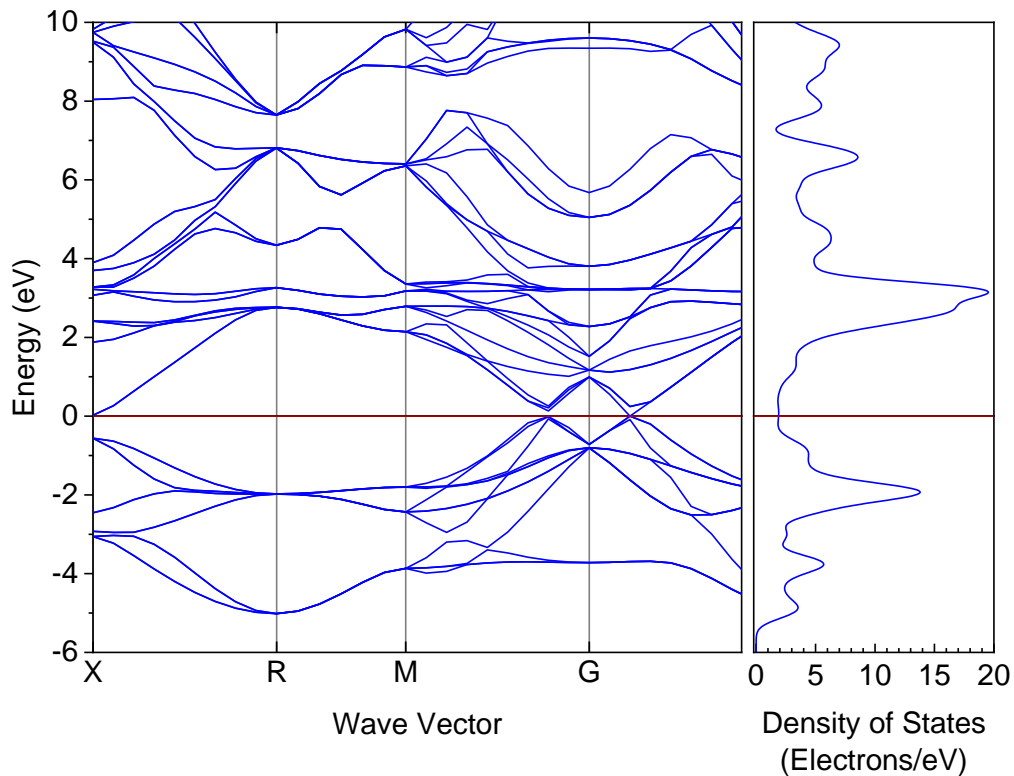


Figure III.5 : Energy spectra obtained along the directions of high symmetry in the Brillouin zone and density of states (DOS) variation as function of energy for ScAs at zero pressure

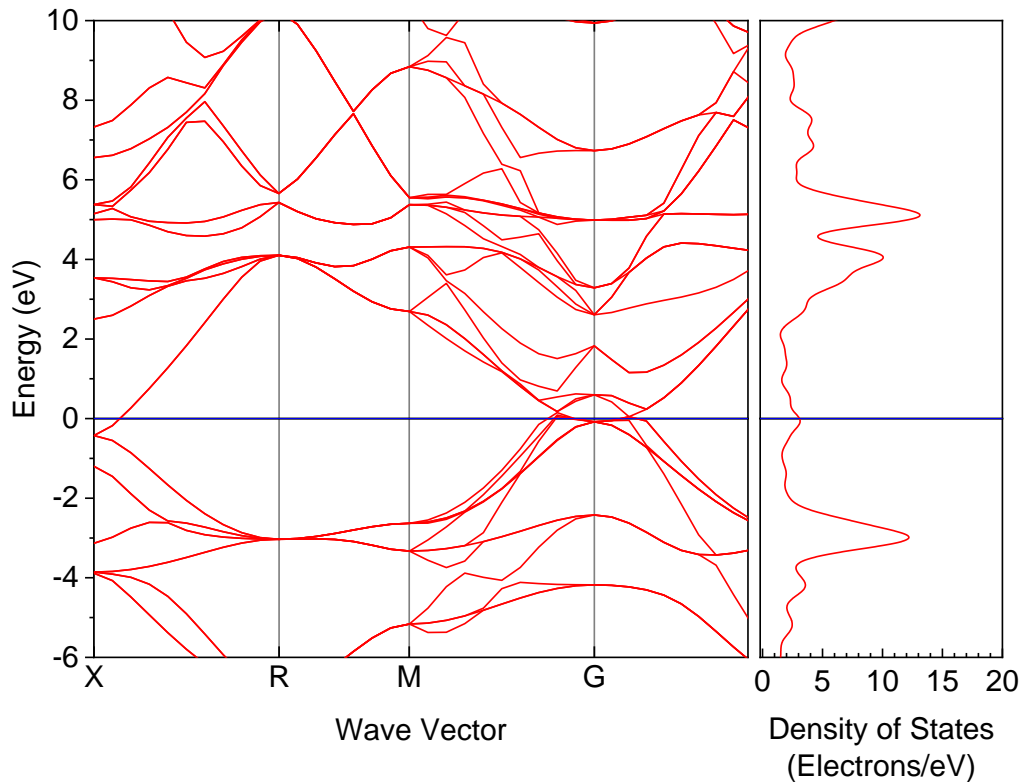


Figure III.6 : Energy spectra obtained along the directions of high symmetry in the Brillouin zone and Density of States (DOS) variation as function of energy for ScAs at 100 GPa pressure

Under the effect of the pressure (figure III.6), we see that the presence of the pressure displaces almost all the bands, rendering our material as semi-metallic. The observed bandgaps (figure III.5 and figure III.6) shows different behaviours, we see a semiconductor behaviour at zero pressure (figure III.5) and it is clearly seen from both the band structure and the total density of states (DOS) curves that the Fermi level E_F crosses the band gap and that DOS is at its minimum (nearly zero) at E_F . This is different from the semimetallic behaviour that we have seen at 100 GPa pressure (figure III.6) where it is clearly seen from both the band structure and the total density of states (DOS) curves that the Fermi level E_F crosses the band gap and that DOS has increased at E_F and unlike when we applied zero pressure we can see a

clear interference between the maximum value of valence band and the minimum value of the conduction band, which lets us conclude that ScAs is a semiconductor in when zero pressure is applied and then changes its behaviours when we apply a pressure of 100 GPa where ScAs shows a semi-metallic behaviour.

III.4 Optical properties of ScAs

In this part, we deal with the optical properties of ScAs semiconducting compound using first-principle calculations in the LDA. Characteristics such as dielectric function, refractive index, reflectivity, optical absorption, optical conductivity, and electron loss function spectra have been reported at zero-pressure and at 100 GPa. The information gathered from this study may be useful for photovoltaic applications.

III.4.1 Dielectric Function

Figure III.7 shows both the real and imaginary optical parts of the dielectric function of ScAs at zero-pressure and at 100 GPa. From figure III.7, it can be seen that the real parts of the dielectric function at the two applied pressures exhibit almost the same qualitative behaviour with some differences in detail and the same for the imaginary parts. We observe that for smaller frequencies, the curve of the real part has a maximum close to the absorption edge. This maximum is followed by regions with the general tendency towards reduced intensity. The applied pressure of 100 GPa seems to increase the maximum of the main peak without affecting the shape of the latter. The increase in the peak can be explained by the interband transitions which change under pressure. The general shape of the real part is that expected for a harmonic oscillator. The latter has a resonant frequency around 33 eV.

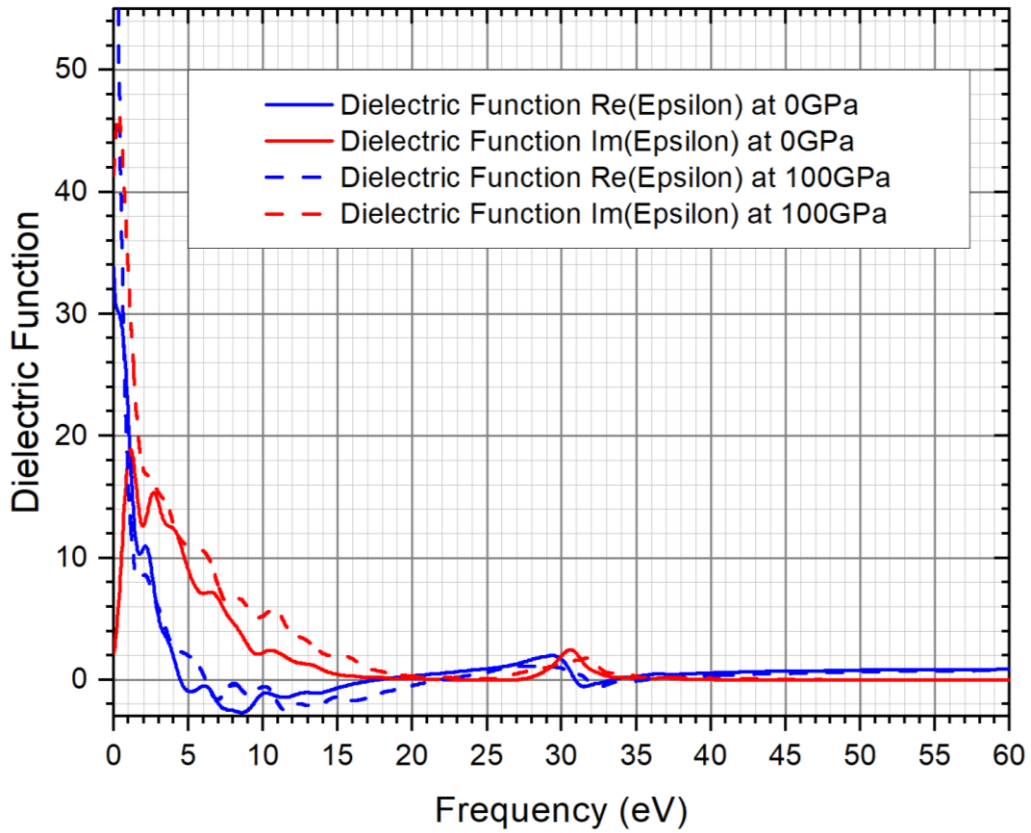


Figure III.7 : Real and imaginary parts of the dielectric function of ScAs in rocksalt phase at zero pressure and under a pressure of 100 GPa

III.4.2 Refractive Index and extinction coefficient

Refractive index n of a material is the measure of its transparency to the incident photons. Both refractive index $n(E)$ and extinction coefficient $k(E)$ spectrums calculated for ScAs at pressures of 0 and 100 GPa are shown in figure III.8. At zero pressure, there is an appearance of peaks from the excitonic transitions that occur at the edges of E_0 . The peaks are affected by the pressure of 100 GPa where a remarkable shift can be observed. This can be attributed to the change in bandgap energy at pressure of 100 GPa compared to that at zero pressure. At zero-pressure, our results predict a value of 5.6 for the static refractive index of ScAs.

Since the band structure of a semiconductor is intimately related to its optical behaviour, there have been attempts to calculate refractive index from energy gaps. Several formulas have been widely used in literature to calculate different opto-electronic properties of semiconductors. Recently, Tripathy has proposed an empirical relation to calculate refractive index of semiconductors from their energy gaps [50]. In his work, he has showed that, the relation (hereafter termed as Tripathy relation) can be successfully used for different group of semiconductors for a wide range of energy gaps. According to the Tripathy relation, the refractive index of semiconductor with energy gap E_g is given by [50]:

$$n = n_0 [1 + \alpha e^{-\beta E_g}] \quad (\text{III. 2})$$

where, $n_0 = 1.73$, $\alpha = 1.9017$ and $\beta = 0.539 \text{ (eV)}^{-1}$ are the constant parameters for a given temperature and pressure.

Replacing our value of E_g in the previous expression, leading to $n = 4.83$, which is slightly lower than the value of 5.6 obtained from the $n(E)$ spectrum.

The $k(E)$ spectrum calculated for ScAs at pressures of 0 and 100 GPa is shown in figure III.8. Note that at zero-pressure, there is an appearance of peaks from the excitonic transitions that occur at the edges of E_0 . The peaks are affected by the pressure of 100 GPa where a remarkable shift can be observed. This can be attributed to the change in bandgap energy at pressure of 100 GPa compared to that at zero pressure. At zero pressure, our results predict a value of 0.2 for the static refractive index of ScAs in the rocksalt structure.

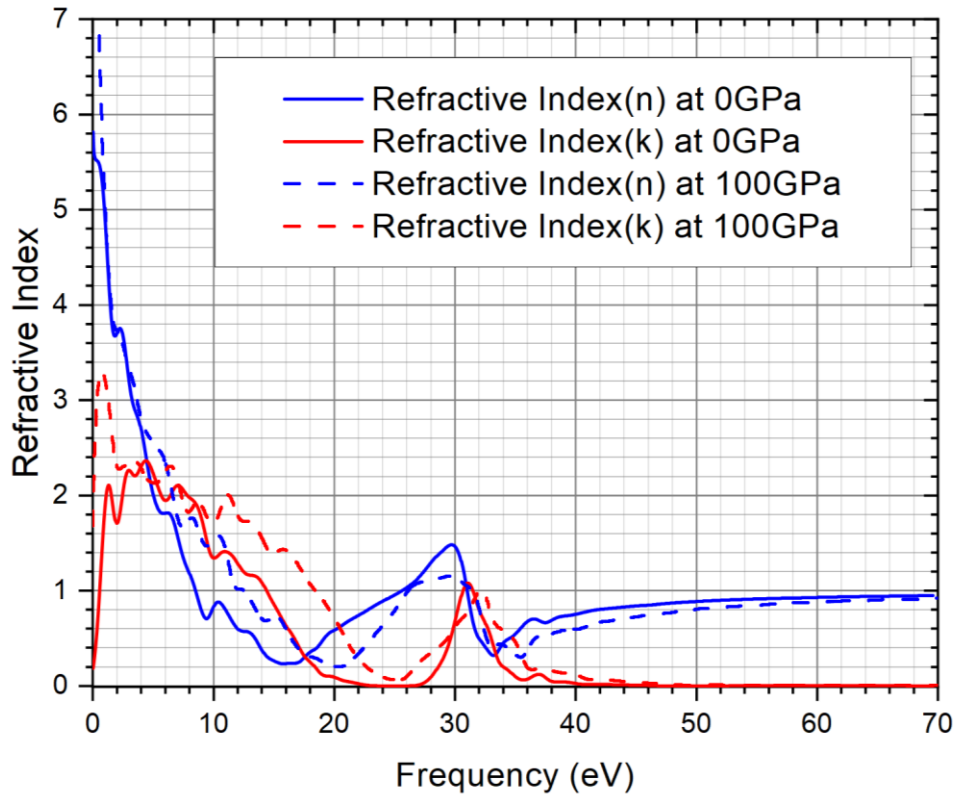


Figure III.8 : Refractive index spectrum (n and k) calculated for ScAs in rocksalt phase at zero pressure and under a pressure of 100 GPa

III.4.3 Optical Reflectivity

The Reflectivity R , defined through the ratio of the reflected power to incident power describes the optical response of the surface of a material. The Knowledge of the complex dielectric function $\varepsilon(E)$ makes it possible to derive another measurable quantity which is the reflectivity spectrum [4]. Our results for ScAs at the pressures of 0 GPa and 100 GPa are shown in figure III.9. Note that the maximum reflectivity has a value of around 72.4% and is at $\hbar\omega = 0$ eV. The peak at this stage is related to interband transitions which are modified by excitonic effects. Generally, the lowest frequency region is dominated by a structure which comes from the energy band gap at point Γ which is of type M_0 . At a higher frequency, the peaks become wider and they are due to interband transitions. The width of

these peaks is due to phonon-phonon scattering. The latter dampens vibrations. An applied pressure of 100 GPa results in an important shift in the reflectivity spectrum to higher frequencies (energies) with a general tendency for reflectivity peaks to become higher. However, the shape of the reflectivity spectrum remains almost the same.

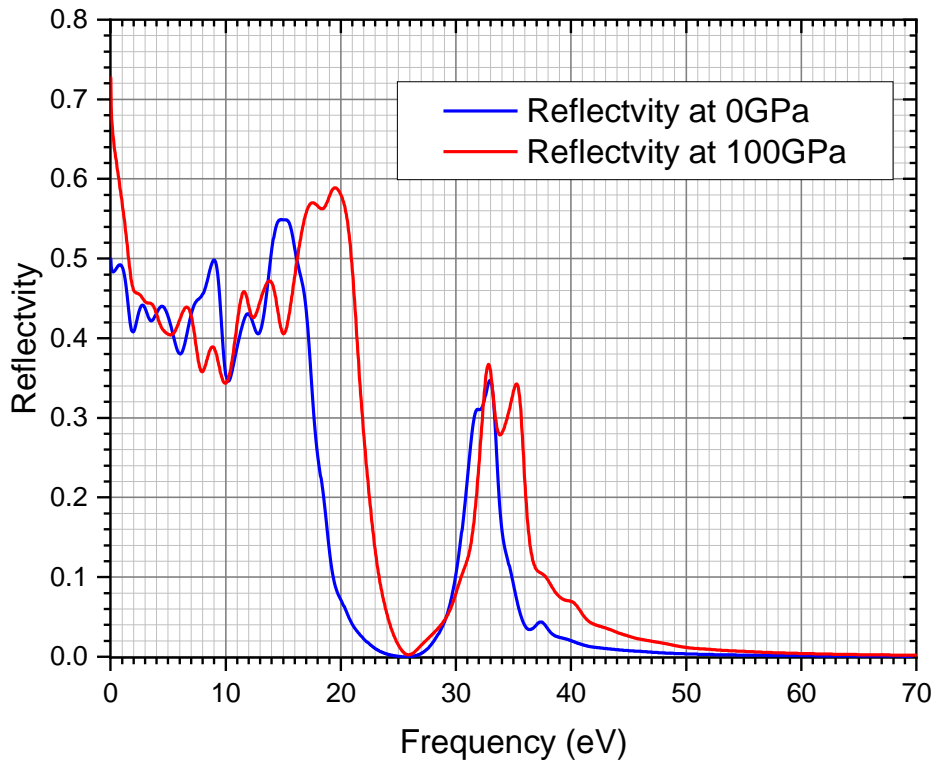


Figure III.9 : Reflectivity spectrum for ScAs in rocksalt phase at zero pressure and under a pressure of 100 GPa

III.4.4 Optical Absorption

Before it is absorbed, the light of a given wavelength penetrates a certain distance into the material. This distance can be determined by a physical parameter called the optical absorption coefficient. In the present work, this coefficient was calculated with the energy of the photons of ScAs in the rocksalt phase at zero pressure and under pressure equals to

100 GPa. Our results are illustrated in figure III.10. Note that at zero pressure, the optical absorption coefficient increases with the increase in the energy of the photons up to about 31.2 eV, then it decreases and vanishes for the energy of the photons above 60 eV. Experimentally, the absorption coefficient α can be calculated simply as $\alpha = (1/t) \ln(I_0/I)$, where t is the thickness, and I_0 and I are the initial and transmitted intensities, respectively [49].

An applied pressure of 100 GPa results in a remarkable shift in the optical absorption coefficient spectrum. From a quantitative point of view, the change of the optical absorption coefficient as shown in figure III.10 (red curve) depends on the energy of the light absorbed.

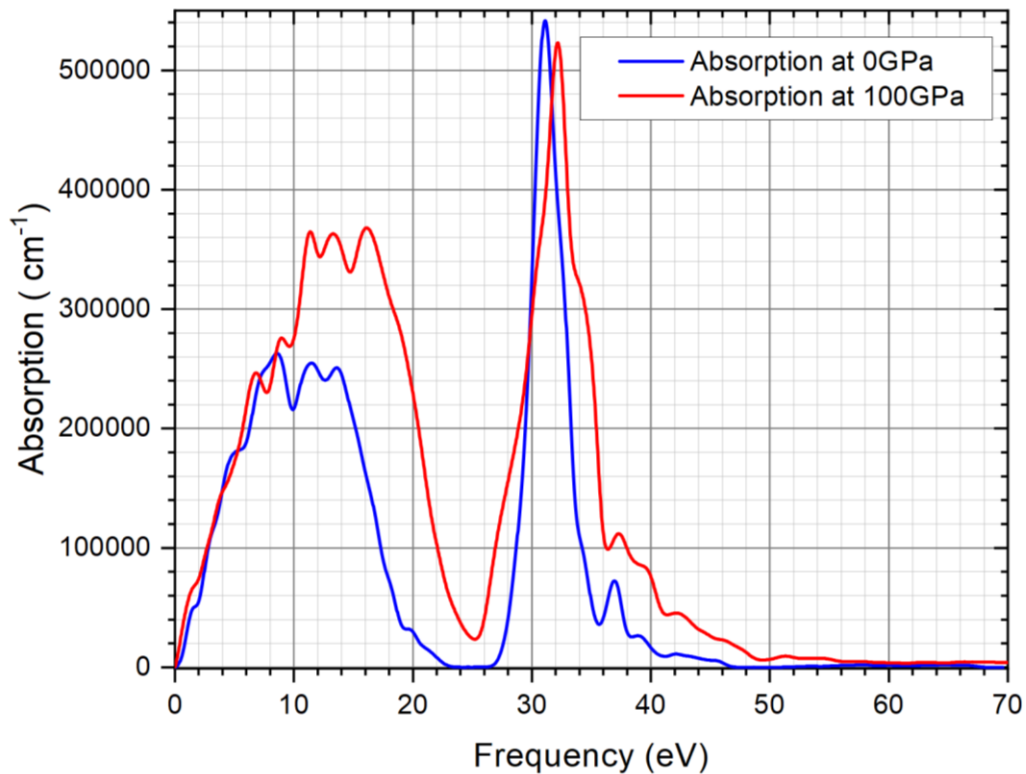


Figure III.10 : Optical absorption coefficient spectrum of ScAs in rocksalt phase at zero pressure and under a pressure of 100 GPa as a function of the energy of the photons

III.4.5 Optical Conductivity

The optical conductivity is a good probe for determining the electronic characteristics of semiconductor materials [4]. For this purpose, the real part of the optical conductivity spectra of ScAs at the pressures of 0 GPa and 100 GPa as a function of the energy of the photons are shown in the figure III.11. As can be seen in this figure, the optical conductivity strongly depends on the wavelength of the photons (energy). Its maximum is reached for a photon energy of about 30.6 eV. When the energy of the photons exceeds 47 eV, the optical conductivity disappears. By applying a pressure of 100 GPa, the conductivity seems to increase (However it can't reach the optical conductivity maximum achieved when zero pressure was applied). Nevertheless, the general shape of the spectrum remains somehow similar to that at zero pressure. Thus, the absorption rate of incident photons by electrons for a given energy should be almost the same.

Now, the imaginary part of the optical conductivity spectra of ScAs at the pressures of 0 GPa and 100 GPa as a function of the energy of the photons are shown in the figure III.11. As can be seen in this figure, the optical conductivity strongly depends on the wavelength of the photons. Its maximum is reached for a photon energy of about 31.2 eV, and also it reaches a minimum that is under the zero for a photon energy of about 29.2 eV. When the energy of the photons exceeds 55 eV, the optical conductivity becomes almost constant at the value 1 of the conductivity. By applying a pressure of 100 GPa, the conductivity seems to increase after reaching the energy of 11 eV. Nevertheless, the general shape of the spectrum remains somehow similar to that at $P = 0$ GPa when the energy is less than 27 eV or more than 30 eV.

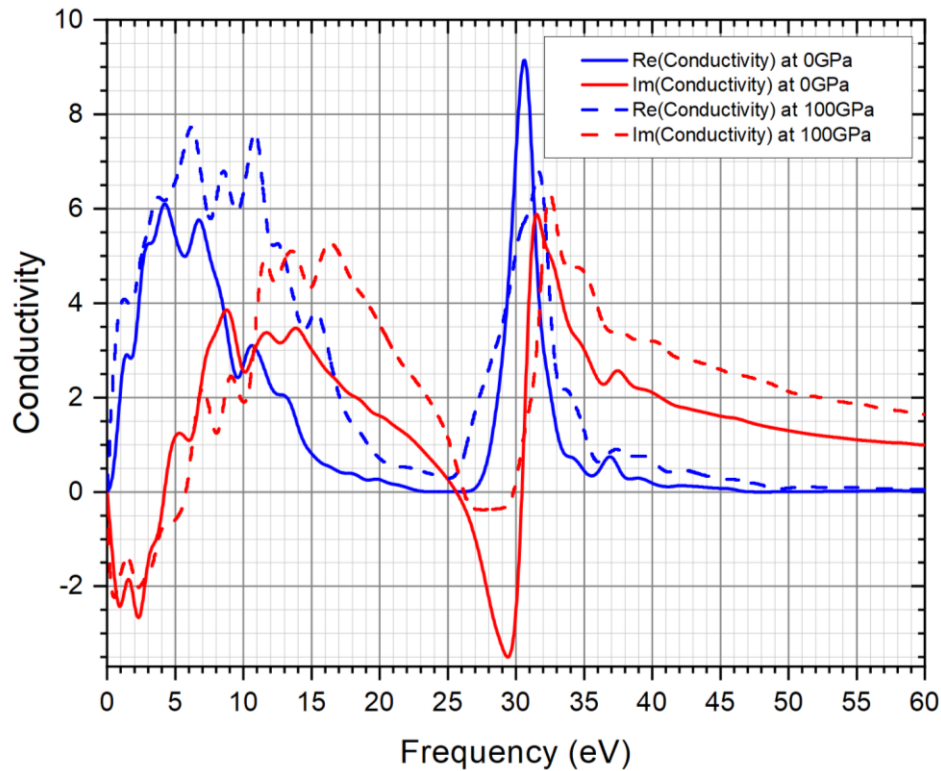


Figure III.11 : Optical conductivity spectra of ScAs in rocksalt phase at zero pressure and under a pressure of 100 GPa as a function of the energy of the photons

III.4.6 Electron energy loss function

The figure III.12 shows the energy loss spectrum of the electron's rapid displacement in the ScAs material at pressures of 0 GPa and 100 GPa. We notice the existence of peaks in these spectra. The most important of these peaks is identified as the plasma peak. The latter is located around an energy of 17.8 eV. In fact, many of the characteristics of the imaginary part of the dielectric function are represented by the electron loss function. In the reflection spectrum, the electron energy loss peaks correspond to the trailing fronts. At 100 GPa compression, the plasma peak is shifted to higher frequencies (energies) and the electron loss energy seems to become bigger.

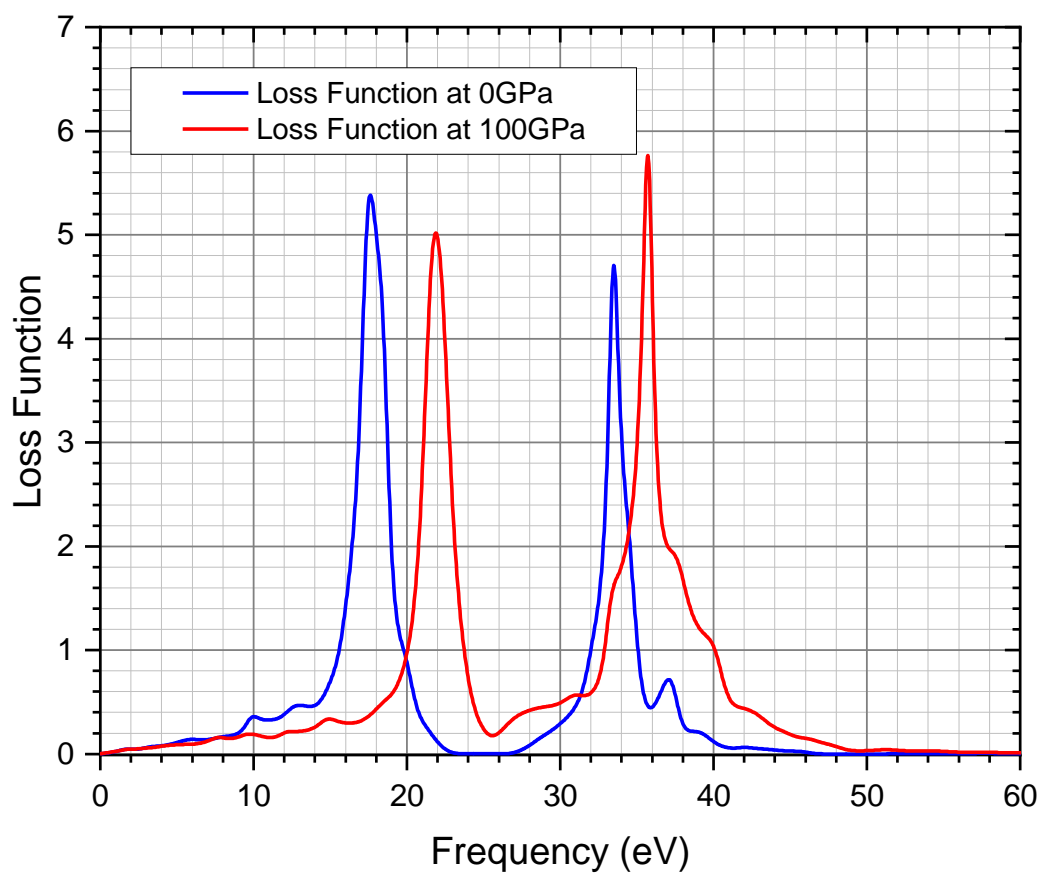


Figure III.12 : ScAs electron energy loss function in rocksalt phase at zero pressure and under a pressure of 100 GPa

General conclusion

General conclusion

In this work of Master's thesis, we have studied the physical properties of the binary compound ScAs in the rocksalt structure (B1). Using a combination of the pseudopotential and the plane-wave methods in the frame of the density functional theory (DFT). the structural parameters, the electronic band structures, the density of state, and several other optical properties have been determined. The different studied properties have been calculated at both a zero and a high pressure. The calculations were proceeded using the local density approximation (LDA) implemented in the CASTEP module of the Materials Studio software and the essential of the achieved results is the next.

To begin, we have realized few ab-initio calculations to choose suitable cut-off energy and sufficient k-points. For the sampling of the first Brillouin zone we have used 60 ($8 \times 8 \times 8$) k-pts in the irreducible Brillouin zone for structural optimization binary compound ScAs in the rocksalt structure.

In our study of structural properties, we have calculated the different values of unit cell volume and the corresponding total energy by changing the value of the applied pressure. We used these achieved results to generate a non-linear fitting curve of the Murnaghan's EOS, and with the help of the Origin software, we obtained the values of V_0 , E_0 (or $E(V_0)$), B_0 and B'_0 , these achieved results are in good agreement with experimental values and other theoretical data of the literature.

And when we studied the electronic properties, the band structures of ScAs compounds showed that it has a semiconductor structure with a direct bandgap at zero-pressure, while at high-pressure, it is semimetal. The analysis of the total density of states (DOS) has explained and supported this result.

We have also studied optical properties, where we have discussed and analyzed the dependence on the applied pressure of the dielectric function, refractive index, reflectivity, optical absorption, conductivity, and electron loss function.

The achieved results are predictive and serve as a good reference for future experimental investigations.

Bibliographical references

Bibliographical references

- [1] Introduction to the history of semiconductors. (2017). In *ULSI Front-End Technology* (pp. 1–43). WORLD SCIENTIFIC.
- [2] Castagne, Duchemin, Gloanec, Ch, R., & Caquot, E. (1990). Circuits intégrés en arséniure de gallium. Physique, technologie et règles de conception. *Ann. Telecommun.*, 45(1–2), 106.
- [3] Pankove, J. I. (1971). *Optical processes in semiconductors*. Old Tappan, NJ: Prentice Hall.
- [4] Khaldi, A. (2019). *Etude des propriétés optoélectroniques et mécaniques des semi-conducteurs magnétiques*. Université Mohamed Khider, Biskra.
- [5] Amer, L., Benbahouche, L., & Imadali, L. (2020). *Simulation et analyse des propriétés et des paramètres de fonctionnement des lasers à semi-conducteurs simple et double hétérojonction AlGaAs/GaAs*. Université Abderahmene Mira, Bejaia.
- [6] Abbad, A. (2014). *Etude et caractérisation des composés binaires, ternaires et quaternaires à base de zinc et de gallium*. Université Abdelhamid Ibn Badis, Mostaganem.
- [7] Sokolich, M. (2018, March). An answer to the question : What is meant by a binary semiconductor?
- [8] Yaddanapudi, K. (2018, April). An answer to the question : What are the advantages and disadvantages of binary semiconductors compared with elemental semiconductors?
- [9] Drago, R. S., & Zumdahl, S. S. (1984). *General Chemistry: V. 1: Problem Solving*. Boston, MA: Houghton Mifflin (Academic).
- [10] The Editors of Encyclopedia Britannica. (2021). Semiconductor. In *Encyclopedia Britannica*. Encyclopedia Britannica.
- [11] Lambrecht, W. R. L. (2000). Electronic structure and optical spectra of the semimetal ScAs and of the indirect-band-gap semiconductors ScN and GdN. *Phys. Rev. B Condens. Matter*, 62(20), 13538–13545.
- [12] The Editors of Encyclopedia Britannica. (2021). Band theory. In *Encyclopedia Britannica*. Encyclopedia Britannica.
- [13] Varshni, Y. P. (1967). Temperature dependence of the energy gap in semiconductors. *Physica*, 34(1), 149–154.
- [14] Singleton, J. (2001). *Band theory and electronic properties of solids* (Vol. 2). Oxford University Press.
- [15] Valavanis, A. (2009). *n-type silicon-germanium based terahertz quantum cascade lasers*. University of Leeds.
- [16] Griffiths David, J., & Schroeter Darrell, F. (1995). Introduction to Quantum Mechanics. *Physics Today*, 48(9), 94.
- [17] Guardian staff reporter. (2013, August). Physicist Erwin Schrödinger's Google doodle marks quantum mechanics work. *The Guardian*. The Guardian.
- [18] Schrödinger, E. (1926). An undulatory theory of the mechanics of atoms and molecules. *The Physical Review*, 28(6), 1049–1070.
- [19] Foiles, C. L., Lerner, R. G., & Trigg, G. L. (1991). Thermoelectric effects. In *Encyclopedia of Physics* (pp. 1263–1264). VCH Publishers.
- [20] Sachs, M., & Grosewald, P. (1964). Solid State Theory. *Physics Today*, 17, 159–160; 238–242. doi: 10.1063/1.3051402
- [21] Gutsev, G. L. (1998). Numerical Pseudopotentials within DV-X α Framework. In *Advances in Quantum Chemistry* (pp. 137–157). Elsevier.
- [22] Bischoff, F. A. (2019). Computing accurate molecular properties in real space using multiresolution analysis. In *State of The Art of Molecular Electronic Structure Computations: Correlation Methods, Basis Sets and More* (pp. 3–52). Elsevier.
- [23] Bylaska, E. J. (2017). Plane-wave DFT methods for chemistry. In *Annual Reports in Computational Chemistry* (pp. 185–228). Elsevier.
- [24] Dayah, M. (1997, October). Periodic Table. *Ptable*.
- [25] Kaur, K., Murali, D., & Nanda B R K. (2019). Stretchable and dynamically stable promising two-dimensional thermoelectric materials : ScP and ScAs. *Journal of Materials Chemistry A, Materials for Energy And*, 7(20), 12604–12615.
- [26] Hahn, T. (2001). The 230 space groups. In *International tables for crystallography : Space group symmetry* (5th ed.,

- pp. 658–660). Tucson, AZ: Kluwer Academic.
- [27] Hahn, T. (2001). The 230 space groups. In *International tables for crystallography: Space group symmetry v* (5th ed., pp. 688–691). Tucson, AZ: Kluwer Academic.
- [28] Tyuterev, V. G., & Vast, N. (2006). Murnaghan's equation of state for the electronic ground state energy. *Computational Materials Science*, 38(2), 350–353.
- [29] Tebboune, A., Rached, D., Benzair Abdelnour and Sekkal, N., & Belbachir A H. (2006). Structural and electronic properties of ScSb, ScAs, ScP and ScN. *Physica Status Solidi B*, 243(12), 2788–2795.
- [30] Dirac P A M. (1927). Note on exchange phenomena in the Thomas atom. *Mathematical Proceedings of the Cambridge Philosophical Society*, 23, 542.
- [31] Perdew John, P. (1985). Accurate density functional for the energy: Real-space cutoff of the gradient expansion for the exchange hole. *Physical Review Letters*, 55, 1665–1668.
- [32] Perdew John, P. (1991). Generalized gradient approximations for exchange and correlation: A look backward and forward. *Physica B: Condensed Matter*, 172(1–2), 1–6.
- [33] Boucetta, S., & Zegrar, F. (2013). Density functional study of elastic, mechanical and thermodynamic properties of MgCu with a CsCl-type structure. *Journal of Magnesium and Alloys*, 1(2), 128–133.
- [34] Paschotta, R. (2019, April). Reflectivity. *Rp-Photonics.Com*. RP Photonics.
- [35] West, W. (2008). *Absorption of electromagnetic radiation*. AccessScience, McGraw-Hill Companies.
- [36] La Rocca G, C. (2005). Semiconductor Optics. In *Encyclopedia of Condensed Matter Physics* (pp. 297–303). Elsevier.
- [37] Pedrotti, F L., Pedrotti, L S., & Pedrotti, L M. (2006). *Introduction to Optics* (3rd ed.). Upper Saddle River, NJ: Pearson.
- [38] Chauhan, R., Kumar Srivastava, A., Mishra, M., & Srivastava K K. (2010). Effect of UV exposure on some optical properties of as-Se based chalcogenide glasses. *Integrated Ferroelectrics*, 119(1), 22–32.
- [39] Swanepoel, R. (1983). Determination of the thickness and optical constants of amorphous silicon. *Journal of Physics E: Scientific Instruments*, 16(12), 1214–1222.
- [40] Kumar Srivastava, A., Thota, S., & Kumar, J. (2008). Preparation, microstructure and optical absorption behaviour of NiO thin films. *Journal of Nanoscience and Nanotechnology*, 8(8), 4111–4115.
- [41] Yagoub, R., Hadjfatih, A., Louhibi-Fasla, S., Daoud, S., Bahlouli, S. (2020). First principles study of rare earth mononitrides ScN and YN under pressure. *Journal of Nano- and Electronic Physics*, 12(5), 5009.
- [42] Petzelt, J., & Rychetský, I. (2005). Dielectric Function. In *Encyclopedia of Condensed Matter Physics* (pp. 426–429). Elsevier.
- [43] Stenzel, O. (2016). The Kramers-Kronig Relations. In *Springer Series in Surface Sciences* (pp. 85–93). Cham, Switzerland: Springer International Publishing.
- [44] Bobrov, V. B., Trigger, S. A., van Heijst, G. J. F., & Schram, P. P. J. M. (2010). Kramers-Kronig relations for the dielectric function and the static conductivity of Coulomb systems. *Europhysics Letters*, 90(1), 10003.
- [45] The optical conductivity of high-temperature superconductors. (2011). In *High-Temperature Superconductors* (103–146).
- [46] Ritchie R H, & Howie, A. (1977). Electron excitation and the optical potential in electron microscopy. *Philosophical Magazine*, 36(2), 463–481.
- [47] Maachou, A., Amrani, B., Driz M. (2007). Structural and electronic properties of III–V scandium compounds. *Physica B*, 388, 384 – 389.
- [48] Ugur, Ş., Soyalp, F. (2008). First principles linear response calculations of phonons for ScP and ScAs, *Solid State Communications* 147, 198–200.
- [49] Yim, W M., Stofko, E J., & Smith, R T. (1972). Vapor growth and properties of ScAs and ScP, *Journal of Applied Physics* 43, 254.
- [50] Tripathy, S. K. (2015). *Optical materials*, 46, 240.

ملخص

يتطرق هذا العمل إلى دراسات المبدأ الأول التي تدور حول الخصائص البنيوية، الإلكترونية والبصرية لمركب ثنائي ينتمي إلى أشباه الموصلات (أنصاف النواقل) وهو ScAs ذو بنية الملح الصخري. تم إجراء الحسابات بإستعمال طريقة أشباه الكمونات للأمواج المستوية في الحساب التقريبي المحلي للكثافة، هذه الطريقة مدمجة في وحدة CASTEP في برنامج Materials Studio لشركة Accelrys. تم فحص تأثير ضغط الموائع الساكنة على الخصائص المدروسة. عندما يكون الضغط معدوماً، تظهر نتائجنا إتفاقاً جيداً مع النتائج المذكورة في الأوراق البحثية وعند تطبيق ضغط قدره 100 GPa تتغير بنية نطاقات المركب المدروس من بنية شبه موصل إلى بنية شبه معدن. النتائج التي تم جمعها في هذه الدراسة بإمكانها أن تكون مفيدة للتطبيقات الكهروضوئية وأيضاً للمجالات الأخرى من تطبيقات أشباه الموصلات.

Abstract

The present work is concerned with the first principle studies of the structural, electronic, and optical properties derived from the binary semiconductor compound ScAs in the rocksalt structure. The calculations are performed using the plane-wave pseudopotential method in the local density approximation implemented in the CASTEP module included in Accelrys's Materials Studio software. The effect of hydrostatic pressure on the studied properties has been investigated and discussed. At zero pressure, our results show good agreement with those reported in the literature and at 100 GPa pressure, the band structure of the studied compound has changed from semiconductor structure to semimetal structure. The results gathered during the present study may be useful for photovoltaic applications and other semiconductor applications.

Résumé

Le présent travail porte sur les études ab initio des propriétés structurales, électroniques et optiques dérivées du composé semi-conducteur binaire ScAs dans la structure rocksalt. Les calculs sont effectués en utilisant la méthode du pseudo-potentiels des ondes planes dans l'approximation de la densité locale implémentée dans le module CASTEP inclus dans le logiciel Materials Studio d'Accelrys. L'effet de la pression hydrostatique sur les propriétés étudiées a été examiné et discuté. À une pression nulle, nos résultats montrent un bon accord avec ceux rapportés dans la littérature et à une pression de 100 GPa la structure de band de composé étudié a été changé sa structure de celle de semi-conducteur à celle de semi-métal. Les résultats recueillis au cours de la présente étude peuvent être utiles pour les applications photovoltaïques et d'autres domaines d'application de semi-conducteur.