THEORETICAL STUDY OF THERMODYNAMIC AND OPTOELECTRONIC PROPERTIES OF NEW INTERMEDIATE BAND PHOTOVOLTAIC MATERIALS

TESIS DOCTORAL

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THEORETICAL STUDY OF THERMODYNAMIC AND OPTOELECTRONIC PROPERTIES OF NEW INTERMEDIATE BAND PHOTOVOLTAIC MATERIALS

ESTUDIO TEÓRICO DE PROPIEDADES TERMODINÁMICAS Y OPTOELECTRONICAS DE NUEVOS MATERIALES FOTOVOLTAICOS DE BANDA INTERMEDIA

TESIS DOCTORAL

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The intermediate-band materials have attracted the attention of the scientific community in the field of the photovoltaics in recent years. Nevertheless, in order to understand the intermediate-band solar cell fundamentals, a profound study of the characteristics of the materials is required. This can be done using theoretical modelling from first-principles. The electronic structure and optical properties of heavily doped semiconductors and their precursor semiconductors are, among others, results that can be obtained from this approach.

In order to unravel the structures of these crystalline systems, this thesis presents a thermodynamic and optoelectronic study of several photovoltaic materials. Specifically advanced intermediate-band materials and their precursor semiconductors were characterized. The study was made in terms of theoretical characterization of the electronic structure, energetics among others. The stability was obtained using site-occupancy-disorder configurations adapted to the symmetry of the system and based on combinatorics. The site-occupancy-disorder method allows the formation of a configurational space of substitutional dopant positions based on the symmetry of the crystalline solid. The result, that can be treated using statistical thermodynamics, gives information of the stability of the whole space of symmetry of the crystalline lattice.

Furthermore, certain other important characteristics of host semiconductors were studied. Specifically, the van der Waal interactions were included in the SnS$_2$ layered semiconductor, and the inversion degree in cases of [M]In$_2$S$_4$ spinels. In this work we also carried out an exhaustive theoretical description of the CdTe:Bi system. This intermediate-band material shows characteristics that are distinct from those of the other studied intermediate-band materials. In addition, Zn was analysed as a modulator of the positions of the sub-band gaps in the CuGaS$_2$:Ti intermediate-band material. The thermodynamic feasibility of the formation of this compound was also carried out. Finally GaN:Cr intermediate-band material was also described both in the zinc-blende and the wurtzite type structures, using the symmetry-adapted-space of configurations. All results, whenever possible, were compared with experimental results.
RESUMEN

Los materiales de banda intermedia han atraído la atención de la comunidad científica en el campo de la energía solar fotovoltaica en los últimos años. Sin embargo, con el objetivo de entender los fundamentos de las células solares de banda intermedia, se debe llevar a cabo un estudio profundo de las características de los materiales. Esto se puede hacer mediante un modelo teórico usando Primeros Principios. A partir de este enfoque se pueden obtener resultados tales como la estructura electrónica y propiedades ópticas, entre otras, de los semiconductores fuertemente dopados y sus precursores.

Con el fin de desentrañar las estructuras de estos sistemas electrónicos, esta tesis presenta un estudio termodinámico y optoelectrónico de varios materiales fotovoltaicos. Específicamente se caracterizaron los materiales avanzados de banda intermedia y sus precursores. El estudio se hizo en términos de caracterización teórica de la estructura electrónica, la energética del sistema, entre otros. Además la estabilidad se obtuvo usando configuraciones adaptadas a la simetría del sistema y basado en la combinatoria. Las configuraciones de los sitios ocupados por defectos permiten obtener información sobre un espacio de configuraciones donde las posiciones de los dopantes sustituidos se basan en la simetría del sólido cristalino. El resultado puede ser tratado usando elementos de termodinámica estadística y da información de la estabilidad de todo el espacio simétrico.

Además se estudiaron otras características importantes de los semiconductores de base. En concreto, el análisis de las interacciones de van der Waals fueron incluidas en el semiconductor en capas SnS$_2$, y el grado de inversión en el caso de las espinelas [M]In$_2$S$_4$. En este trabajo además realizamos una descripción teórica exhaustiva del sistema CdTe:Bi. Este material de banda-intermedia muestra características que son distintas a las de los otros materiales estudiados. También se analizó el Zn como agente modulador de la posición de las sub-bandas prohibidas en el material de banda-intermedia CuGaS$_2$:Ti. Analizándose además la viabilidad termodinámica de la formación de este compuesto. Finalmente, también se describió el GaN:Cr como material de banda intermedia, en la estructura zinc-blenda y en wurtztite, usando configuraciones de sitios ocupados de acuerdo a la simetría del sistema cristalino del semiconductor de base. Todos los resultados, siempre que fue posible, fueron comparados con los resultados experimentales.
Acknowledgments

Esta tesis ha sido el fruto de un intenso esfuerzo no solo por mi parte, sino que también ha sido producida a raíz del trabajo en conjunto con mis dos directores de tesis Prof. Dr. Perla Wahnon y Dr. Pablo Palacios a quienes dedico los resultados que han sido obtenidos a lo largo de estos cuatro años. Además debo mencionar la importante colaboración con el Dr. Ricardo Grau-Crespo en University College London, con la que también ha sido posible obtener una parte importante de nuestros resultados. Durante todo este tiempo he aprendido para mi trabajo futuro, puntos claves dentro de la modelación de sólidos para materiales fotovoltaicos, y teoría dentro de química cuántica avanzada. Me gustaría agradecer al Dr. Jose Carlos Conesa por sus muy valiosos aportes en los temas relacionados con los semiconductores en capas, así como su intensa colaboración en temas que también fueron parte del desarrollo de este trabajo. A Raquel Lucena, algunos aportes también fueron puntos claves para darle una ruta efectiva a este trabajo, sobre todo en la identificación experimental de los materiales sintetizados. Además debo dar las gracias a todo el profesorado del Master de Energía Solar Fotovoltaica con los que aprendí sobre los temas importantes dentro de los sistemas fotovoltaicos y al personal del Departamento de Tecnologías Especiales Aplicadas a la Telecomunicación. Agradezco además al Ministerio de Economía y Competitividad por la beca FPI concedida a través del proyecto MAT2006-10618 para poder realizar este trabajo. The author thankfully acknowledges the computer resources, technical expertise and assistance provided by the Centro de Supercomputación y Visualización de Madrid (CeSViMa) and the Spanish Supercomputing Network. I also would like to thank the UK’s Materials Chemistry Consortium for allowing access to the HECToR supercomputing service via EPSRC grant EP/F067496.
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Introduction
Introduction

Human civilization needs energy to live not only because life as we know it is based on solar energy but also by the use of electrical energy in almost every activity of modern life. Energy has been a concern of society due to the shortages of oil in many parts of the world added to the increased prices. Nowadays, the fossil-fuel era of non-renewable resources is gradually coming to an end. The renewable energies derived from the Sun are one of the promising options. These types of energies can be used both directly and indirectly. Indirectly the Sun provokes several processes in nature that transforms energies as (e.g.) in winds that blow, plants that grow or rain that falls. Besides, temperature differences occur while water gradients in the oceans move. The Sun’s energy can also be used directly in a variety of thermal applications like heating air or water, drying, distillation and space heating. And finally through the photovoltaic effect it can be used as electrical energy through a two-steps process [1,2].

These two steps that transform solar energy into electricity can be described as, for instance, a chemical process first (which is an excitation process \(^1\)), then the transport of the chemically photogenerated carriers. The former chemical dynamics

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Introduction

is obtained through excitation of the electrons using the photon energies. The efficiency of the excitation process is constrained when the recombination processes appear. Shockley and Queisser [3] defined the ultimate efficiency of a single gap solar cell as 40.7%. This value is reported for semiconductors with 1.1 eV band-gap. After this first step, the effective transports are limited to exact timings under which carriers are moving at a velocity that allows them not to recombine and therefore without loosing the extracted energy from the photons. Even avoiding all non-radiative recombination processes in solar cells, efficiencies are far from reaching the theoretical maximum value of solar cell efficiency. The losses by thermalization and the non-absorption of low-energy photons are identified as some of the causes. In order to improve the solar cell efficiencies, these two factors should be minimized through several enhancements of the solar cells and the photovoltaic processes within them. The development of new materials has opened new perspectives for the production of potential low-cost and high-efficient devices.

The improvement of the solar-cell efficiency can be obtained, for instance, through irradiating the solar cell only photons within a narrow energy-gap and processing the other photons by solar-cells with different band-gaps in the tandem solar cell [4]. Other improvements of the devices can be obtained through the control in the concentration of incident radiation combined with a good cooling system for the solar panels. Besides, through filtering the incident photons in a thermo-photovoltaic device that possesses a filter with a high quality material the overall system should also be more efficient. Other theories included in ongoing investigations, like the hot carrier solar cells [5], can hypothetically enhance the photovoltaic efficiency while extracting the just-generated carrier, avoiding, in this way, the thermalization processes.

Furthermore, the intermediate-band solar cell [6] is also a concept that allows the efficiency improvement in the solar cells. In this, the ultimate efficiency that can be reached, in principle, overcomes that of the single-junction solar cell. The unravelling of intermediate-band materials is theoretically treated in this thesis.

While, some improvements have been made toward the research of quantum-dot solar cells with intermediate-band [7–9], those bulk based or thin film based solar cells have also demonstrated the increase of the photon absorption using the intermediate-band concept [10–18]. The candidates to be proposed as precursors of intermediate-band materials in bulk are semiconductors with around 2 eV of band-gap. Among the most promising intermediate-band photovoltaic materials
are those based on the [M]In$_2$S$_4$ spinels, defective spinels as In$_2$S$_3$, CuGaS$_2$ chalcopyrite and SnS$_2$ layered semiconductors.

The characterization of these candidates have been performed both, theoretically and experimentally. While the theoretical characterization is very important for the description of these materials, the experimental findings have also constituted key aspects in the development of the research of these types of intermediate-band cells [18, 19]. Yet, even though some intermediate-band materials in bulk sometimes are neither obtained as a solar cell nor as a thin film, the properties that have been found acknowledged absorptions with values below the main energy gap of the host semiconductor, which is a response of their enhanced characteristics.

The experimental characterization of bulk intermediate-band materials should show good optoelectronic properties. Thus, the experimental characterization included not only the analysis of optical absorption through diffuse reflectance UV-Vis-NIR spectra and overall efficiency with photocatalytic degradation [20] but also other properties of the materials (e.g.) magnetic behaviour using Electron Paramagnetic Resonance (EPR) spectra. If in the experimental findings the carrier lifetimes on the heavily doped semiconductors show increased values, therefore it is demonstrated that, in fact, the intermediate-band formation annihilates the Shockley-Read-Hall recombination and instead, the promotion of extra carriers takes place [21]. Materials with high resistivity while also showing high photon absorption with clear enhancement of the absorption below the fundamental optical band-gap is also an indication of an intermediate-band formation [22]. In addition, certain materials [23, 24] show a behaviour that demonstrates that while, at high concentration of the dopants, non-radiative recombination might deteriorate the material, at low dopant concentration an increased photoresponse might be related with the formation of an intermediate-band material.

Furthermore, some other materials which are obtained as solar-cells, almost by chance, have shown enhanced electrical properties while also exhibit photon absorptions with values below the main energy gap of the host semiconductor when compared both spectra, that of the host and also that of the doped material. That is the case of the CdTe doped with Bi [24, 25].

In addition, not only the characterization of the material properties is important but also the structural analysis. While XRD diagrams show exactly the positions of the atoms as appear in the host semiconductor the positions of the dopants are not accurately described in this method. Experimentally these types of characterizations are not as easy to obtain as could be obtained by using a
Introduction

Theoretical approach through *ab-initio* calculations.

The description of the electronic structure of these periodic systems is obtained at a quantum-mechanical level using Density Functional Theory (DFT) with accurate results in the majority of cases. The DFT nowadays is a well-known approach to treat condensed matter, as well as other systems. The results obtained with DFT in the majority of cases are alike those experimental findings, which is a proof of the validity of this method to describe electronic systems on the condensed matter and foremost, its derived characteristics. Experimental observations confirm certain characteristics of matter that are predicted through DFT.

Briefly, the DFT, as its name indicates, is described using mathematical functionals which are operators that act upon the atomic structure. The interactions and correlations of the "structure parts" are obtained through the solution of the Schrödinger equation that includes these operators. While standard DFT is very helpful in the description of certain electronic systems, some others are not so well described. This is because, DFT lacks (e.g.) description for weak forces (van der Waals type), and also strong correlations (like those that appear in d-orbitals). In addition the correct values for the band-gaps are not achieved in standard DFT. Nevertheless, improved theories can overcome these problems separately. For instance, while hybrid functional [26] are used for the corrected value of the band-gap (and total energies), dispersion correction [27], among others [28, 29] describes weak interactions. In addition Coulomb interactions through Hubbard parameter included for certain atomic orbitals correct the correlation energy which is considered in the GGA+U method [30–32]. Furthermore, the optical properties of intermediate-band materials can also be obtained and compared with the experimental results.

In addition, vibrational energies plus configurational energies are considered for the determination of thermodynamic processes in these systems. Particularly, the vibrational properties are obtained through the calculation of the phonon spectra within the harmonic-oscillator limit in the lattice. These calculations can be made both, using linear displacements or by using Density Functional Perturbation Theory, which is less computationally demanding than the former. While in certain systems the configurational energies are obtained directly in others this energy should be achieved through site-occupancy-disorder method (SOD) [33, 34]. This has proved itself as an useful tool for the characterisation of disordered materials upon the addition of a dopant in the host semiconductor.

The lack of experimental data in some systems, together with the necessity for
developing characterisation tools for these intermediate-band materials, led to our group to undertake the present work. The main objective of this work has been the optoelectronic and thermodynamic characterisation of intermediate-band materials and its precursors by means of theoretical calculations. We also present an study of the intermediate-band precursor properties and its influence on intermediate-band materials. Specifically the influence of the inversion degree of [M]In$_2$S$_4$ spinels on the resulting material and the van der Waals (vdW) interactions between layers in the SnS$_2$:V doped semiconductor. Besides new intermediate-band material systems are also unravelled as CdTe doped with Bi. In order to obtain the intermediate-band, the materials were calculated through the dopant inclusion in cationic or interstitial sites of the semiconductor lattices. The effect of the disordered sites and the defect compensation upon the DFT electronic calculations have been investigated in detail. The introduction of Zn as a band-gap modulator in the CuGaS$_2$:Ti has also been studied. Besides the interpretation of the configurations in the site-occupancy-disorder method, was also necessary to deepen in the statistic thermodynamic properties of the doped materials.

This work is divided into ten chapters. Chapter two provides a general overview about the current status of intermediate-band materials, the intermediate-band hypothesis and previous theoretical and experimental findings. Chapter three includes the description of the DFT and beyond and also the methodology applied to obtain the optical properties, among other theories. Since most of the findings presented in this work are related to SOD method, I included a chapter dealing with this topic. Therefore chapter four gives an insight into these theories used as a tool for the description of the atomic systems.

Following chapters constitute the cores of the work in which the most relevant theoretical results are presented and discussed. Chapter five provides the configurational and vibrational thermodynamics concerned in disordered [M]In$_2$S$_4$ spinels. The influence of the change in the inversion degree in each spinel on intermediate-band materials was determined. Chapter six introduces the thermodynamic study of Zn band-gap modulator in the CuGaS$_2$:Ti. Chapter seven deals with the description of SnS$_2$ layered material, that includes vdW interactions. The resulting anisotropy influence of vdW in SnS$_2$ while doped with V is described. The two final chapters include the thermodynamic and electronic characterization of new prospect intermediate-band materials, that have also been experimentally obtained as solar cells. These systems are CdTe:Bi and GaN:Cr.
Intermediate Band Materials and Precursors
Chapter 2

Intermediate-Band Materials and Precursors

2.1 Features of Intermediate-Band Materials

In order to enhance the efficiency of solar-cells, the intermediate-band materials constitute new proposals to be used in the photovoltaic systems. The limit of Shockley-Queisser or detailed balance limit [3] determines the highest efficiency of a single-junction solar cell around 40.7\% for a semiconductor with 1.1 eV of band-gap. However, the efficiency in intermediate-band solar cells is reported as high as 63.2\% for a semiconductor with 1.98 eV [6,36]. It is predicted that this type of solar cells exceeds the ultimate-efficiency of Shockley - Queisser through special optoelectronic properties of the intermediate-band materials. When compared with standard solar cells, the intermediate-band solar cell converts into electricity low energy photons (photons below the band-gap, $E_G$) which increases photo-current without loosing voltage [21]. While in single-junction solar cells the photons of energy lower than the semiconductor band-gap are unused, in intermediate-band solar cells are eliminated some efficiency losses that are unavoidable in the formers. The predicted mechanism includes absorption of two extra low energy photons that results in one extra electron promoted from the
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Valence Band Maximum (VBM)

Conduction Band Minimum (CBM)

Intermediate Band (IB)

Absorption $h\nu_1$

Absorption $h\nu_2$

Internal Transition, $S_{1(IB)} \rightarrow S_{2(IB)}$ non-radiative transition.

Vibrational Relaxation.

Figure 2.1: Scheme of an intermediate-band material showing (a) its chemical electronic excitation processes and (b) the intermediate-band solar cell outside from the equilibrium position \[6, 35\]
valence band to the intermediate-band and from that to the conduction band. Therefore, this mechanism generates an extra electron-hole pair.

The scheme of this intermediate-band material is shown in Fig. 2.1 where the inherent processes that allows the increase of the solar cell efficiency are shown. In the Fig. 2.1 (a) the chemical electronic excitation processes that result in one extra electron promoted from the valence band (VB) to the intermediate-band (IB) and from that to the conduction band (CB), in addition to those promoted from the main band-gap of the host semiconductor can be seen. Furthermore, the vibrational relaxations (e.g.) thermalization and also the internal conversion (IC) are also shown. This IC cannot be considered for the gaining in the photo-current as this remains internally in this level for the two-steps process that promotes the extra electron. The intermediate-band shown metallic character. The Fermi energy level ($E_F$) is located in this partially filled intermediate-band while the structure is in equilibrium.

In the Fig. 2.1 (b) [6, 35] the intermediate-band solar cell is outside from the equilibrium position where its quasi-Fermi energy levels can be seen. These correspond to each subband-gap ($\varepsilon_{Fe}$ and $\varepsilon_{Fh}$) which are depicted with electrical connections. The quasi-Fermi energy level assigned to the intermediate-band ($\varepsilon_{Fib}$) is considered unaffected outside equilibrium.

The materials that might be candidates for intermediate-band solar cells can be separated in two groups, these that are obtained to be used as quantum-dot (QD) solar cells [7–9] and those bulk materials based on heavily doped semiconductors. In QD intermediate-band solar cells two materials with different band-gaps allow the confinement of the carriers forming with these connected levels the intermediate-band. Some others more exotic propositions [37] that also includes quantum confinement have also arise. The other group, those bulk based or thin film based solar cells have been extensively experimental-theoretically studied in the last decades [10–18]. These results, that have been obtained in our group, have been considered as the basis for this thesis.

Theoretical approaches regarding these bulk materials have been focused in the characterization of the nature of the dopant materials, its orbital configurations and the possibility of the particular orbital-splitting while certain distortion occurs. The need for introducing a high dopant proportion, in order to avoid non radiative recombination obtained through the formation of a highly localized discrete energy level of the impurity, has also been detailed. The intermediate-band should be narrow, slightly disperse, delocalized and isolated from the host semiconductor.
bands. Specifically, dopants are transition-metals which, while substituting the semiconductor cations, might introduce their \(d\) orbitals in the band-gap of semiconductors, and this allow the formation of isolated energy band. The basis of this non-bonded crystalline band formation lies in the symmetry of the \(d\) orbitals which is different from those \(s\) and \(p\)-type orbitals that form the VBs and the CBs in almost all III-V and II-VI semiconductors.

Several doped photovoltaic materials have been proposed in order to enhance the photon absorption of solar cells and increase the generated power through the formation of an intermediate-band material. However, it has been realized that, in experimental situations, the nature of the dopant and the high concentrations that are needed, represent challenges for the synthesis of these relatively new materials.

### 2.2 State of The Art of the Studied Materials.

In previous works transition-metal substituted semiconductors in which the metal generates a new band in the semiconductor band-gap, have been proposed to develop solar cells with a greater efficiency and lower cost. In an intermediate-band material of this type the electron delocalization occurs along the transition-metal orbitals. While these extra electrons are located in these orbitals, separated from the host semiconductor bands, the increased concentration is such that allows the Mott transition [31]. This refers to the case in which the material can undergo an evolution from the insulator (or semiconductor) to the metallic structure through shortening of the band-gap to that extreme in which an overlapping of energy levels is exhibited. Nevertheless, the transition-metal dopants allow the formation of a narrow band which is separated and isolated, as they include \(d\)-orbitals, therefore the metallic character is "confined" only to this narrow space, while the formed subband-gaps correspond with the main structure band-gap.

External parameters such as composition, pressure [38], temperature [39] and external magnetic field have been proposed as the causes of the formation of this metallic compound from the insulating. Moreover, changes in carrier concentration of semiconductors not only can be affected through these causes but also by chemical doping. This is the case of an intermediate-band formation, in which the concentration of the impurity is such that avoids that recombination that takes place in isolated energy levels. While surpassing Mott limit [31], carriers
from impurities are delocalized and forms a band with other impurity-states. Moreover, not only theoretical predictions have been done for the description of these types of materials, but also experimental findings have demonstrated that intermediate-band materials can actually be synthesized. Some of the examples of these types of materials are:

- V doped In$_2$S$_3$ [10, 19],
- V doped SnS$_2$ [18],
- GaN doped with Cr [40],
- Ti implanted in Si [41–48],
- *thin film* CuGaS$_2$ doped with Cr [49], Fe [23] or Sn [50],
- oxygen doped ZnTe [51, 52] or ZnCdTe [53],
- Cu$_2$O with N [22] and
- N doped GaP [54, 55]

The intermedite-band formed through a high dopant addition to semiconductors is based on the regular arrangement of certain dopants and resulting local distortion of the surrounding bonds. Transition metal cations show $d$ orbitals in the outer shell of each atom. In the $d$ orbitals there is a strong tendency to produce a Jahn-Teller Effect. The symmetry of $d$ orbitals is such that in some compounds is not possible the total hybridization of these orbitals and instead a distortion of the surrounding bond appears. This effect lowers the overall energy of the compound stabilizing the system.

Intermediate-band materials using a heavily doped semiconductor with a transition metal might be regarded as a coordination-complex which bonding type are explained using the *Crystal Field Theory* [56]. This theory exposes that there is an interaction between a transition-metal atom and the ligands. This, in ligand field theory, is a strong ionic interaction between a positive charged transition metal cation and the negative ligands. In the former the energies of the five degenerated $d$ orbitals change upon the ligands point charges. Therefore, the particular geometry of $d$ orbitals allows the stabilization of the system through a distortion in bond distances, electrons from the ligand will be closer to some of the $d$ orbitals and
farther from others causing a loss of degeneracy. The $d$ orbitals that are farther from the ligands will have a lower energy, and those less separated from the ligands will have a higher energy. The result is an energy-splitting in $d$ orbitals. In addition, the nature of both the transition-metal atom and the surrounding ligands will affect this splitting. The oxidation state of the transition-metal atom will also influence, in a way that a higher oxidation state leads to a larger splitting. The symmetry of the ligands around the metal ion will affect. The complexes formed with transition-metal with ligands will have octahedral or tetrahedral symmetry.

In octahedral symmetry the $d$ orbitals split into two sets with an energy difference $\Delta_{\text{oct}}$. The degenerated $t_{2g}$ triplet ($d_{xy}$, $d_{xz}$, and $d_{yz}$ orbitals) will have lower energy than the degenerated $e_g$ doublet ($d_{z^2}$ and $d_{x^2−y^2}$ orbitals). The triplet is further away from the ligands than the doublet and this is a result from the symmetry of the ligands arrangement around the transition-metal [57].

In distorted systems, like heavily doped semiconductors that form an intermediate-band material, the $t_{2g}$ triplet and $e_g$ doublet also have a degeneracy breaking. The intermediate-band materials obtained through the Jahn-Teller distortion in a transition-metal doped semiconductor are rather similar in the local environment to the complex with transition-metal and the ligands. In these systems the resulting environment in the lattice will affect the configuration of the orbital splitting [10].

2.2.1 Spinels

Certain wide gap indium spinels, as MgIn$_2$S$_4$, CdIn$_2$S$_4$ and also the defective In$_2$S$_3$, have been used as host semiconductor to obtain intermediate-band materials [10,19, 58–61].

The In atoms in octahedral sites are substituted by transition metal atoms (Ti and V) with $d$-orbitals to form the intermediate-band. The isolated partially filled narrow band allows the absorption of photons with energy below the band-gap, in addition to the normal light absorption of a semiconductor. The enhanced optical absorption of the intermediate-band material formed was theoretically and experimentally studied. The theoretical study was obtained through the contribution of the optical properties of both, the transition-metal doped semiconductor and the host semiconductor, in the range of high solar emission, and comparing them.
In these structures not only DFT theoretical study but also $GW$ calculation was used in order to characterize the substituted spinels [58]. Particularly, the structures were analysed using a series of standard functionals and the screened hybrid of Heyd, Scuseria, and Ernzerhof (HSE). All these calculations were performed using the normal, full inverse, and intermediate configurations of $\text{MgIn}_2\text{S}_4$ and $\text{CdIn}_2\text{S}_4$. Despite the fact that using either inverse, normal or an intermediate configuration of these spinels is fair enough for the study of this complex structure, accurate results will be obtained upon considering an equilibration inversion degree using thermodynamic parameters through a profound configuration study.

In this thesis we get an insight into the influence of the inversion degree of spinels in different characteristics of $\text{MgIn}_2\text{S}_4$ and $\text{CdIn}_2\text{S}_4$ semiconductors. In addition, the influence of inversion degree in the intermediate-band materials will be exposed.

### 2.2.2 Chalcopyrites

$\text{CuGaS}_2$ has an experimental wide gap around the most efficient theoretical band-gap found for intermediate-band materials. Ti or Cr-substituted $\text{CuGaS}_2$ had been proposed for enhanced efficiency in photovoltaic cells [14, 16, 17, 62]. A half metallic intermediate-band appears forming a non-isolated intermediate-band material. The intermediate-band slightly overlaps the conduction band. Nevertheless when Hubbard-type empirical correction (GGA + $U$ method) is applied in this system, the well isolated and filled narrow band is obtained.

Moreover, the thermodynamic viability of these Ga-chalcopyrites, which are partially-substituted with Ti or Cr, was obtained through calculations of the total energy, disorder entropy, and vibration (phonon) contributions [63]. The free energy of formation of those materials is obtained using those closely related binary or ternary compounds into which they could decompose. The solubility was lower for Ti than for Cr; the latter also has a tendency to form aggregates. Unless low substituent concentrations and high temperatures were involved, the Cr and Ti-chalcopyrites structures are less stable than the combination of simpler compounds. Nevertheless, the metastability that mostly characterize these four element compounds is related with the possibility of the formation of these compounds outside thermodynamic equilibrium.

On the other hand, certain experimental evidences of Zn occupying cationic positions in $\text{CuGaS}_2$ show that the semiconductor band-gap reduces from 2.53 eV [64], to
2.1-2.3 eV [65, 66] in doped compound, taking the form of (CuGaS$_2$)$_{1-x}$ZnS$_x$, with $x$ ranging from 0.05 to 0.0005 respectively.

### 2.2.3 Layered semiconductors.

Layered semiconductors of the type MX$_2$, (X = chalcogen) are considered promising alternative materials for solar energy conversion. The *van der Waals* (vdW) cleavage plane (001) of layered semiconductors as SnS$_2$ is characterized by hexagonal arrays of close packed X-M-X sandwiches (X=chalcogenide and M=cation). This is an ideal substrate to study fundamental aspects of the metal/semiconductor interaction as the perfect (001) plane is considered to be free of surface states and intercalation of adsorbed metals may occur in stoichiometric amounts. In photovoltaic applications the doped semiconductors play a major roll, and one of the studied layered semiconductors is SnS$_2$ which has been considered as a precursor of intermediate-band materials doped with vanadium [67–69].

SnS$_2$ structure consists of sheets of tin atoms in the basal plane octahedrally coordinated between close packed sheets of sulphur atoms. The three-atomic-layer sandwich is repeated in the $c$ direction. SnS$_2$ can exist in a number of different polytypes where the stacking sequences of these sandwiches vary. The simplest structure 2H has a stacking sequence, $A\gamma B-A\gamma B$ where the Greek letter represents the metal atom. There is one layer, and one molecular unit per unit cell. The 4H structure has a stacking sequence $A\gamma B-C\gamma D$. It has two layers and two molecular units per unit cell. The $a$ lattice parameter is the same and the $c$ lattice parameter approximately doubled with respect to the 2H structure. In the results of our work some remarks about the vdW interaction influences in SnS$_2$ is exposed, and its influence in the intermediate-band materials.

### 2.2.4 Defects in CdTe

Nowadays, CdTe is among the most promising thin film photovoltaic materials. Several extrinsic dopant elements have been used to balance the non-stoichiometry formed in the synthesis of this compound. In recent years the use of bismuth in CdTe lattice has shown a high photoconductivity and low resistivity, a perspective material for photovoltaic applications.

The Bi insertion in CdTe lattice has been described through experimental characterization [24, 25]. Results have demonstrated an enhancement in the photon absorption when Bi is inserted in CdTe. Authors explains that this enhancement in
the concentration range of $10^{17}$ cm$^{-3}$ is due to a deep level found under this concentration level of Bi. In this synthesized material, while the resistivity in the dark is high, the photo-resistivity is lower which result in a great photo-response. Therefore in the quest of finding an answer for this phenomenon, the theoretical calculations might help in the description of the CdTe:Bi electronic structure at the concentration level and with feasible interactions between the dopant and intrinsic defects. Electronic-band structures, densities of states and optical absorption coefficient of doped and non-doped CdTe can be used to describe this system. This might predict in which situation an intermediate-band material is formed, explaining the relationship of this deep level with the enhancement of the photo-response.

2.2.5 Clusters of Cr substituting Ga in GaN

An intermediate-band material is formed in Cr doped GaN using radio-frequency-sputtering technique [40]. Even though the wurtzite type GaN has been theoretically studied by using standard DFT, there is a lack of evidence of an intermediate-band formation in those theoretical works [70]. Results of optical absorption, hard x-ray photoemission spectroscopy, and charge transport measurements demonstrated that an additional energy band is formed in the intrinsic band-gap of GaN upon Cr doping, and that charge carriers in the material move into the inserted band [40, 71]. Recently the optical absorption of Cr doped GaN has also been theoretically obtained [72].

Electronic structure, energy bands, and magnetic properties of Cr-doped GaN have been calculated from inArst principles. The coupling between Cr atoms is found to be ferromagnetic and this result is shown either theoretically and experimentally [70, 73].

In addition, enhanced short circuit current and open circuit voltage in the n-GaN/GaCrN/p-GaN structure compared to the GaCrN/p-GaN structure corroborates the concept of an intermediate-band material formation. There are extensive DFT results which provide direct evidence that Cr atoms in Cr:GaN has a strong tendency to form embedded clusters, occupying Ga sites [74, 75]. These results showed that in Cr doped GaN the magnetic ions prefer to occupy Ga sites and have a strong tendency to form embedded clusters while maintaining the wurtzite structure.

In other works [76] it is provided evidence that the distribution of the Cr atoms is
neither homogeneous nor random. Local structural distortions on the Cr-bonded N atoms are shown. Besides, the metallic, half-metallic, or semiconducting properties depend on the dopant concentration. Some other theoretical studies in GaN:Cr were focussed in the formation of defects and defects interactions. In Refs. [77, 78] the N vacancies were studied and in Refs. [79, 80] the Mn co-doping was also used for obtaining interesting magnetic materials.
Theoretical Approach I: DFT Method
3.1 *Ab-Initio* calculations in Density Functional Theory

In quantum-mechanics one of the most useful and interesting topic is Density functional theory (DFT). This is a powerful theoretical tool that allows to obtain *ad hoc* insight of materials and their physical and chemical properties. The electronic structure and total-energy calculations that can be obtained with DFT are very important for the description of the electronic structure of compounds. The exchange and correlation interactions are the key aspects inside DFT, and the correct description of the electronic systems necessarily needs the best variety of exchange and correlation functionals. The simplest form of the DFT method should be carefully used in certain systems as (e.g) these with *van der Waals* forces, or those including strong correlation.

Among the disadvantages of using a regular DFT functional are:

- The underestimation of the band-gap.
The incorrect description of electronic systems that include extremely localized states (or strongly correlated) [81].

The incorrect description of excited states.

DFT also fails in some metallic or magnetic systems.

Nevertheless in recent years, certain improvements of the exchange-correlation functionals have been made to solve these mentioned problems. In some of these theories the corrected terms are included in the integrals of the exchange-correlation functional, but others just apply a "post-integration" implementation. Particularly, a brief list of these recent methods which are these that are going to be used for this thesis, includes:

- GGA+U method to better describe the certain localized states of $d$ and $f$ orbitals.
- Hybrid functionals as screened HSE06 functional for the description of the corrected band-gap of insulators (and semiconductors), among other advantages that are going to be later described.
- Improvements in the van der Waals (vdW) forces either using the functional of Lundqvist and Langreth or the Grimme’s dispersion correction.
- The Density Functional Perturbation Theory for the description of optical transitions, phonons and Raman intensities.

The complete list also have different approach and particularities that are rather specific and/or are beyond the topics of this thesis.

3.1.1 Theoretical Basis

If we should characterize certain crystalline compounds, therefore we might start to explain this through the description of the isolated atoms that define the crystal. For the description of the atoms and their fundamental characteristics we should take into account the energy and how their energy changes. This is defined through the description of the location of nuclei and atom’s electrons in the time-independent Schrodinger equation, as:
For Ab-Initio calculations in Density Functional Theory, the Hamiltonian is given by:

\[
[T_N + T_e + V_{ee}(r) + V_{NN}(R) + V_{Ne}(r, R)]\Psi(r, \sigma, R) = E_{tot}\Psi(r, \sigma, R)
\] (3.1)

were the terms are:

- \(T_N\) and \(T_e\) respectively for kinetic energy of nuclei and electrons.
- \(V_{ee}(r), V_{NN}(R)\) and \(V_{Ne}(r, R)\) respectively for the interaction potentials between electrons, nuclei, and both in the spatial coordinates of electrons \(r\) and nuclei \(R\).
- \(\Psi(r, \sigma, R)\) is the wavefunction of the particular state that should be described.

The coordinates of all electrons and nuclei and all the spin components \(\sigma\) of electrons are involved in this equation. The solution of left part of the equation gives the eigenvalues \(E_{tot}\) and eigenvectors \(\Psi(r, \sigma, R)\) of the time-independent Schrödinger equation.

A keystone in the description of the system composed by nuclei and electrons of atoms, is that mass difference between these particles is very large. Each proton or neutron in a nuclei has more than 1800 times the mass of an electron [82]. Therefore, nuclei are heavy and move slower than electrons, while these are moving so fast that its mass is neglected, and its trajectory is what matters. As a result, the physical problems is separately analysed. This adiabatic separation of nuclei and electrons is the Born-Oppenheimer approximation. Thus, the Schrödinger equation in Eq. 3.1 can be rewritten and terms \(T_N\) and \(V_{NN}(R)\) will not appear. The many-body problem is now represented by a system of interacting electrons in the external field \(V_{ext} = V_{Ne}\).

On one hand, we obtain the description of electron motion using some equations while nuclei constitute fixed positions. On the other hand, we find the lowest energy configuration, or state, of the electrons that move in the force field of a set of nuclei. Therefore, we solved part of the problem, the lowest energy found in this system corresponds with the ground-state of electrons \(E_{tot}\) and the ground-state wavefunction \((\Psi(r, \sigma, R))\) describes this state.

Nevertheless, the approximations are not enough yet. The Bloch periodicity theorem [83, 84] constrains the calculation just within the Brillouin Zone (BZ) but the challenge of solving the electronic equation is a many-body problem even in a calculation restricted to a BZ. If the number of electrons \((N)\) increase then the higher the difficulties to solve the Schrödinger equation.
3.1.2 Density functional theory

DFT is a solution for a many-body problem, which is intractable even in not so big systems. The interacting electrons in independent potentials are reduced in DFT to a tractable problem of non-interacting electrons moving in an effective potential. Therefore DFT treat the conjunct of electrons as a whole. This method has also another advantage which is that is rather simple in terms of computational cost. Its central principle, which is that the total ground-state energy of a system of electrons acted on by a potential (in practice, the electrostatic potential due to the nuclei) is uniquely determined by the electronic density distribution $\rho(r)$.

$$\rho(r) = N \int |\Psi_0(r_1, r_2, \ldots, r_N)|^2 dr_1 \ldots dr_N \quad (3.2)$$

or better described:

$$\rho(r) = \sum_{i=1}^{N} \left| \psi_i(r) \right|^2 \quad (3.3)$$

DFT is based on the works of Pierre Hohenberg, Walter Kohn and Lu J. Sham [85, 86]. They demonstrated that an electronic system is described using an electron density through a functional $E[\rho]$.

**Hohenberg and Kohn theorems**

Hohenberg and Kohn [85] exposed two theorems related to any system consisting and interacting electron gas moving under the influence of an external potential $V_{ext}(r)$

**Theorem 1**

- The external potential $V_{ext}(r)$ and hence the total energy, is a unique
Ab-Initio calculations in Density Functional Theory

functional of the electron density $\rho(r)$

- The energy functional $E[\rho(r)]$ can be written in terms of the external potential $V_{\text{ext}}(r)$

$$E[\rho(r)] = \int \rho(r) v_{\text{ext}}(r) \, dr + F[\rho(r)]$$

(3.4)

- $F[\rho]$ contains the kinetic energy $T[\rho]$ and the interaction of electrons $V_{ee}[\rho]$.

**Theorem 2**

- The minimised electronic density corresponds with the groundstate density and allows to obtain the total energy of the groundstate.

- The groundstate energy is variationally obtained.

This means that every functional energy higher than that of the minimised density will lead to the groundstate total energy through a variational method. They proved that there exists a universal functional of the density, independent of the external potential. This theorem states its application only to the groundstate. However, not yet been tested in actual physical problems they develop a theory of the electronic ground state. Regardless of the outcome of this test, they shed some new light on the problem of the inhomogeneous electron gas and suggested further developments that were overcome somehow by Kohn and Sham through several approximations.

**The Kohn-Sham formulations**

Kohn and Sham [86] proposed an approach which is the Schrödinger equation of a fictitious system (the "Kohn-Sham system") of non-interacting particles that generates the same density as any given system of interacting particles. The Kohn-Sham equation is defined by a local effective (fictitious) external potential in which the non-interacting particles move, called the Kohn-Sham potential. As the particles in the Kohn-Sham system are non-interacting, the Kohn-Sham wavefunction is a single Slater determinant constructed from a set of orbitals that are the lowest energy solutions to:
Theoretical Approach I: DFT Method

\[
\left( -\frac{\hbar^2}{2m} \nabla^2 + v_{\text{eff}}(\mathbf{r}) \right) \phi_i(\mathbf{r}) = \varepsilon_i \phi_i(\mathbf{r}) \tag{3.5}
\]

This eigenvalue equation is the typical representation of the Kohn-Sham equations. Here, \( \varepsilon_i \) is the orbital energy of the corresponding Kohn-Sham orbital, \( \phi_i \), and the density for an \( N \)-particle system was just described before (Eq. 3.3).

In DFT, the total energy of a system is expressed as a functional of the charge density as

\[
E[\rho] = T_s[\rho] + \int d\mathbf{r} \, v_{\text{ext}}(\mathbf{r}) \rho(\mathbf{r}) + V_H[\rho] + E_{\text{xc}}[\rho] \tag{3.6}
\]

where \( T_s \) is the Kohn-Sham kinetic energy which is expressed in terms of the Kohn-Sham orbitals as

\[
T_s[\rho] = \sum_{i=1}^{N} \int d\mathbf{r} \, \phi_i^*(\mathbf{r}) \left( -\frac{\hbar^2}{2m} \nabla^2 \right) \phi_i(\mathbf{r}) \tag{3.7}
\]

\( v_{\text{ext}} \) is the external potential acting on the interacting system (at minimum, for a molecular system, the electron-nuclei interaction), \( V_H \) is the Hartree (or Coulomb) energy,

\[
V_H = \frac{e^2}{2} \int d\mathbf{r} \int d\mathbf{r}' \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \tag{3.8}
\]

and \( E_{\text{xc}} \) is the exchange-correlation energy. The Kohn-Sham equations are found by varying the total energy expression with respect to a set of orbitals to yield the Kohn-Sham potential as

\[
v_{\text{eff}}(\mathbf{r}) = v_{\text{ext}}(\mathbf{r}) + e^2 \int \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' + \frac{\delta E_{\text{xc}}[\rho]}{\delta \rho(\mathbf{r})} \tag{3.9}
\]

where the last term

\[
v_{\text{xc}}(\mathbf{r}) = \frac{\delta E_{\text{xc}}[\rho]}{\delta \rho(\mathbf{r})} \tag{3.10}
\]
is the exchange-correlation potential. This term, and the corresponding energy expression, are the only unknowns in the Kohn-Sham approach to density functional theory.

Finally, the DFT equation that should be solved is:

\[
\left( -\frac{\hbar^2}{2m} \nabla^2 + V_{\text{ext}}(r) + e^2 \int \frac{\rho(r')}{|r - r'|} dr' + \frac{\delta E_{\text{xc}}[\rho]}{\delta \rho(r)}(r) \right) \phi_i(r) = \epsilon_i \phi_i(r) \tag{3.11}
\]

Even though the description of Kohn and Sham of the electronic systems was very helpful in the beginning, the approximations for the exchange-correlation energy are still under development. There is a necessity to improve the exchange-correlation functionals in order to get a better description of the electronic systems. As was enumerated before, so far regular DFT exchange-correlation functionals give an underestimation of the band-gap of semiconductors, and a wrong localization of energy levels around the Fermi energy for metallic compounds. These are two major problems that nowadays can only be partially solved with hybrid functionals.

**Approximations (exchange-correlation functionals)**

All the approximations in DFT are concentrated in the exchange-correlation component \( E_{\text{xc}} \) of the total energy. The major problem with DFT is that the exact functionals for exchange and correlation correction are not known except for the free electron gas.

However, approximations exist which permit the calculation of certain physical quantities quite accurately. Initially, the local density approximation (LDA), which assumes that there is a exchange-correlation energy density that is related to the local density \( \rho(r) \) in exactly the same way as in an uniform electron gas, was always used for \( E_{\text{xc}} \) [87]. This functional depends only on the density at the coordinate where the functional is evaluated:

\[
E^{\text{LDA}}_{\text{xc}}[\rho] = \int \epsilon_{\text{xc}}(\rho) \rho(\vec{r}) d^3r \tag{3.12}
\]

In addition, the local spin-density approximation (LSDA) is a straightforward generalization of the LDA to include electron spin:
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\[ E_{xc}^{\text{LSDA}}[\rho_{\uparrow}, \rho_{\downarrow}] = \int \varepsilon_{xc}(\rho_{\uparrow}, \rho_{\downarrow}) n(\vec{r}) d^3r \] (3.13)

Other versions of the exchange-correlation functional are the Generalized Gradient Approximations (GGA) [88] which take into account the gradient of the density at the same coordinates:

\[ E_{xc}^{\text{GGA}}[\rho_{\uparrow}, \rho_{\downarrow}] = \int \varepsilon_{xc}(\rho_{\uparrow}, \rho_{\downarrow}, \vec{\nabla}\rho_{\uparrow}, \vec{\nabla}\rho_{\downarrow}) \rho(\vec{r}) d^3r \] (3.14)

Within this approach, there are relevant exchange-correlation functionals to be mentioned:

- The Perdew-Burke-Ernzerhof parametrization [89]
- The Perdew-Wang parametrization [90]

Furthermore, within the Perdew-Burke-Ernzerhof parametrization there are other enhancements like PBE-sol functional which is particularly suitable for solid [91]. This improves the description of cell geometries and of phonon frequencies in solids, compared to the standard PBE functional.

3.2 Beyond Density Functional Theory

The improvements of the exchange-correlation functionals came about to solve the lack of effectiveness that the standard DFT has, as (e.g.) improvement of correlation energies, or actual semiconductor band-gaps. Those theories are beyond DFT and are useful in separated systems with their particularities.

3.2.1 The DFT+U approach.

DFT+U (GGA+U alike LDA+U) leads to the enhancement of the DFT calculation results for those strongly correlated orbitals inside the same system. LDA+U method [30–32] concerns mainly the LDA approximation but is also applied in the GGA approach, which will be used in this thesis.

\( U \) Hubbard parameter introduces Coulomb and exchange terms upon electrons found in d-orbitals of certain systems that are strongly correlated, as (e.g.) oxides.
This method is also particularly important when transition metal atoms are included in the semiconductor systems. The transition metals with partially filled d or f-orbitals include properties that depend on the partial occupancies. Nevertheless standard DFT is unable to describe the localized interactions that appears in d-orbitals or f-orbitals. This is because, standard DFT allows the calculation of a functional for a delocalized exchange-correlation potential of a homogeneous electron gas, and the rather exotic symmetries that are sometimes in systems with d or f-orbitals in doped semiconductors lead to strong localization of electrons in these levels. The electrons are separated in a way that these in d or f-orbitals are different from those in s or p-orbitals. Localized electrons which are in d and f-orbitals should move in a different potential than delocalized electrons in s or p-orbitals. Therefore partially occupied d-orbitals and f-orbitals with non-local electrons in the valence levels are described as electronic structure of a metal and these materials are considered Mott insulator [92]. The LDA Coulomb interaction between d orbitals is replaced by an on-site Coulomb repulsion energy $U$. The interaction of electrons in d-orbitals is subtracted from the LDA energy functional avoiding in this way double-counting [93]: In order to better describe the d or f-orbitals in systems with transition metal atoms, a Hubbard term is included in the integrals of the standard DFT, added to the other terms. A general version of this addition looks like this:

$$E^{LDA+U} = E^{LDA} + E^U - E^{dc} \quad (3.15)$$

The $E^{LDA}$ term describes the delocalized electrons in the system located in e.g. s and p-orbitals, or its hybrid states. The second term is the Coulomb interaction energy of electrons in d-orbitals, the third term is the Hubbard term, which depends on the orbital occupancies $n_i$. A more detailed expression of this equation is:

$$E = E^{LDA} - \frac{UN(N-1)}{2} + \frac{1}{2} \sum_{i \neq j} n_i n_j \quad (3.16)$$

where $N$ is the number of electrons and $U$ is the value of Hubbard correlation energy. This $U$ is described as the energy needed for extracting an electron located in a d-orbital between two atoms with electrons in d-orbitals, renormalized by the screening due to the other electrons of s and p-orbitals [94]. This results in the
screening of the Coulomb interactions between \( d \) orbitals which reduces the \( U \) value.

In the LDA+U approximation the potential within \( E^{LDA} \) is \( V^{LDA} = V^{\text{ext}} + V^H + V^{xc,LDA} \) which is the potential that is used for electrons in \( s \)- and \( p \)-orbitals while for \( d \) and \( f \)-orbitals the potential acting on electrons is \( V_{LDA} + U (1/2 - n_i) \). If the orbital is occupied then \( n_i = 1 \) for unoccupied orbitals \( n_i = 0 \).

This method is specially good in the treatment of the transition metal doped semiconductors in the theoretical approach of this thesis. Yet despite this, the assignation of the \( U \) exact value in each case is difficult. This is because the treated materials in this thesis are still under study. Nevertheless, we used the effective \( U \) (\( U_{\text{eff}} = U - J \)) \(^1\).

3.2.2 Heyd-Scuseria-Ernzerhof Hybrid Screened Functional

Hybrid functionals constitutes those approximations to the exchange-correlation energy functional in DFT that incorporates a portion of exact exchange from Hartree-Fock theory with exchange and correlation from other sources (\textit{ab initio} or empirical).

While Kohn-Sham density functional theory has proven to be a highly competitive method, hybrid density functionals further improve upon the GGA results. Included in advanced functionals is also the meta-GGA which have been shown to yield accuracy comparable to hybrid functionals in solids. A comparison with hybrid functionals in solids is difficult due to elevated computational costs, but Heyd-Scuseria-Ernzerhof (HSE) functional shows improvements upon GGA and meta-GGA results for structural parameters such as lattice constants and bulk moduli \([95]\).

The exact exchange energy functional is expressed in terms of the Kohn-Sham orbitals rather than the density, so is determined with an implicit density functional. Therefore, a hybrid exchange-correlation functional is usually constructed as a contribution of exchange and correlation density functionals with a linear combination of the Hartree-Fock exact exchange functional, \( E^\text{HF} \) and using the following equation:

\[ E_{\text{HSE}} = E^\text{HF} + a \cdot E^\text{H} + (1 - a) \cdot E^\text{XC} \]

\(^1\)The \( U_{\text{eff}} \) value was introduced by Dudarev approach and this value was that had a correct meaning in the equations, instead of just the \( U \). (S. L. Dudarev, G. A. Botton, S. Y. Savrasov, C. J. Humphreys and A. P. Sutton, Phys. Rev. B 57, 1505 (1998))
Treatment of van der Waals interactions

\[ E_{x}^{\text{HF}} = \frac{1}{2} \sum_{i,j} \int \int \psi_i^*(r_1) \psi_j^*(r_1) \frac{1}{r_{12}} \psi_i(r_2) \psi_j(r_2) dr_1 dr_2 \quad (3.17) \]

The parameters determining the weight of each individual functional are typically specified by fitting the functional’s predictions to experimental or accurately calculated thermochemical data.

The HSE (Heyd-Scuseria-Ernzerhof) \([26, 96, 97]\) exchange-correlation functional uses an error function which is a screened Coulomb potential to calculate the exchange portion of the energy in order to improve computationally efficiency, specially for metallic systems. In this theory they apply a screened Coulomb potential only to the exchange interaction in order to screen the long-range part of the HF exchange. All other Coulomb interactions of the Hamiltonian, such as the Coulomb repulsion of the electrons, will not use a screened potential. They split the Coulomb operator into short-range SR and large-range LR components.

If HF and PBE long-range exchange contributions of this functional are neglected and work under the assumption that this approximation may be compensated by other terms in the functional, we obtain a screened Coulomb potential hybrid density functional of the form:

\[ E_{\omega}^{\text{PBEh}} = a E_{x}^{\text{HF,SR}}(\omega) + (1-a) E_{x}^{\text{PBE,SR}}(\omega) + E_{x}^{\text{PBE,LR}}(\omega) + E_{c}^{\text{PBE}} \quad (3.18) \]

where \(a\) is the mixing coefficient (\(a=1/4\)) and is determined by perturbation theory, and \(\omega\) is an adjustable parameter that control the short-range in the interactions. \(E_{x}^{\text{HF,SR}}(\omega)\) is the short range Hartree-Fock exact exchange functional, \(E_{x}^{\text{PBE,SR}}(\omega)\) and \(E_{x}^{\text{PBE,LR}}(\omega)\) are the short and long range components of the PBE exchange functional, and \(E_{c}^{\text{PBE}}(\omega)\) is the PBE correlation functional. The HSE exchange-correlation functional is reduced to the PBE0 hybrid functional for \(\omega = 0\).

3.3 Treatment of van der Waals interactions

Van der Waals (vdW) interactions appears when covalent bonds between molecules form dipoles. In addition, for a crystalline system, these forces appear between layers in the layered materials, where the permanent dipoles stabilize the whole system. The distance among layers is high enough and therefore these types
3.3.1 The Grimme’s dispersion correction

Density functionals fail when trying to describe correctly van der Waals interactions. The dynamical correlations between fluctuating charge distributions when a weak force is involved are not suited inside DFT integrals. In layered materials the result is that the layers are not conserving the distance, and instead the expansion of the cell parameter in the direction of the layer stacking is what is obtained, and the resulting structure is far from the reality. Grimme’s DFT-D dispersion correction [27, 101–103] allow the corrected cell parameter in the direction of the layer stacking for layered solids, with great results.

This is a pragmatic method which consists in adding to the conventional Kohn-Sham DFT energy ($E_{KS-DFT}$) a semi-empirical dispersion potential:

$$E_{DFT-D} = E_{KS-DFT} - \frac{s_0}{2} \sum_{i=1}^{N_{at}} \sum_{j=1}^{N_{at}} \sum_{L} \frac{C_{ij}}{|r^{i,0} - r^{j,L}|^6} f(|r^{i,0} - r^{j,L}|)$$

(3.19)

In the DFT-D2 method of Grimme [27], the van der Waals interactions are described
Treatment of van der Waals interactions

via a simple pair-wise force field where the summations are over all atoms $N_{\text{at}}$ and all translations of the unit cell $L = (l_1, l_2, l_3)$. The atoms $i \neq j$ for $L = 0$, $s_6$ is a global scaling factor that has been optimized for several different DFT functionals and in PBE $s_6 = 0.75$. $C_6^{ij}$ are the dispersion coefficient for the atom pair $ij$ which value is obtained with:

\[
C_6^{ij} = \sqrt{C_6^i C_6^j},
\]

and $r^{L}$ is a position vector of atom $i$ after performing $L$ translations of the unit cell along lattice vectors.

The term $f(r_{ij})$ is a damping function which scale the force field in order to minimize contributions from interactions within typical bonding distances.

\[
f(r_{ij}) = \frac{1}{1 + e^{-d(r_{ij}/R_{ij}^0 - 1)}}
\]

vdW radii $R_{ij}$ are:

\[
R_{ij}^0 = R_{i}^0 + R_{j}^0,
\]

### 3.3.2 vdW-DF functional

The vdW-DF functional was originally proposed by Dion et al. [29] for accounting the vdW weak interactions (Eq. 3.23).

\[
E_{xc} = E_{x}^{\text{GGA}} + E_{c}^{\text{LDA}} + E_{c}^{\text{nl}}
\]

In Eq. 3.23, $E_{x}^{\text{GGA}}$ is an exchange functional using the generalized gradient approximation (GGA) and $E_{c}^{\text{LDA}}$ is the local correlation energy of the local density approximation (LDA) (LDA instead of GGA in this case in order to avoid the inclusion of doubled correlation) The non-local correlation energy describing the vdW interaction is given by a six-dimensional integral [29]. The non-local term is calculated as suggested in the original vdW-DF from Dion et al. [29] but using the exchange functional from revPBE [104]. In the former vdW-DF functional from Dion et al. [29] the $E_{c}^{\text{nl}}$ vanishes for a uniform electron density, hence, the correlation energy is complemented by the LDA contribution. Since $E_{c}^{\text{nl}}$ contains the necessary ingredients for vdW forces, an additional attraction stemming from the exchange functional as in LDA is undesirable. For this reason,
the original choice for the exchange to be used with $E_{\text{vdW}}$ was the revPBE functional [104], which is almost free from any spurious binding.

The vdW interaction is obtained from the electron density $\rho(r)$ via the genuinely non-local correlation functional:

$$E_{\text{nl}}^c = \int dr dr' \rho(r) \Phi_c(r,r') \rho(r'),$$

(3.24)

where $\Phi_c(r,r')$ is a kernel function derived from a local polarizability model [105] using a number of approximations [29, 106–108].

This revPBE is nevertheless too repulsive in the vdW regime [109, 110], and a large number of other options for the exchange part of the functional have been proposed, including a revised version of the PW86 functional, PW86R [106, 107, 110], PBE [109], optimized versions of PBE [98] and long-range corrected hybrid functionals [107, 111].

While in vdW-DF the foremost optimization for vdW forces rely on correlation in the optimized version by Michaelides et al [28] and named optPBE-vdW the parameters of the exchange are enhanced using the S22 database [98]. These functionals can be applied in layered semiconductors using also stress forces to optimize the volume relaxation.

After applying the adiabatic-connection fluctuation-dissipation theorem [112], that allows the inclusion of the vdW forces, the exact correlation energy can be expressed as

$$E_c = -\text{Tr} \int_0^\infty \frac{d\omega}{2\pi} \int_0^1 \frac{d\lambda}{\lambda} (\chi_\lambda(i\omega) - \chi_{KS}(i\omega)) V_\lambda,$$

(3.25)

where $V_\lambda$ is $\lambda$ times the Coulomb potential and $\chi_\lambda$ and $\chi_{KS}$ are the frequency-dependent density-response functions for the interacting and Kohn-Sham systems, respectively. If the so-called exchange-correlation kernel [113], $f_{xc}^\lambda$, is known, we can obtain $\chi_\lambda$ from Dyson’s equation

$$\chi_\lambda = \chi_{KS} + \chi_{KS}(V_\lambda + f_{xc}^\lambda) \chi_\lambda,$$

(3.26)

but in practice, (3.25) is untractable for real systems, unless $f_{xc}^\lambda$ is approximated.
3.4 Thermodynamic properties

Thermodynamic properties of compounds allow us to describe the feasibility of the synthesis of the materials. These are obtained through quantum calculation of the energy eigenvalues of the compounds \( E_n \).

\textit{Ab-initio} calculations in condensed phases treat systems of many atoms and might explore large regions of configuration space to obtain the energy eigenvalues. There is an effective way to do this at present through DFT method. In this topic, DFT is highly competitive in accuracy with other quantum chemistry methods and is widely used for calculating the ground-state energetics.

In general terms, \textit{ab initio} calculations in DFT allows to obtain the energy eigenvalues \( E_n \) from a Kohn-Sham hamiltonian \( \mathcal{H}_{KS} \). We assumed general terms of the DFT theory, but should be clarified that \( \mathcal{H}_{KS} = \left( -\frac{\hbar^2}{2m} \nabla^2 + v_{\text{eff}}(r) \right) \) of equation 3.5. Similarly to a macroscopic system, thermodynamics in a Kohn-Sham hamiltonian might be described as a sum of Kinetic Energy (\( \mathcal{T} \)), Potential Energy (\( \mathcal{V} \)), and Internal Energy (\( \mathcal{U} \)):

\[
\mathcal{H}_{KS} = \mathcal{T} + \mathcal{V} + \mathcal{U},
\]

(3.27)

On the other hand the partition function allows the description of the system using the different states in certain ensemble:

\[
\mathcal{Z}' = \sum_n e^{-\beta E_n},
\]

(3.28)

where: \( \beta \equiv \frac{1}{k_B T} \)

The partition function constitutes the basis to obtain other thermodynamic functions, and particularly, the Helmholtz free energy:

\[
F = -k_B T \ln Z
\]

(3.29)

### 3.4.1 Vibrational Energies and Phonons

Even with an accurate \textit{ab initio} energy function the calculation of the vibrational free energies is very difficult, except in one case: the harmonic system.
The phonon frequencies are described through displacements of the ions in the periodic lattice in the force-constant matrix \( \Lambda_{is\alpha,jt\beta} \) in which atoms \( i, j \) within a \( s, t \) small displacement vector positions respectively are moving in the \( \alpha, \beta \) Cartesian directions, therefore atom \( i \) moves only within \( \mathbf{R}_i^0 + \tau_s \) positions and atom \( j \) within \( \mathbf{R}_j^0 + \tau_t \) positions. This force-constant matrix is described through the harmonic approximation.

A \( u_{jt\beta} \) displacement of the atom \( j \) within \( \mathbf{R}_j^0 + \tau_t \) zone along the direction \( \beta \) allows the description of the force exerted on the atom at position \( \mathbf{R}_i^0 + \tau_s \) in the \( \alpha \) Cartesian direction in harmonic approximation:

\[
F_{i\alpha}^{j\beta} = -\sum_{j\beta} \Lambda_{is\alpha,jt\beta} u_{jt\beta}
\]

(3.31)

This force-constant matrix should remain symmetric:

\[
\Lambda_{\alpha,\beta}(\mathbf{R}_j + \tau_t - \mathbf{R}_i - \tau_s) = \Lambda_{\beta,\alpha}(-[\mathbf{R}_j + \tau_t - \mathbf{R}_i - \tau_s])
\]

(3.32)

Each displacement in \( x, y \) and \( z \) Cartesian coordinates provides a number of \( 3N \) vibration forces (where \( N \) is the number of atoms) with which are calculated the vibration frequencies. The total computation of these frequencies result in the total vibrational energy [114]. In this equation the entropic term and also the vibrational enthalpy are included.

\[
F_{\text{vib}} = k_B T \sum \ln \left[ 2 \sinh \left( \frac{hv_i(x)}{2k_B T} \right) \right]
\]

(3.33)

This calculation should be done in each \( k \)-point within the Brillouin Zone instead of confining it to the center of the cell.
3.5 Optical Properties

The interaction between a photon and an electron leads to the excitation of the later to higher levels of energy inside the materials. The optical properties are theoretically obtained using relation equations from the imaginary part of the dielectric function. The frequency dependent dielectric matrix after the electronic ground state can be determined upon a summation over empty states for the calculation of the imaginary part by using the equation:

\[
\varepsilon^{(2)}_{\alpha\beta}(\omega) = \frac{4\pi^2e^2}{\Omega} \lim_{q \to 0} \frac{1}{q^2} \sum_{c,v,k} 2w_k \delta(\varepsilon_c - \varepsilon_v - \omega) \times \langle u_{c,k+e_\alpha q} | u_{v,k} \rangle \langle u_{c,k+e_\beta q} | u_{v,k} \rangle^*,
\]

(3.34)

where the indices \(c\) and \(v\) refer to conduction and valence band states respectively, and \(u_{c,k}\) is the cell periodic part of the orbitals at the \(k\)-point. The real part of the dielectric tensor \(\varepsilon^{(1)}\) is obtained by the usual Kramers-Kronig transformation

\[
\varepsilon^{(1)}_{\alpha\beta}(\omega) = 1 + \frac{2}{\pi} P \int_0^\infty \frac{\varepsilon^{(2)}_{\alpha\beta}(\omega') \omega'}{\omega'^2 - \omega^2 - i\eta} d\omega',
\]

(3.35)

where \(P\) denotes the principle value. The complex shift \(\eta\) is 0.1, which is perfectly acceptable for most calculations and causes a slight smoothing of the real part of the dielectric function.

The adsorption coefficient is related with the dielectric matrix with:

\[
\alpha = \left[ 2 \left( \sqrt{\varepsilon_1^2 + \varepsilon_2^2} - \varepsilon_1 \right) \right]^{\frac{1}{2}}
\]

(3.36)

The reflectivity for normal incidence is the percentage of the intensity of the field that is reflected by the surface. It can be deduced from classical optics in terms of the refraction index and the extinction coefficient:

\[
R = \frac{I_{\text{reflected}}}{I_{\text{incident}}} = \frac{(1-n)^2 + \kappa^2}{(1+n)^2 + \kappa^2}
\]

(3.37)

\(^1\text{For a wider explanation of the theoretical description of optical properties of materials see.} \ [115]\)
assuming that the first medium is the vacuum (or approximately, air). The refraction index is:

\[
n = \left[ \frac{\sqrt{\varepsilon_1^2 + \varepsilon_2^2 + \varepsilon_1}}{2} \right]^2
\]

(3.38)

Other equations that relates the optical properties of refractive index \( n \) which is the real part of the complex refractive index: \( \text{Re}(\mathcal{N}) \) and the extinction coefficient \( \kappa \) is \( \text{Im}(\mathcal{N}) \). They are related to the dielectric function by:

\[
\varepsilon_2 = 2n \kappa \quad \text{(3.39)}
\]

\[
\varepsilon_1 = n^2 - \kappa^2 \quad \text{(3.40)}
\]
Theoretical Approach II: SOD Method
Chapter 4

Theoretical Approach II - SOD Method

4.1 Theoretical approach of SOD

Site occupancy disorder (SOD) program [33, 34] came about to solve the problem of defective site calculations, when a non straightforward way of obtaining thermodynamic results is available. The simplest algorithm implemented in SOD considers the equivalent configurations when they are related by an isometric operation, while those unequally in terms of symmetry are considered non-equivalent. A list of all possible isometric transformations is provided in the parent structure (the original structure without any substitution). These provided elements are those that allow the differentiation of each non-equivalent configurations. On the other hand the SOD method not only allow us to obtain the non-equivalent configurations through combinatorics, but also this might be characterized through the associated statistical thermodynamic data. In order to describe the disordered sites that appear in intermediate-band materials, SOD is a powerful tool that allows us to get an insight into the properties of these yet unknown doped structures.
4.1.1 Disordered Sites in Solids

In a periodic lattice, the defect formation is a ubiquitous phenomenon. Certain intrinsic defects or dopant atoms are located in disordered sites, which are forming a non-periodic occupation of lattice sites (Fig. 4.1). There are several examples that can be mentioned: metallic alloys, mineral solid solutions, and synthetic non-stoichiometric compounds.

In general terms, the appearance of defects in solid compounds is well described from a thermodynamic point of view. At equilibrium in the solid, we should have a chemical potential $\Theta = 0$ and $\partial \Theta / \partial n = 0$. [83] Two cases, therefore, are

![Scheme exhibiting some general intrinsic defects and some extrinsic dopant interactions](image)

**Figure 4.1**: Scheme exhibiting some general intrinsic defects and some extrinsic dopant interactions that might occur in a 2D lattice of an AB binary compound (analogous to that of a 3D lattice). These are: vacancies $V_A$ and $V_B$ and interstitial sites $A_i$ and $B_i$ which are intrinsic defects while C, D and E are dopants in different situations. C represents a dopant inserted in a substitutional site with no distortion in the surrounding bonds while D dopant interacts with the atoms in a distortion. Distortion in these cases is related with the nature of the inserted atom and its valence orbitals. F dopant is interacting with a neighbouring atom of the same nature, forming an aggregate.
distinguishable with the constrained heat $q$ which should always be positive in order to maintain the stability of the bonds, otherwise the solid would be unstable. The degree of local disorder generated produce an entropy $s$. If the process of creating the defects is a non-equilibrium process, i.e. if the defects are created fast enough in comparison with the relaxation time of the solid, then $q < sT$ and, from the equilibrium condition, we have

$$n = N_0 e^{-q/T}$$  \hspace{1cm} (4.1)$$

and $\Theta_0 = T n$. This demonstrates that there will always be the defects in solid (for any $T \neq 0$). In addition, in this equation is shown that defect concentration increases with temperature. Furthermore in a process that is slow enough in comparison with the relaxation time of the solid, so that $q = sT$, the defects may be created under equilibrium condition:

$$n = N_0 e^{-s} ,$$  \hspace{1cm} (4.2)$$

This equation shows that there will always appear a finite concentration of defects which is independent of temperature (for any $T \neq 0$). In general, for any realistic value of $q$ and $s$, and normal temperatures, the defect concentration given by both equations is extremely low, but this is only a general statement. If we would like to obtain a very high concentration of defects in a solid compound, therefore the controlled preparation of compounds would be somehow difficult in experimental conditions.

Moreover, the aperiodicity in the local environment in a bulk periodic lattice provides interesting features to the host system, as e.g. an intermediate-band formation among others. The study of this and also the study of the resulting defective structure are important. Nevertheless, the theoretical modelling of these disordered sites involves a high computational cost [116]. Site disorder modelling can be described as a non-periodic occupation of lattice sites in a crystal structure. The computational modelling of site disorder is challenging because periodic boundary conditions cannot be applied in the same straightforward way as in perfect crystals [116].

4.1.2 Methods for treating site-disordered solids

There are three types of methods for treating site-disordered solids. In general terms the characteristics of each are described as following [34]:

The first group:

- Interatomic potential methods:
  - These are implemented in programs like GULP [117,118]
  - Accounts average atom allowing the recover of the perfect periodicity in the crystal.
  - Classical calculations with analytical interatomic potentials.
  - Each disordered site experiences a potential which is average of all configurations of disordered positions. This can also be accounted for virtual crystal approximation (VCA)
  - Include geometric relaxations explicitly while electronic effects are implicit.
  - Useful for preliminary simulations of very disordered systems.
  - VCA: One potential generated by average atoms working upon electrons in the Schrödinger equation.

The main drawback of these methods is the lack of local structural representation around each ion. In other words they lack descriptions of electronic potentials in detailed manner as other methods allow.

The second group:

- Special quasi-random structure [119]
  - A large supercell with a more or less random distribution of ions in the sites.
  - Computationally expensive.
  - Provides a better description of the local geometries found in the real system.
  - The ion positions in the supercell mimic the most relevant close-neighbor pair and multisite correlation functions of the random substitutional alloy.
  - Useful in the evaluation of the electronic structure of site-disordered solids.
The main drawback of these methods are the inflexibility of the fixed ion distribution. The varying degree of disorder as a function of temperature, for example, needs a more flexible representation.

The third group:

- The multi-configurational supercell approach (Fig. 4.2)
  - Set of configurations in supercells.
  - Each configuration corresponds to a particular arrangement of atoms within the supercell.
  - There is a probability of occurrence associated.

The main drawback is that the supercell size is fixed. Strictly speaking, each of the configuration energies depends on the configuration of the ions in the neighboring cells. Only for large supercells, where *intracell* interactions are much more important than *intercell* interactions this can be neglected and this is the consideration made in this thesis.

In the multi-configurational supercell approach we calculate the probabilities of occurrence of the configurations within assumption of configurational equilibrium. Energy (electronic total energy) of each configuration is used in the sub-conjunct applying a formalism based on Boltzmann-Gibbs statistical mechanics. Lower energies of configurations have higher probabilities. The dispersion of the distribution is controlled by the temperature as (e.g.) at low temperatures only the most stable configurations appear, whereas at high temperatures more configurations are accessible to the ions, leading to higher disorder.

**Approximations in the energy evaluation**

The approximations in the energy evaluation can be divided into several groups, the first, where the energy is only a function of the site occupancies, and the second where the energy is obtained after considering electrons and ions. In between, there is a group of methods like GULP which explicitly do not consider electrons. Some characteristics of the main methods are as follow:

- Metropolis - Monte Carlo, Ising-type models of alloys, and cluster expansion methods
Figure 4.2: Schematic representation of total and reduced space of configurations obtained with SOD. (The change in the color of configurations from the whole population, that of the non-screened set, have been kept intentionally with changed colors from that of the selected structures, i.e. those that conform the sub-set of the non-equivalent configurations)

- Computationally cheaper.
- The energy is only a function of the site occupancies.
- It can be integrated with sampling algorithms (e.g.) within a single computer program, all the configurations calculated at a time.
- The energy is obtained from nearest-neighbor (NN), next-nearest-neighbor (NNN) configurations or longer-distance effective pair interactions, or including terms for clusters of more than two ions.

Main Drawback: Electronic and geometrical degrees of freedom are not included. The lack of accounting long range interactions provides sometimes inaccuracies or would require a large number of terms and parameters.

- Tight-binding method, DFT, Hartree-Fock (HF), post-HF, hybrid DFT/HF (e.g.) HSE
– Include geometric and electronic relaxation for each configuration.
– Provide access to vibrational properties of the solid.
– These vibrational properties respond to external pressure.
– Any property that can be obtained for each configuration can be averaged over the ensemble to obtain effective values for the disordered solid.

The main drawback is that the calculations are more expensive and can be done using only one geometric configuration at a time. Configurational sampling in these cases requires multiple calls to the quantum-mechanical or interatomic potential code from an external program, and very long running times.

4.2 Modelling Approach for the Configurational Space

The configurational space can be modelled by using three approaches: one, by using a random sampling; two, through an importance sampling using Metropolis-Monte Carlo algorithms and, three, using the crystal symmetry to discriminate configurations [34]. The latter is which is going to be treated in this thesis.

4.2.1 Combinatorial in SOD using crystal symmetry

The Fig. 4.2 showed before, represents an example of configurations that can be obtained when more than one disordered sites are modelled in the same supercell size and different samples. The first row corresponds to the total number of configurations \( N \) that can be obtained using all the disordered sites. This total number is sometimes very large and the solution is difficult to handle. Therefore, we obtain a reduced space of configurations denoted by \( n \). This reduced space, represented in Fig. 4.2 by rows with colour differentiation, is smaller than the former. Each configuration within each representative part is considered identical to the chosen model, even though the positions of the disordered sites are not identical, of course.

According with Grau-Crespo et al [33] the fundamental theory in SOD can be explained as if every subset of configurations owning identical symmetry is represented by one of them, we should say any of them \(^1\). Therefore Fig. 4.2

\(^1\)http://www.ucl.ac.uk/uccargr/sod.htm
representation applied for SOD method is a good example as how SOD can be implemented.

Briefly, if we represent each symmetry element as an operator matrix and the atoms that contribute to each of them as a vector \((x_1, x_2, x_3)\), therefore we can obtain the information of whether this atom (vector) is equivalent or not to the others through the translation vector \((o_1, o_2, o_3)\). There is an extensive theory that lies in beyond this simplest statement.

\[
\hat{O} \cdot \bar{x} = \overline{O} \cdot \bar{x} + \sigma = \begin{pmatrix} a_{11} & a_{12} & a_{13} \\ a_{21} & a_{22} & a_{23} \\ a_{31} & a_{32} & a_{33} \end{pmatrix} \begin{pmatrix} x_1 \\ x_2 \\ x_3 \end{pmatrix} + \begin{pmatrix} o_1 \\ o_2 \\ o_3 \end{pmatrix} \tag{4.3}
\]

The simplest way to look at solid crystalline materials is in a way of its symmetry. Crystal, with an ordered internal arrangement of atoms shows symmetry, and symmetry operators also can be related with the set of ordered atoms by applying a symmetry operator over the matrix that conforms the set of ordered atoms. If a crystal lattice is formed by a highly symmetric ordered set of atoms then a highly amount of symmetry operator matrices is shown. Therefore symmetry of any crystal structure can be described by one of the 230 crystallographic space groups. Each of those crystallographic space groups is represented through a number of symmetry elements which are symmetry operators. These groups are which describe the isometric transformation that converts each configuration of the disorder into the other, and this is true for the unit cell. Therefore in the supercell, the symmetry operators in the space group of the unit cell are reproduced and it is also possible to find the set of all the symmetry operators of the supercell. Beyond the fact that all the symmetry information of the supercell is contained in the space group description, the translations are not included once a supercell is created.

Within this approach, two configurations are considered equivalent when they are related by an isometric operation. A list of all possible isometric transformations is provided by the group of symmetry operators in the parent structure (the original structure without any substitutions).

They include the symmetry operators in the space group of the crystal unit cell (scaled in an appropriate way to account for the cell multiplication in the supercell), the supercell internal translational operators, and the combinations between them. We also need to keep track of the degeneracy of each independent configuration, that is, how many times it repeats in the whole configurational space. Then it is possible
to screen all possible configurations and select those which are symmetrically non-equivalent for energy/properties evaluation.

Site occupancy disorder is considered a partial occupation of lattice sites in a crystal structure in which an element of disorder or defect can be identified, but conserving the periodicity. The combinatorial can be applied to reduce the number of site-occupancy of atomic configurations, of this atomic disordered sites, and this is done using the crystal symmetry of the lattice, taking into account that every identical set of two atoms, related with each other by a symmetry operator give us the same result. The information that can be obtained is related with the statistical probability of a defect appearance into a lattice, and the thermodynamical terms associated.

4.2.2 Thermodynamic parameters within SOD method

The equations for configurational statistics within the reduced space of inequivalent configurations \[34\] are slightly adapted from the canonical ensemble (see appendix ??). Each independent configuration \(m (m = 1,.M)\), has an energy \((E_m)\) and a degeneracy \((\Omega_m)\) associated and the probability of each of them will be:

\[
P_m = \frac{\varepsilon_m}{Z} e^{-E_m/k_B T} \tag{4.4}
\]

which means that if we want to compare the stability of two independent configurations in energetic terms, we should not use their energies but instead the value \(E_m\). Average properties within the configurational space are also obtained:

\[
A = \sum_{m=1}^{M} P_m A_m \tag{4.5}
\]

but only if \(A_m\) is the same for all the \(\Omega_m\) equivalent configurations that the inequivalent configuration \(m\) represents. For example, if we are modelling a cubic system, we cannot obtain the average cell parameter \(a\) from the cell parameters of the inequivalent configurations, as this result could be different from the direct average of the \(b_m\) or \(c_m\) values, breaking the cubic symmetry. We therefore need to find first a related magnitude that is invariant in the subspace of equivalent configurations, e.g. the volume \(V_m\) in the given example. We can then define the average cell parameter of the cubic system as:
\[ a = \left( \sum_{m=1}^{M} P_m V_m \right) \] (4.6)

Symmetry reduction is only practical when working with relatively small supercells. This is typically the case when properties other than the energy are being evaluated. When evaluating the thermodynamic functions of the solution, the enthalpy tends to converge very quickly with supercell size, but the convergence of the entropy, which depends on configuration counting, is much slower.

### 4.3 Computational Details in SOD Method

Fig. 4.3 represents the schematic diagram of SOD implementation, where the first step is the use of the combinatorics explained in the above sections. In the outputs of SOD combinatorics (sod\_comb), the configurations are used for the input data in the calculation of electronic properties with VASP code. Of course, certain other codes of this type might also be used. The final step is the use of the statistical part of the SOD code (sod\_stat). Using sod\_stat one can obtain results like the calculations of thermodynamic probabilities of configurations or the average properties of the studied systems (geometric parameters, energies, etc.) and all these data might be obtained using different degree of disorder (e.g.) through the use of different temperatures within the assumption of thermodynamic equilibrium. Yet, the output also gives the data outside thermodynamic equilibrium.
Figure 4.3: Schematic representation of SOD implementation using the electronic calculations as an intermediate step in between the two steps that are included in the SOD code.
Results I: $MIn_2S_4$ Spinel type materials
Chapter 5

Results I- Spinel type materials

5.1 Intrinsic-disorder in spinels.

Spinel materials have rather complex structures. Empirical observations have been used for explaining cation distributions in spinels, which is interpreted in terms of the thermodynamic energetics [120]. While their stoichiometry of cations may have different oxidation states, in the case of MIn$_2$S$_4$ II-III spinels, these exhibit an intrinsic disorder which corresponds with the equilibration exchange between tetrahedral (M$^2+$) and octahedral (In$^3+$) cations. Spectral data, as that of Infrared or Raman active modes, would constitute important tools in deciphering the actual cation distributions that can appear in certain spinel materials [121]. Nevertheless In$^3+$ and Cd$^{2+}$ are isoelectronic, and for this reason these are not distinguishable in an Infrared spectra of CdIn$_2$S$_4$ [122].

The (Cd$_{1-x}$In$_x$)[In$_2$–$x$Cd$_x$]S$_4$ structure agrees with the nomenclature in which tetrahedral sites are in parentheses ( ) while octahedral are in brackets [ ] where M=Mg,Cd. The extent under which this exchange takes place is known as inversion degree $x$ which $x=0$ is a non exchanged configuration while $x=1$ is a fully inverted one.
Figure 5.1: Spinel structure exhibiting tetrahedral (central atom color light salmon is M$^{2+}$ in direct spinel) and octahedral cationic sites (color dark brown is In$^{3+}$ in direct spinel) in [Cd/Mg]In$_2$S$_4$.

In the MgIn$_2$S$_4$ the $x$ is reported as 0.84 [123] while the $x$ in CdIn$_2$S$_4$ is reported approximately 0.20 [124].

We determined the cation distribution in CdIn$_2$S$_4$ and MgIn$_2$S$_4$ 2:3 spinel sulphide by a thermodynamic model including a configurational approach and combined with the vibration energy from the vibration frequencies of the lattice based on the \textit{ab initio} energy results.

The MgIn$_2$S$_4$ and CdIn$_2$S$_4$ primitive cell contains two formula units, which allows us to consider inversion degrees $x = 0, 0.5$ and 1 (Fig.5.2). This imply that for each $x$ there is only one symmetrically different configuration of cations.

Order-disorder transition behaviors are examined using calculation of supercell in a symmetry-adapted configurational set and the transition temperatures under which the experimental inversion degree is obtained are evaluated.
5.2 Study of CdIn$_2$S$_4$ inversion-degree, bandgap control.

The PBE and PBEsol results are very similar in terms of energy, therefore the discussion below refers to the PBEsol results, unless otherwise stated.

The total energies for the three different $x$ values allow the calculation of the energy $\Delta E_{\text{conf}}$ as $\Delta E_{\text{conf}}(x) = E(x) - E(0)$, where the subscript $\text{conf}$ indicates that this is the configurational contribution only. A quadratic dependence of the inversion energy with $x$ has been empirically recognised by Kriessman and Harrison [120] and theoretically justified by O’Neill and Navrotsky [125] based on the linear dependences with $x$ of both the cell parameter $a$ and the anion position parameter $u$. Therefore, our three calculated inversion energies allow us to interpolate for any value of $x$ using a quadratic function (Fig. 5.3 (a)).

The inversion energies are positive for the whole range of $x$, and the curvature is slightly negative. In order to test the approximation of using only one configuration for the calculation of the energy for each $x > 0$, we have calculated the inversion energy for $x=0.25$ by taking the symmetry-adapted ensemble average of all different cation configurations [33] in a cell doubled along one axis. The result represented

Figure 5.2: Structures associated with the inversion degree in the CdIn$_2$S$_4$ and MgIn$_2$S$_4$. 
as an empty circle is in good agreement with our quadratic interpolation based on
the primitive cell results (Fig. 5.3 (a)).
Furthermore, we estimated the configurational free energy of inversion as \( \Delta F_{\text{conf}} = \Delta E_{\text{conf}} - T\Delta S_{\text{conf}} \), where:

\[
S_{\text{conf}} = -R\left[x\ln x + (1-x)\ln(1-x) + \frac{x\ln x}{2} + (2-x)\ln(1-\frac{x}{2})\right]
\]

(5.1)
is the ideal configurational entropy of inversion [126, 127].
In practice, some excess (non-ideal) contributions to the configurational entropy can be expected. Our test calculations for the ensemble of configurations with \( x=0.25 \) in the double cell show that these excess contributions are indeed small.
The difference between the temperature-dependent entropy (as calculated using Boltzmann statistics, e.g. [128]) and the maximum entropy for the given cell and composition, is only 2%.
In the absence of inversion energies, the minimum of the inversion free energy corresponds to the maximum of the configurational entropy, which occurs at \( x = 2/3 \) (full disorder of the cations among all sites). However, the positive and relatively high inversion energies imply that the minima of the inversion free energy actually occur at much lower values of \( x \) (e.g. \( x=0.04 \) at \( T=1000 \text{ K} \)), as shown in Fig 5.3 b).
Therefore, according to the analysis so far, which ignores vibrational effects, the CdIn\(_2\)S\(_4\) spinel would be expected to be almost fully direct, while experimental measurements suggest inversion degrees of \(~20\%\) [124].

5.2.1 Phonon frequencies in CdIn\(_2\)S\(_4\)
In order to discuss the effect of vibrations in the thermodynamics of inversion, we now examine the phonon modes in CdIn\(_2\)S\(_4\) with different degrees of inversion.
For these calculations, we employ density functional perturbation theory, as implemented in VASP. We first compare the calculated zone-centre frequencies for the direct spinel with the experimental values measured using infrared and Raman spectroscopy [129, 130]. Table 5.1 shows that the vibrational modes are well described by our PBEsol calculations, with average discrepancy of only 2.5%.
We then calculated the phonon frequencies in a \( 2 \times 2 \times 2 \) supercell, which is equivalent to a \( \Gamma \)-centered \( 2 \times 2 \times 2 \) sampling of the reciprocal space, thus
allowing (linear) dispersion of the modes. From resulting frequencies we obtained the vibrational contributions to the inversion free energy in the harmonic approximation:
Table 5.1: Calculated zone-centre phonon frequencies of normal CdIn$_2$S$_4$ spinel in comparison with experimental values [129, 130]

<table>
<thead>
<tr>
<th>Mode</th>
<th>$\tilde{\nu}_{\text{exp}}$ (cm$^{-1}$)</th>
<th>$\tilde{\nu}_{\text{theo}}$ (cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$T_{1u}$ (IR)</td>
<td>68</td>
<td>67</td>
</tr>
<tr>
<td>$T_{2g}$ (Raman)</td>
<td>93</td>
<td>92</td>
</tr>
<tr>
<td>$T_{1u}$ (IR)</td>
<td>171</td>
<td>171</td>
</tr>
<tr>
<td>$E_g$ (Raman)</td>
<td>185</td>
<td>189</td>
</tr>
<tr>
<td>$T_{1u}$ (IR)</td>
<td>215</td>
<td>221</td>
</tr>
<tr>
<td>$T_{2g}$ (Raman)</td>
<td>247</td>
<td>239</td>
</tr>
<tr>
<td>$T_{1u}$ (IR)</td>
<td>307</td>
<td>296</td>
</tr>
<tr>
<td>$T_{2g}$ (Raman)</td>
<td>312</td>
<td>297</td>
</tr>
<tr>
<td>$A_{1g}$ (Raman)</td>
<td>366</td>
<td>355</td>
</tr>
</tbody>
</table>

$$
\Delta F_{\text{vib}} = k_B T \left\{ \sum \ln \left[ 2 \sinh \left( \frac{h\nu_i(x)}{2k_B T} \right) \right] - \sum \ln \left[ 2 \sinh \left( \frac{h\nu_i(0)}{2k_B T} \right) \right] \right\}
$$

(5.2)

for configurations with inversion degrees $x = 0, 0.5$ and 1. Fig. 5.3 (c) shows that the vibrational contribution to the free energy exhibits an almost linear variation with $x$. The negative slope means that vibrational effects will shift the equilibrium inversion degree towards values higher than those expected based on configurational contributions only. The total (configural + vibrational) free energy is then plotted in Fig. 5.3d as a function of $x$ for temperatures between 900 and 1200 K. At a temperature $T = 1200$ K, which is typical for the synthesis of this type of material [131, 132], the equilibrium degree of inversion is very close to the experimentally observed value $x = 0.20$. This result suggests that the degree of inversion in CdIn$_2$S$_4$ is thermodynamically controlled during the solid formation.

### 5.2.2 Band-gap control in CdIn$_2$S$_4$

The sensitivity of the equilibrium inversion degree to the temperature indicates that it is possible to tune the cation distribution via temperature control during the
Study of CdIn$_2$S$_4$ inversion-degree, bandgap control.

sample preparation. For example, if the equilibration temperature is reduced from 1200 K to 1100 K, the degree of inversion decreases to $x=0.15$. From these results, it can also be expected that the degree of inversion will be higher when the sample is quenched (cooled rapidly) instead of annealed (cooled slowly) after its formation. In the latter case, the slow cooling will allow the equilibration of the cation distribution at lower temperatures. Experimental studies have indeed shown a variation in the electronic and optical properties of CdIn$_2$S$_4$ with the cooling rate after synthesis [133].

We therefore consider the effect that a change of inversion degree has in the electronic properties of the material. The electronic structure was calculated here using the Heyd-Scuseria-Ernzerhof (HSE06) screened hybrid functional, which includes 25% of Hartree-Fock exchange [26], yielding better band gap predictions (although at a higher computational cost) than standard DFT functionals [134]. In fact, recent work has shown that HSE06 gives band structures for Mg/In and Cd/In thiospinels that are very similar to those obtained from more computationally demanding many-body techniques [59]. The calculated values for the direct and indirect band gap are close to, although somewhat lower than, the experimental values measured in samples with degree of inversion $x=0.20$ (2.1-2.4 for indirect and 2.5-2.7 for direct band gap [135]). The effect of inversion on the band gap is found to be quite drastic, with a decrease of almost 1 eV in both the direct and indirect band gaps when $x$ changes from 0 to 0.5 (Fig. ??).

This result means that any small change in the inversion degree, achieved via temperature control during the sample preparation, will be reflected significantly in the electronic and optical properties of the material. The connection between the band gap and the equilibration temperature for the cation distribution is illustrated in the inset of Fig. 5.4. Lower temperatures of formation, or slower cooling rates after sample preparation, should lead to wider band gaps. Therefore our simulations results indicate a possible route to tune the electronic properties of this interesting photovoltaic material.

While there is some controversy as to whether CdIn$_2$S$_4$ gap is direct or indirect, we obtained a range of band-gaps in which the indirect band-gap was smaller than the direct band-gap. Therefore, we conclude that the CdIn$_2$S$_4$ show a indirect band-gap in all the range of inversion degree under which it might be synthesized.
Figure 5.4: Direct and indirect band gaps as a function of inversion degree, from screened hybrid functional calculations. In the inset, the band gaps as a function of the configurational equilibration temperature.

5.2.3 High Pressure Influence in Band-Gap and Lattice Parameters.

The calculations of CdIn$_2$S$_4$ at a high pressure was investigated in order to analyse the behaviour of the inversion degree under these conditions. Our hypothesis was that this might change under these conditions, as was previously investigated for the variation of temperature in our previous work. The inversion degree was obtained under different temperatures and was interpreted through the use of inversion degree energetics. Using high external pressure the conditions under which the inversion degree might change should be somehow similar to that obtained without external stress. We used the same model for the interpretation of
Study of CdIn$_2$S$_4$ inversion-degree, bandgap control.

Figure 5.5: a) Inversion energies as obtained from PBEsol calculations in CdIn$_2$S$_4$ under 3GPa conditions. b) Configurational and c) vibrational contributions to the inversion free energy. d) Total inversion free energy; the vertical line marks the experimental value of the inversion degree.

The theoretical thermodynamic parameters associated with the inversion degree were obtained under 3GPa conditions (Fig. 5.5). In this figure the configurational energy ($\Delta E_{\text{conf}}$), configurational total energy with the entropical term included ($\Delta F_{\text{conf}}$), the vibrational total energy ($\Delta F_{\text{vib}}$) and the total energy ($\Delta F$) associated with the inversion degree are shown.
In these calculations the configurational energy (Fig. 5.5 a)) was slightly higher than that of the calculations held under 0GPa of external pressure, so was the configurational total energy (Fig. 5.5 b)), but in general terms we can consider these values as very similar. In addition, the vibrational total energy calculations of 3GPa results (Fig. 5.5 c)) were far greater than those of 0GPa results. This was expected, the vibration of the lattice increase when a higher tension obligates the structure to be less stabilized. Therefore, the entropical part is more affected and the result is a higher vibrational total energy. Besides, the distance among atoms under 3GPa of pressure is smaller than that considered for the cells calculated without stress.

Finally the total energy (Fig. 5.5 d)) is affected by both the configurational and vibrational total energies. The slightly higher configurational total energy is smaller than the great increase of the vibrational contribution. The result is that the overall total energy is smaller and the system under 3GPa appears as stabilized by the external pressure and more importantly the inversion degree is greatly affected. This result is even more pronounced at higher temperatures due to the synergism of the two factors acting upon the structure: temperature and pressure.

An unsuccessful attempt to obtain these values for a higher external pressure demonstrated that the range under which the inversion degree might appear is narrowed under pressures that are higher than 3GPa. Therefore the calculations greater values of pressures were made using the direct cell only.

The comparison of the theoretical calculations with the experimental results using the electronic band-gap width and also the geometrical volume obtained under different pressures is shown (Fig. 5.6). The experimental geometrical volume [137] was compared with the value we obtained theoretically. The difference between them is very small, and can be considered as a very accurate result. Besides, although we obtained an underestimated value of band-gap using this functional, the relative total energies are considered as good as those that can be obtained with e.g. HSE functional, which is more reliable. The band-gap of CdIn$_2$S$_4$ we also obtained using HSE functional and results were compared with the experimental values. These experimental band-gaps [136] were obtained using a method that depends on the Urbach’tail. These type of methods introduce a range of energies in what the real band-gap is located, yet our theoretical values for the indirect and direct band-gaps at different pressures were located in between this range.

CdIn$_2$S$_4$ spinel have been studied under a range of pressure and results
Study of CdIn$_2$S$_4$ inversion-degree, bandgap control.

Figure 5.6: Theoretical (a) geometrical volume and (b) band-gap obtained in a range of pressure up to 9GPa. The theoretical calculations were compared with experimental results of Refs. [136, 137].
demonstrated that the inversion degree of this structure is not as variable under high external pressure as it is under normal conditions. The thermodynamic parameters associated with the inversion degree were obtained under 3GPa. Higher external pressure demonstrated that the range under which the inversion degree might appear is narrowed under pressures that are higher than this value. The geometrical volumes and also the electronic band-gaps were obtained under a range of pressures. The obtained theoretical volumes were accurately alike the experimental values while the indirect and direct theoretical band-gaps are in between the two extremes found in the experimental Urbach rule.

5.3 Study of MgIn$_2$S$_4$ inversion degree

MgIn$_2$S$_4$ has a band gap within a range of 2.1-2.28 eV. While it is known that the structure has an inversion degree around 0.80 there is needed some further results in order to clarify if the actual band-gap is direct or inverse \[136, 138, 139\]. Therefore, further study is needed. Lattice energy calculations, as well as the experimental observation of different cation distributions in spinels containing ions of similar charge and size have been done \[126\]. In some cases the conclusion lies in the van der waals radius of the cations.

The thermodynamic parameters were obtained for MgIn$_2$S$_4$ as was aforementioned explained. Different from what happens in the CdIn$_2$S$_4$ case, the inversion energies are not positive for the whole range of $x$, and the curvature is strongly negative around 0.84, its experimental value for the inversion degree (Fig. 5.3 (a)). The change of sign around the experimental inversion degree correspond exactly with 0.84. In addition, the whole range of configurational energy is not as wide as was found for CdIn$_2$S$_4$. These two factors demonstrates that the cation exchange in MgIn$_2$S$_4$ is in thermodynamic equilibrium.

5.3.1 Cation Exchange in MgIn$_2$S$_4$

The covalent radii for Mg and In are respectively reported as 141 and 142 pm \[140\] which are almost identical and the equilibrium exchange of these cations in the spinel is really what occurs. As was made in CdIn$_2$S$_4$, we tested the approximation of using only one configuration for the calculation of the energy for each $x > 0$. We calculated the inversion energy for $x=0.75$ by taking the symmetry-adapted
ensemble average of all different cation configurations [33] in a cell doubled along one axis. The result is not in good agreement with our quadratic interpolation based on the primitive cell results, instead we found a very scattered pattern. We realized that the model is not wrong, the particularities of this inverted spinel, which has an equilibrium between its cations, make impossible the adjustment. The configurational and vibrational free energy of inversion were calculated (Fig. 5.7 (b) and (c)). In the vibrational free energy of inversion there is a non-linear adjustment of the data which is different from the results found in CdIn$_2$S$_4$. 

Figure 5.7: a) Inversion energies as obtained from PBEsol calculations in MgIn$_2$S$_4$. b) Configurational and c) vibrational contributions to the inversion free energy. d) Total inversion free energy; the vertical line marks the experimental value of the inversion degree.
Furthermore the form of the data of the configurational free energy is not so different from that of the total free energy to obtain the minima of inversion degree in each case. This demonstrates that the vibrational data might be neglected. The vertical bar that shows the experimental value for the inversion degree (Fig. 5.7 (d)) is near the values found in our calculations, which also agrees that the model is as valid for this spinel as was previously obtained in the CdIn$_2$S$_4$.

5.4 Consequences of inversion degree in the IB materials

The MgIn$_2$S$_4$ and CdIn$_2$S$_4$ thiospinels are potential candidates for intermediate-band materials. Their characteristic band-gaps are in the region of optimum values for a high efficiency intermediate-band material. Several calculations were made using supercells with different inversion degrees of MgIn$_2$S$_4$ and CdIn$_2$S$_4$ doped with V. In order to better obtain a result that is coherent with the actual inversion degree, a doubled primitive cell in which the inversion degree is 0.25 for CdIn$_2$S$_4$ and 0.75 for MgIn$_2$S$_4$ were chosen. The electronic results demonstrated that the intermediate-band remains unaltered even though the inversion degree is changed. This is because, the intermediate-band is composed by V orbital contributions, and all the cases have V atoms bonded to S atoms.
Results II: Zn band-gap modulator in Chalcopyrites with Ti
Chapter 6

Results II- Zn band-gap modulator in Chalcopyrites with Ti

6.1 Chalcopyrites tetragonal structures.

Chalcopyrite materials have the \( A^I B^{III} C^{VI} \) structure. These materials have been widely investigated for many years to be used in photovoltaic solar cells [141–143]. In these materials, among the most important characteristics is that they combine advantages of thin film technology with the efficiency and stability of conventional crystalline silicon cells.

This attractive behavior makes great expectation around future widespread use of solar cell chalcopyrites. Therefore, these materials are included in the proposed semiconductors that are studied as host systems of the intermediate-band materials. Among these compounds CuGaS\(_2\) (Fig. 6.1) has thoroughly been studied. Particularly, in our group we have proposed some transition metal doped CuGaS\(_2\) as intermediate-band materials [14–17, 62]. These earlier works have revealed that the insertion of Ti into a chalcopyrite semiconductor such as CuGaS\(_2\), with a band-gap found experimentally as 2.53 eV depicts a separated intermediate-band.
6.1.1 Ti in CuGaS$_2$

Thermodynamic study for the feasibility of the Ti insertion in CuGaS$_2$ was carried out in a previous work [63]. The results demonstrated that substitution by Cr or Ti at Ga sites in CuGaS$_2$ is energetically unfavorable with respect to phase segregation or decomposition into known, simpler stable compounds. In addition, the study also comprised the contribution of thermal vibrations to the free energy balance which was found to be more significant for Ti than for Cr.

The solubility limits are low at the whole range of temperatures, indicating that preparation methods controlled by kinetics must be used to obtain large dopant concentrations in this metal-substituted chalcopyrite. The limit is lower for Ti than for Cr, which might be related to the respective values of the ionic radii and to the different stability of the trivalent state in these elements. Although these

Figure 6.1: CuGaS$_2$ structure, yellow tetrahedra are around S atoms which exhibit two corners with Ga cations and the other two with Cu cations.
unfavorable perspectives for material preparation could be intuitively anticipated purely on chemical grounds, it is proper to recall that these energies are less unfavorable than that of the substitution of Ga by Mn in GaAs, a process that has been experimentally achieved [13]. Therefore, Ti insertion in CuGaS$_2$ should not be less feasible. The validity of the hypothesis that assumes ideal mixing (random substitution) has been checked with preliminary calculations by evaluating the tendency of Cr and Ti to cluster in this system. This tendency appears to be negligible for Ti but not for Cr, which implies that for medium to large substitution levels the results obtained for the latter element must be corrected by taking this factor into account.

6.1.2 Zn in CuGaS$_2$

Several previous studies have demonstrated that Zn in CuGaS$_2$ exhibits interesting characteristics for photovoltaic applications. Zn in CuGaS$_2$ photoluminescence spectra having the form of (CuGaS$_2$)$_{1-x}$(2ZnS)$_x$ have been experimentally measured [65, 66] where a photoluminescence transition of 2.1-2.3 eV is reported (when $x$ is 0.05-0.0005, respectively). This transition is ascribed to the band-gap of the heavily Zn doped CuGaS$_2$ in the Ga position, showing that there is a dependence of band-gap constriction when Zn concentration increases. Furthermore ZnS has the same D$_2$D$_{12}$ tetragonal space group of CuGaS$_2$ [144]. Nevertheless, even though other doped chalcopyrite synthesis, including Ti doped ones have been reported in literature [145–147] and CuGaS$_2$:Ti formation has also been theoretically predicted, an experimental synthesis of CuGaS$_2$:Ti has not been reported yet. In addition, some of these doped-chalcopyrites using binary sulphides as precursors in thin film chalcopyrite solar cell obtainment [148, 149] can also be found in literature.

6.2 Zn insertion into CuGaS$_2$:Ti

The Zn modulation effect might be seen as well in CuGaS$_2$:Ti where Zn insertion in the intermediate-band material CuGaS$_2$:Ti not only modulates the band-gap value but also the position of the intermediate-band and consequently the sub band-gaps created by the intermediate-band.

In agreement with the scope previously reviewed, which involves chalcopyrite characteristics combined with intermediate-band formation in transition metal
Results II: Zn band-gap modulator in Chalcopyrites with Ti
doped semiconductors and Zn effect into CuGaS$_2$, we present Zn addition effect on Ti doped CuGaS$_2$ intermediate-band systems, and its influence in the modulation of intermediate-band inside doped semiconductors [150]. We have to remark, that there is a necessity to isolate the intermediate-band from the conduction band lower level in systems like Ti doped CuGaS$_2$, to avoid non-radiative recombination.

Ab-initio density functional theory (DFT) calculations were carried out on a representative structure consisting on a supercell derived from the parent body-centered tetragonal CuGaS$_2$ structure. Different dilutions of the proposed dopants inside the host semiconductor were computed. Supercells of different sizes were constructed to achieve the desired proportion inside the semiconductor material. Particularly calculations with 32, 48 and 64 atom cells were carried out and compared. The dilutions proposed were achieved by substituting Ti in a Ga position inside a CuGaS$_2$ supercell. Moreover, further substitution with Zn as dopant was also performed replacing Zn in the Ga position.

Relaxed calculations and subsequent total and projected densities of states (DOS and PDOS) for different dilutions of the two metal dopants were carried out using the DFT VASP code including spin polarization with PAW potentials and the PW91 GGA functional [90, 151–154]. A cut-off energy of 280 eV was applied for the plane-wave expansion and the Brillouin zone was sampled using 8x8x8, 6x6x6 and 8x8x6 Monkhorst-Pack grids respectively for the 32, 48 and 64 atom supercells. In all the densities of states (DOS) figures the Fermi energy level in the x-axis is set up at zero, and in y-axes, majority and minority spin states are positive and negative values respectively. In 32 and 48 atom supercells were used correspondingly 256 and 144 irreducible k points; 96 k points for the Ti in Ga symmetrical positions and 192 irreducible k points using Ti in Ga non-symmetrical positions were observed for the 64 atom supercells. In order to compare subsequent results the same k point grid was taken for the two 64 atom supercells and a comparative visualization of the two structures found after calculations is shown in Fig. 6.2.

We named Ti$_2$Cu$_{16}$Ga$_{14}$S$_{32}$ and ZnTi$_2$Cu$_{16}$Ga$_{13}$S$_{32}$ respectively to the 64 atom supercells with Ti in Ga symmetrical positions, and these with an "*" for those with Ti in Ga non-symmetrical positions. Table 6.1, 6.2 and 6.3 respectively show the Ti doped CuGaS$_2$ atomic distances and the Zn in Ti doped CuGaS$_2$ atomic distances. The comparison shows that Ti-Ti distances have almost the same value in 32 and 48 atom supercells and the Ti-Ti distance value in Ti$_2$Cu$_{16}$Ga$_{14}$S$_{32}$ is greater than the distances in Ti$_2$Cu$_{16}$Ga$_{14}$S$_{32}$*. 
Zn insertion into CuGaS$_2$:Ti

Figure 6.2: 64 atom supercells with Ti (gray) substituted in different Ga (salmon) positions. In figures the atoms are: Zn (blue), Cu (orange), and S (yellow). a) ZnTi$_2$Cu$_{16}$Ga$_{13}$S$_{32}$ and b) ZnTi$_2$Cu$_{16}$Ga$_{13}$S$_{32}$.

Zn is added to the Ti doped CuGaS$_2$ in a way that forms the largest possible Zn-Ti distance, and Ti-Ti initial distances have been equally modelled in the systems with and without Zn doping. Besides, Zn-Ti distances are equal for the 32 and 48 atom supercells, and greater than those of 64 atom supercells. Also Zn-Zn distances are almost equivalent for the 32 and 64 atom supercells and different from the one with 48 atoms. Further discussion of the obtained distances after relaxing is presented in Table 6.2 and 6.3.

The structure of the CuGaS$_2$ host semiconductor was studied to compare with the further inclusion of the Zn and Ti dopants. The bond distances Ga-S and Cu-S mean values in CuGaS$_2$ were respectively found, after relaxation, to be 2.33 and 2.31 Å. These values are consistent with previously found experimental and
Table 6.1: Bond lengths in Ti doped CuGaS$_2$ structures for different dilutions found after relaxation (in Å).

<table>
<thead>
<tr>
<th></th>
<th>Ti-Ti</th>
<th>Ti-S</th>
<th>Ga-S$_{\text{min}}$</th>
<th>Ga-S$_{\text{max}}$</th>
<th>Cu-S$_{\text{min}}$</th>
<th>Cu-S$_{\text{max}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti$<em>2$Cu$</em>{16}$Ga$<em>{14}$S$</em>{32}$</td>
<td>7.58</td>
<td>2.35</td>
<td>2.32</td>
<td>2.33</td>
<td>2.3</td>
<td>2.32</td>
</tr>
<tr>
<td>Ti$<em>2$Cu$</em>{16}$Ga$<em>{14}$S$</em>{32}$</td>
<td>5.35</td>
<td>2.35</td>
<td>2.32</td>
<td>2.33</td>
<td>2.3</td>
<td>2.32</td>
</tr>
<tr>
<td>Ti$<em>2$Cu$</em>{12}$Ga$<em>{10}$S$</em>{24}$</td>
<td>6.56</td>
<td>2.35</td>
<td>2.31</td>
<td>2.34</td>
<td>2.29</td>
<td>2.32</td>
</tr>
<tr>
<td>Ti$<em>3$Cu$</em>{12}$Ga$<em>9$S$</em>{24}$</td>
<td>6.56</td>
<td>2.35</td>
<td>2.32</td>
<td>2.34</td>
<td>2.3</td>
<td>2.33</td>
</tr>
<tr>
<td>Ti$_2$Cu$_8$Ga$<em>6$S$</em>{16}$</td>
<td>6.57</td>
<td>2.35</td>
<td>2.32</td>
<td>2.34</td>
<td>2.3</td>
<td>2.32</td>
</tr>
</tbody>
</table>

Table 6.2: Bond lengths in Zn and Ti doped CuGaS$_2$ structures for different dilutions found after relaxation (in Å).

<table>
<thead>
<tr>
<th></th>
<th>Ti-Zn</th>
<th>Zn-Zn</th>
<th>Ti-Ti</th>
<th>Zn-S</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnTi$<em>2$Cu$</em>{16}$Ga$<em>{13}$S$</em>{32}$</td>
<td>6.53</td>
<td>7.58</td>
<td>7.58</td>
<td>2.34</td>
</tr>
<tr>
<td>ZnTi$<em>2$Cu$</em>{16}$Ga$<em>{13}$S$</em>{32}$</td>
<td>6.56</td>
<td>7.58</td>
<td>5.36</td>
<td>2.34</td>
</tr>
<tr>
<td>ZnTi$<em>2$Cu$</em>{12}$Ga$<em>9$S$</em>{24}$</td>
<td>5.32</td>
<td>10.7</td>
<td>6.53</td>
<td>2.34</td>
</tr>
<tr>
<td>ZnTi$<em>3$Cu$</em>{12}$Ga$<em>8$S$</em>{24}$</td>
<td>5.34</td>
<td>10.71</td>
<td>6.48</td>
<td>2.34</td>
</tr>
<tr>
<td>ZnTi$_2$Cu$_8$Ga$<em>5$S$</em>{16}$</td>
<td>5.34</td>
<td>7.55</td>
<td>6.58</td>
<td>2.31</td>
</tr>
</tbody>
</table>

Theoretical values [144, 155]. Table 6.1 shows comparison of Ga-S and Cu-S minimal and maximal distances found after relaxation in Ti doped compounds. No great differences are found when metal dilution changes. Also, the minimal and maximal values for each bond length have no significant difference between them. Tables 6.2 and 6.3 shows distances for the Zn and Ti doped CuGaS$_2$ structures. In this system, Ti-S, Cu-S and Ga-S bond length values have broader distribution than those found in Ti doped CuGaS$_2$, shown in Table 1. The minimal Cu-S and Ga-S bond length values were found for the nearest neighbors of Zn atoms. Each bond length distribution in studied cells was found similar excluding 32 atom supercells where Zn and Ti atoms are substituting Ga position. It is important to point out that
Table 6.3: Distorted Bond lengths, minimum and maximum values in Ti and Zn doped CuGaS$_2$ for different dilutions found after relaxation (in Å).

<table>
<thead>
<tr>
<th></th>
<th>Ti-S$_{\text{min}}$</th>
<th>Ti-S$_{\text{max}}$</th>
<th>Ga-S$_{\text{min}}$</th>
<th>Ga-S$_{\text{max}}$</th>
<th>Cu-S$_{\text{min}}$</th>
<th>Cu-S$_{\text{max}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnTi$<em>2$Cu$</em>{16}$Ga$<em>{13}$S$</em>{32}$</td>
<td>2.32</td>
<td>2.35</td>
<td>2.27</td>
<td>2.36</td>
<td>2.28</td>
<td>2.33</td>
</tr>
<tr>
<td>ZnTi$<em>2$Cu$</em>{16}$Ga$<em>{13}$S$</em>{32}$*</td>
<td>2.32</td>
<td>2.34</td>
<td>2.27</td>
<td>2.37</td>
<td>2.28</td>
<td>2.33</td>
</tr>
<tr>
<td>ZnTi$<em>2$Cu$</em>{12}$Ga$<em>9$S$</em>{24}$</td>
<td>2.33</td>
<td>2.35</td>
<td>2.28</td>
<td>2.35</td>
<td>2.28</td>
<td>2.33</td>
</tr>
<tr>
<td>ZnTi$<em>3$Cu$</em>{12}$Ga$<em>8$S$</em>{24}$</td>
<td>2.33</td>
<td>2.35</td>
<td>2.28</td>
<td>2.36</td>
<td>2.29</td>
<td>2.34</td>
</tr>
<tr>
<td>ZnTi$_2$Cu$_8$Ga$<em>5$S$</em>{16}$</td>
<td>2.35</td>
<td>2.36</td>
<td>2.30</td>
<td>2.33</td>
<td>2.31</td>
<td>2.33</td>
</tr>
</tbody>
</table>

There are 8 total Ga atom positions and three of them are substituted by two Ti and one Zn which is a high doped proportion.

The obtained DFT values for CuGaS$_2$ and ZnS band-gaps respectively are 0.91 eV and 2.18 eV demonstrating the consistency with chalcopyrite anomaly, due to the notable reduction on the CuGaS$_2$ band-gap compared with ZnS band-gap, which has the same symmetry. Besides, the obtained band-gap value of Zn doped CuGaS$_2$ is 0.51 eV which is a significant band-gap reduction for this system. This is consistent with a previous report of Zn in CuGaS$_2$ in the form of (CuGaS$_2$)$_{1-x}$(2ZnS)$_x$ where the band-gap reduction is in a range of 0.23-0.43 eV related to the semiconductor band-gap. In this work, a band-gap shortening of 0.35 eV was obtained when 0.25% of Zn is added to the CuGaS$_2$ in a form of ZnCu$_8$Ga$_7$S$_{16}$.

Ti doped CuGaS$_2$ structures have been found highly spin polarized in all cases in agreement with previous works. The intermediate-band was also found, as is shown in Fig 6.3 a) and Fig 6.3 b), 6.25% concentration of Ti doped CuGaS$_2$ for the two different symmetries. These energy levels are potentially an intermediate-band, even though a small density of states still appears between the upper intermediate-band level and the lower level of the conduction band.

One extra electron per Ti in the primitive unit cell in all Ti doped structures was also found, demonstrating that Ti in the structure is in an oxidation state of Ti$^{3+}$ and has an excess carrier of one electron per Ti substituted in the whole system. However, when Zn is added to Ti doped CuGaS$_2$, the unpaired spin disappears due
Figure 6.3: DOS and PDOS for a) 6.25% Ti doped CuGaS$_2$ and b) 3.13% Zn in 6.25% Ti doped CuGaS$_2$ with Ti in Ga symmetrical positions.

to the expected Zn$^{2+}$ oxidation state involved. Tables 6.4, 6.5 show the energy differences obtained in the DOS calculations for the intermediate-band of Ti doped CuGaS$_2$, and Zn in Ti doped CuGaS$_2$ for the equivalent structures, respectively. The obtained intermediate-band width is also shown in Tables 6.4 and 6.6. In these tables, $\epsilon_C - \epsilon_V$ is the value of the corresponding band-gap calculated using the spin down levels, $\epsilon_C - \epsilon_{IBU}$ the energy difference between the conduction band lower level and the intermediate-band upper level and $\epsilon_{IBB} - \epsilon_V$ is the energy difference between the intermediate-band lower level and the valence band upper level. The last two energy differences were computed using the spin up levels. IBwidth corresponds to the intermediate-band width. We can infer from the comparison of the equivalent Zn in Ti doped CuGaS$_2$ and Ti doped CuGaS$_2$ structure results, that when Zn is added in high proportion further isolation of the intermediate-band occurs. In
Zn insertion into CuGaS$_2$:Ti

Figure 6.4: DOS and PDOS for a) 6.25% Ti doped CuGaS$_2$ and b) 3.13% Zn in 6.25% Ti doped CuGaS$_2$ with Ti in Ga non-symmetrical positions.

Table 6.4, we can also compare the obtained band-gap value of different Ti doped CuGaS$_2$ structures with the computed CuGaS$_2$ band-gap of $\varepsilon_C - \varepsilon_V = 0.91$ eV calculated in a similar way. This comparison leads to the conclusion that, when Ti is added to the semiconductor, all obtained band-gaps have a characteristic broadening. Therefore, when Zn is added to the already Ti doped CuGaS$_2$ chalcopyrite a band-gap reduction, showing the modulation effect of Zn, in Ti doped CuGaS$_2$ band-gap is observed.

As we can deduce from Table 6.4, for the same Ti/Zn ratio in the compounds and excluding the ZnTi$_2$Cu$_{16}$Ga$_{13}$S$_{32}$* structure, when the Zn proportion increases an increase of the $\varepsilon_C - \varepsilon_{IBU}$ width, a slight reduction in $\varepsilon_{IBB} - \varepsilon_V$ and a broadening of intermediate-band are shown. If the Zn proportion increases from 3.3% to 4.17% we can see an increment in $\varepsilon_C - \varepsilon_V$ but, when the Zn proportion increases from 4.17% to 6.25% the band-gap is reduced by 0.12 eV.
Results II: Zn band-gap modulator in Chalcopyrites with Ti

Table 6.4: Energy level differences (in eV) in Ti doped CuGaS$_2$ structures for different dilutions. Symbols are explained in the text.

<table>
<thead>
<tr>
<th>%Ti</th>
<th>$\varepsilon_{C}-\varepsilon_{V}$</th>
<th>$\varepsilon_{IBB}-\varepsilon_{V}$</th>
<th>IBwidth</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti$<em>2$Cu$</em>{16}$Ga$<em>{14}$S$</em>{32}$</td>
<td>6.25</td>
<td>1.05</td>
<td>0.8</td>
</tr>
<tr>
<td>Ti$<em>2$Cu$</em>{16}$Ga$<em>{14}$S$</em>{32}^*$</td>
<td>6.25</td>
<td>0.99</td>
<td>0.605</td>
</tr>
<tr>
<td>Ti$<em>2$Cu$</em>{12}$Ga$<em>{10}$S$</em>{24}$</td>
<td>8.3</td>
<td>1.1</td>
<td>0.77</td>
</tr>
<tr>
<td>Ti$<em>3$Cu$</em>{12}$Ga$<em>9$S$</em>{24}$</td>
<td>12.5</td>
<td>1.16</td>
<td>0.775</td>
</tr>
<tr>
<td>Ti$_2$Cu$_8$Ga$<em>6$S$</em>{16}$</td>
<td>12.5</td>
<td>1.18</td>
<td>0.775</td>
</tr>
</tbody>
</table>

Table 6.5: Energy level differences (in eV) in Zn and Ti doped CuGaS$_2$ structures for different dilutions. Symbols are explained in the text.

<table>
<thead>
<tr>
<th>Ratio</th>
<th>Zn/Ti</th>
<th>%Ti</th>
<th>%Zn</th>
<th>$\varepsilon_{C}-\varepsilon_{IBU}$</th>
<th>$\varepsilon_{IBB}-\varepsilon_{V}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnTi$<em>2$Cu$</em>{16}$Ga$<em>{13}$S$</em>{32}$</td>
<td>0.5</td>
<td>6.3</td>
<td>3.13</td>
<td>0.79</td>
<td>0.045</td>
</tr>
<tr>
<td>ZnTi$<em>2$Cu$</em>{16}$Ga$<em>{13}$S$</em>{32}^*$</td>
<td>0.5</td>
<td>6.3</td>
<td>3.13</td>
<td>0.49</td>
<td>0.125</td>
</tr>
<tr>
<td>ZnTi$<em>2$Cu$</em>{12}$Ga$<em>9$S$</em>{24}$</td>
<td>0.5</td>
<td>8.3</td>
<td>4.17</td>
<td>0.90</td>
<td>0.060</td>
</tr>
<tr>
<td>ZnTi$<em>3$Cu$</em>{12}$Ga$<em>8$S$</em>{24}$</td>
<td>0.3</td>
<td>12.5</td>
<td>4.17</td>
<td>0.94</td>
<td>0.120</td>
</tr>
<tr>
<td>ZnTi$_2$Cu$_8$Ga$<em>5$S$</em>{16}$</td>
<td>0.5</td>
<td>12.5</td>
<td>6.25</td>
<td>0.82</td>
<td>0.115</td>
</tr>
</tbody>
</table>

The resulting DOS of Zn in Ti doped CuGaS$_2$ is depicted in Fig. 6.5 for 32 and 48 atom supercells. As it was demonstrated in the aforementioned tables, these systems show a displacement of the intermediate-band to energies away from the conduction band level and keeping the same intermediate-band width. This fact can be explained as the Zn energy levels in the formed materials are interacting directly in these intermediate-band. Although the intermediate-band is mainly constituted of Ti atomic $e_g$ orbitals, a slight proportion of Zn projected DOS appears contributing also in the intermediate-band features of each dilution.

Variation of the substituent positions implies a variation of the band-gap and variation in the intermediate-band features. This is shown for ZnTi$_2$Cu$_{16}$Ga$_{13}$S$_{32}$
Thermodynamic of Zn insertion into CuGaS$_2$:Ti

Table 6.6: Width of the intermediate-band in CuGaS$_2$:Ti:Zn (IBwidth).

<table>
<thead>
<tr>
<th>IBwidth (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnTi$<em>2$Cu$</em>{16}$Ga$<em>{13}$S$</em>{32}$</td>
</tr>
<tr>
<td>ZnTi$<em>2$Cu$</em>{16}$Ga$<em>{13}$S$</em>{32}$*</td>
</tr>
<tr>
<td>ZnTi$<em>2$Cu$</em>{12}$Ga$<em>9$S$</em>{24}$</td>
</tr>
<tr>
<td>ZnTi$<em>3$Cu$</em>{12}$Ga$<em>8$S$</em>{24}$</td>
</tr>
<tr>
<td>ZnTi$_2$Cu$_8$Ga$<em>5$S$</em>{16}$</td>
</tr>
</tbody>
</table>

and ZnTi$_2$Cu$_{16}$Ga$_{13}$S$_{32}$* in Fig. 6.3 and 6.4, where a comparison between both compounds shows a wider intermediate-band and also a wider difference $\varepsilon_C - \varepsilon_{IBU}$ for ZnTi$_2$Cu$_{16}$Ga$_{13}$S$_{32}$*. Furthermore $\varepsilon_{IBB} - \varepsilon_V$ energy difference in Ti$_2$Cu$_{16}$Ga$_{14}$S$_{32}$* and ZnTi$_2$Cu$_{16}$Ga$_{13}$S$_{32}$* has been found shorter than $\varepsilon_{IBB} - \varepsilon_V$ energy difference in the other calculated dilution. Moreover, greatly symmetric intermediate-band peaks have been found, which can be related with the shorter Ti-Ti distance involved. Nevertheless, total energies of Ti$_2$Cu$_{16}$Ga$_{14}$S$_{32}$* and ZnTi$_2$Cu$_{16}$Ga$_{13}$S$_{32}$* have been found smaller than the corresponding total energies in Ti$_2$Cu$_{16}$Ga$_{14}$S$_{32}$* and ZnTi$_2$Cu$_{16}$Ga$_{13}$S$_{32}$*.

6.3 Thermodynamic of Zn insertion into CuGaS$_2$:Ti

We intend to predict using the energetics of several reaction schemes whether Zn in CuGaS$_2$:Ti is termodinamically stable. Modelled supercells were made using 32 atoms in which Zn and Ti atom substitute Ga atom positions and starting with CuGaS$_2$ experimental parameters.

The constructed structures were relaxed in both atomic coordinates and lattice dimensions using density functional theory (DFT) with GGA PW91 functional [90] implemented in VASP program [151, 152], where the presence of spin polarization was also considered. Atomic core regions of the electronic structure in the periodic systems were represented with PAW potentials [154, 156]. The cut-off energy used, 374 eV, was high enough to evaluate the convergence of each of the studied materials, and the reciprocal space was sampled according to a dense Monkhorst-Pack grid increased until total energy difference was less than 1
meV. After relaxation the calculations were taken as a starting point to obtain energy minimization using tetrahedron method. The k-point values were also increased to confirm that convergence was achieved.

The straightforward way of assessing the compound stability is to compare its energy with that of a sum of simpler known compounds in which it could possibly decompose. Besides it is well known that the type of crystalline structure could have an influence on the reaction dynamics. According to this a combination of ZnS, Cu$_2$S, TiS$_2$ and CuGaS$_2$ the first CuGaS$_2$:Ti:Zn decomposition reaction
scheme proposed might be found favorable. The compound total energy gives a negative energy difference of $\text{ZnTi}_2\text{Cu}_8\text{Ga}_5\text{S}_{16}$ decomposition (Table 6.7). This negative energy difference, $\Delta E$, means that $\text{CuGaS}_2$:Ti:Zn compound decomposition is predicted favorably.

Different Ti-Ti and Ti-Zn distances and the same Zn-Zn distance, 7.53 Å were modelled in the 32 atom supercells (Fig. 6.6) to compare the influence of substituent distances in total energy difference of reaction 6.2. In these supercells the substituent distances were taken as is shown in Table 1.

The total energy in supercell A was 0.013 eV lower than the value found in supercell B. This means that the largest possible Ti-Ti distance gives a more stable compound formation but in decomposition processes the smallest Ti-Ti distance is preferred. In the following $\Delta E$ values will refer to the most stable supercell A.

Figure 6.6: Structure of CuGaS$_2$ (32 atoms) doped with Ti and Zn
Table 6.7: Substituent distances in two ZnTi$_2$Cu$_8$Ga$_5$S$_{16}$ supercells in Å, and corresponding $\Delta E$ of equation 6.1 in eV.

<table>
<thead>
<tr>
<th></th>
<th>Zn-Ti</th>
<th>Ti-Ti</th>
<th>$\Delta E$</th>
</tr>
</thead>
<tbody>
<tr>
<td>supercell A</td>
<td>5.3</td>
<td>6.6</td>
<td>-0.43</td>
</tr>
<tr>
<td>supercell B</td>
<td>6.6</td>
<td>5.3</td>
<td>-0.44</td>
</tr>
</tbody>
</table>

6.3.1 Two decomposition schemes using non-binary sulfides.

We may also consider decomposition schemes using more complex compounds, such as Cu$_{2/3}$TiS$_2$ suggested in our previous study of Ti insertion in CuGaS$_2$ [63] and others like Cu$_4$TiS$_4$ [157] or ZnGa$_2$S$_4$ [158] which are tetragonal chalcogenides as CuGaS$_2$.

As an example of a decomposition path of reaction using the aforementioned compounds, we calculated the following reaction scheme,

$$ZnTi_2Cu_8Ga_5S_{16} \rightarrow 3CuGaS_2 + ZnGa_2S_4 + 1/3Cu + Cu_{2/3}TiS_2 + Cu_4TiS_4$$ (6.1)

For the energy balance of reaction 6.1 the DFT calculations give $\Delta E = -0.87$ eV, confirming that $(Zn,Ti_{1-y})_xCa_{1-x}S_2$ compounds are metastable and only exist under kinetically controlled conditions.

Another possible decomposition scheme has also been analyzed,

$$ZnTi_2Cu_8Ga_5S_{16} \rightarrow 5CuGaS_2 + ZnS + (3/2)Cu_{2/3}TiS_2 + (1/2)Cu_4TiS_4$$ (6.2)

and the result of the calculation shows that this is even more spontaneous than the two previous ones: $\Delta E = -1.30$ eV.

However this energy difference is negative as that previously found for the
Thermodynamic of Zn insertion into CuGaS$_2$:Ti

Figure 6.7: Thermodynamic parameters of reaction equation 6.1 a) $\Delta F_{\text{configurational}}$ at different $x$ dilutions of Zn and Ti atoms substituting Ga atoms. b) $\Delta F_{\text{configurational}}$ at different temperatures $T$.

CuGaS$_2$:Ti decomposition [63]. This $\Delta E$ is also negative as that found for decomposition of intermediate-band material such as In$_2$S$_3$:V [159], -0.58eV / per V atom, or for a doped semiconductor such as Mn substituting Ga in GaAs [13], and these two systems have been successfully synthesized [19, 160]. Nevertheless, we have to point out that, even though the reaction schemes proposed in this work could constitute viable decomposition paths of CuGaS$_2$:Ti:Zn systems, other proposed reactions might make decomposition energy balances less negative,
Results II: Zn band-gap modulator in Chalcopyrites with Ti

Figure 6.8: Thermodynamic parameters of reaction equation 6.2 a) $\Delta F_{\text{configurational}}$ at different x dilutions of Zn and Ti atoms substituting Ga atoms. b) $\Delta F_{\text{configurational}}$ at different temperatures T.

i.e. more favorable. The present results can be taken therefore as a lower limit for free energy balances.
6.3.2 Configurational entropy contribution to the free energy balance, of disordered compounds.

We know that Cu\(_{2/3}\)TiS\(_2\), a disordered compound, and the structure of Zn- and Ti-substituted material (which if synthesized should also be disordered), would introduce configurational entropy to the whole system. In order to show the possible effects on thermodynamical stability, we calculated the configurational entropy contribution following the standard equation,

\[
S = -k[x_1 \ln(x_1) + (1 - x_1) \ln(1 - x_1)]
\]  

(6.3)

This configurational entropy formula can be applied due to the presence of a disordered Cu atom located in interstitial positions of Cu\(_{2/3}\)TiS\(_2\) and in this case the \(x_1\) value corresponds to \(x_1 = 2/3\). On the other hand in \((Zn_{y}Ti_{1-y})_{x}CuGa_{1-x}S_{2}\), random Ga positions are occupied by Zn and Ti atom substituents and as a result of this argument the configurational entropy has a more complex equation,

![Graph](image_url)

Figure 6.9: \(\Delta F_{total}\) of equation 6.2 at different x dilutions.
\[ S = -k\{[x\ln(x) + (1-x)\ln(1-x)] + x[y\ln(y) + (1-y)\ln(1-y)]\} \] (6.4)

In this equation the complexity of evaluating configurational entropy includes not only the effect of substituents localized in random Ga positions but also a competition between Zn and Ti atoms to occupy a minimal energy Ga site. In agreement with these two factors and regarding \((\text{Zn}_y\text{Ti}_{1-y})_x\text{CuGa}_{1-x}\text{S}_2\) stoichiometry in equation 6.4 we evaluated \(x = 3/8\), and \(y = 1/3\) of the total random positions in these systems.

The Helmholtz free energy, \(\Delta F\), calculation results of equation 6.1 in Fig 6.7 a) shows the configurational entropy contribution to the free energy when the temperature increases and in fig. 6.7 b) the configurational free energy, \(\Delta F_{\text{configurational}}\) when \(x\) concentration of Zn and Ti atoms located at random positions rises is shown.

Fig. 6.8 shows these results for equation 6.2 in which the configurational entropy contribution is smaller than that corresponding to equation 6.1.

This leads us to infer that \(\Delta F_{\text{configurational}}\) contribution reduces instability in the whole system of interest when the temperature increases and also using low Ti and Zn concentrations. As was previously found for a CuGaS\(_2\):Ti formation [63] vibrational entropy might also be involved here as another factor that contributes to instability reduction but this factor is likely to be negligible in total free energy calculations. The resulting total free energy of equation 6.2, \(\Delta F_{\text{total}}\) (Fig 6.9) which is the more negative one of the two proposed reaction scheme having disordered Cu\(_{2/3}\)TiS\(_2\) shows that \((\text{Zn}_y\text{Ti}_{1-y})_x\text{CuGa}_{1-x}\text{S}_2\) compounds are unstable even at high temperatures.

In summary, we presented first principle calculations of Zn insertion effect in Ti:CuGaS\(_2\) intermediate-band materials. In agreement with previous experimental findings our results confirm than Zn reduces the host CuGaS\(_2\) band-gap. Densities of states of different dilutions of Zn in Ti doped CuGaS\(_2\) have been studied and discussed. The Zn substitution in Ti doped CuGaS\(_2\) produces a distortion of the formed cell bond lengths, leading to changes in the densities of states inside the doped semiconductor.

Moreover, we found that Zn modulates energies around the band-gap vicinity. In particular, the modulation effect consists in a separation of the intermediate-band
Thermodynamic of Zn insertion into CuGaS$_2$:Ti

from the conduction band lower level, forming an isolated band structure. For a given Ti% and raising Zn concentration, results show approximately the same energy difference except for the $\epsilon_C - \epsilon_{IBU}$ value that shows a significant increase, caused mainly by Zn addition. This argument is also supported when we compare equal Ti doped CuGaS$_2$ structures with and without Zn doping. These statements show the Zn modulation effect in Ti doped CuGaS$_2$ and make the resulting Zn and Ti doped structures good materials to be proposed as intermediate-band solar cells.

On the other hand, the thermodynamic analysis through different proposals of spontaneous $(Zn_y Ti_{1-y})_x CuGa_{1-x}S_2$ system decomposition analysed were considered. We observed that the reaction scheme of binary sulphides gives the least negative $\Delta E$ value of all the studied reaction. We can conclude that the decomposition scheme via non-binary sulphides is a spontaneous process even at high temperatures and at low Zn and Ti concentrations. However, the energy of reaction, considered per substituent atom is smaller than that found for previous predicted intermediate-band materials which have also been synthesized. The results presented in this work show that it is thermodynamically unfavorable to obtain the Zn and Ti substituted CuGaS$_2$ but this does not exclude that the material may be obtained using kinetically controlled methods. In addition, the wide intermediate band obtained is not suitable for an intermediate band material.
Results III: Layered Materials: \( \text{SnS}_2 \) and \( \text{SnS}_2:V \)
Chapter 7

Results III-Layered Materials: SnS$_2$ and SnS$_2$:V

7.1 Layered SnS$_2$: 2H and 4H structures

The SnS$_2$ presents a CdI$_2$ layered type structure, and also has polytypism [67, 161] in which the perpendicular stacking of the layers is different in each polytype. In this hexagonal unit cell, the positions of Sn atoms are (000) while S are in (0.33, 0.67, $u$) and (0.67, 0.33, -$u$) positions, with $u$=0.25 [162]. Intra-layer bonds are rather strong due to the covalent nature within, thus the \textit{van der Waals} (vdW) interaction among the layers is weaker than that of the intra-layer bonds. Nevertheless, despite the fact that vdw interactions are weak the correction of these forces in the DFT calculation is very important for reliable results. This phenomenon of vdw interaction in between layers, allows a deformation of the structure by using a slightly strong force [68, 163–165] which can be translated as a phase equilibrium named polytypism. It is reported that the 2H polytype is the most stable when the synthesis occurs at low temperature, 18R at medium temperature and 4H when the synthesis temperature is above 800°C [69, 166].
These 2H and 4H polytypes respectively crystallize in hexagonal P-3m1 and P63mc space group and the structures are depicted in Fig. 7.1.

Figure 7.1: 2x2x2 expansion of the primitive unit cell of 2H and 4H symmetry in SnS$_2$ polytypes. Interlayer distance ($d$) can be observed in the 2H case.

Low cost and easy synthesis routes in SnS$_2$ [167] make the possibility of using this material in different applications among which there is the use of SnS$_2$ as a photovoltaic material [168–170] and in this area, recently SnS$_2$ doped with V had been proposed as an intermediate-band material for solar cells [18]. The 2H and 4H SnS$_2$ polytypes are theoretically studied and compared using DFT with and without the inclusion of a vdW dispersion correction in the calculations.
Layered SnS$\textsubscript{2}$: $2H$ and $4H$ structures

The need of this term will be demonstrated with geometric and electronic structure results. DFT VASP code calculations with PAW potentials [154, 156] and PBE-GGA functional [89] using a 8x8x6 Monkhorst-Pack grid of k points, including volume relaxation were made for the SnS$\textsubscript{2}$ polytypes. Band and projected band calculations were made using the high symmetry k point that corresponds to each polytype. The cut-off energy used, 360 eV, was high enough to evaluate the convergence of each of the studied materials. The small energy difference to consider convergence was $\pm 1 \cdot 10^{-3} eV$ and the energy difference to achieve the lowest energy in the system was $\pm 1 \cdot 10^{-7} eV$. Further HSE06 calculations without additional relaxation [26, 96, 97] were held to obtain SnS$\textsubscript{2}$ 2H and 4H accurate band-gaps.

Grimme empirical dispersion correction [27, 101–103] was made using identical $s_6 = 0.75$ parametrization in both the methods PBE and HSE. The used cells in each case correspond with the unit cell of each structure, taking into account the experimental parameters.

The results obtained were corroborated using different sized supercells up to hundred of atoms. We can observe in Fig. 7.1 that the stacking of the layers appears along the c parameter of the cells. Furthermore, 2H and 4H polytypes are identical except for the displacement of the second layer in the latter. The interlayer distance is the same in the two cases, and the reported experimental value is 5.86 Å.

The band diagrams of SnS$\textsubscript{2}$ 2H and 4H polytypes are shown in Fig. 7.2. The projections of the atomic orbitals are depicted: Sn and S s-orbital in green and Sn and S p-orbitals in dark blue. The band dispersion in the 4H compared with that of the 2H polytype is split into two which is a result of the displacement of the half-bond of the second layer respecting the first. Furthermore, a complete comparison of these band diagrams was made by Powell et al [171]. These results obtained with Grimme’s dispersion correction are comparable with the reported in literature [162, 171, 172]

### 7.1.1 Different methods for the van der Waals interactions.

After geometric and electronic convergence of all supercell structures, the resulting geometric $a$ and $c$ lattice parameters within the two SnS$\textsubscript{2}$ polytypes studied, 2H and 4H and using DFT method with and without vdW dispersion correction, can be seen
Figure 7.2: Band diagram SnS$_2$ 2H and 4H polytypes with projections of orbitals in the PAW spheres inside each band.

We can observe that the best fit of the geometry corresponds with the cases that

in Table 7.1.
Layered SnS$_2$: 2H and 4H structures

Table 7.1: Lattice parameters of SnS$_2$ 2H and 4H using different methods.

<table>
<thead>
<tr>
<th></th>
<th>a(Å)</th>
<th>c(Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>EXP [163]</td>
<td>3.64</td>
<td>11.80</td>
</tr>
<tr>
<td>2H (PBE)</td>
<td>3.70</td>
<td>13.33</td>
</tr>
<tr>
<td>2H (PBE+D2)</td>
<td>3.69</td>
<td>11.78</td>
</tr>
<tr>
<td>4H (PBE)</td>
<td>3.70</td>
<td>13.38</td>
</tr>
<tr>
<td>4H (PBE+D2)</td>
<td>3.69</td>
<td>11.78</td>
</tr>
</tbody>
</table>

include vdW dispersion correction, comparing with the experimental values [163]. The calculations without taking into account the vdW interactions have an increased \(c\) lattice parameter as a result of the dismissed weak vdW interaction between the layers, due to the fact that no chemical bonds are attached to the layers. Furthermore, the lattice parameter perpendicular to the stacking direction is quite well reproduced in GGA calculations.

The evolution of lattice parameters in the calculations through relaxation can be clearly seen in Fig. 7.3. These demonstrate that GGA (without using dispersion corrections) gives a volume expansion for the \(c\) lattice parameter and the resulting interaction between the layers is a repulsion. This tendency is corrected using Grimme empirical method after each auto-consistent cycle. For the \(a\) parameter direction we do not have predominant dispersion forces, so both approaches give a similar result. The good agreement found between experimental and computed \(c\) parameters when Grimme’s correction is introduced means that the possible inadequacy [159] of applying to a strongly polar or ionic compound (as is the case here) of the original Grimme’s parameters, which are appropriate for neutral atoms, is not a problem in the present case [173].

We also have obtained the band diagrams of the two polytypes using GGA (PBE) and GGA with dispersion correction (PBE+D2). The effect of the Grimme dispersion correction in the band dispersion is only related with a decreased energy of each band relative to the upper edge of the valence band VB, but the shape of the dispersion remains similar. Furthermore after the geometry optimization with PBE and PBE+D2, the HSE update of the density matrix was obtained and included also the dispersion correction HSE+D2.
Figure 7.3: Evolution of lattice parameters $a$, $c$ through relaxation calculations.

Table 7.2: Indirect energy gap ($E_{g,\text{ind}}$) in SnS$_2$ 2H and 4H polytypes in PBE respectively calculated from $\Gamma$-L and $\Gamma$-M transition for 2H and 4H.

<table>
<thead>
<tr>
<th>SnS$_2$</th>
<th>Method</th>
<th>$E_{g,\text{ind}}$ PBE (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2H</td>
<td>DFT</td>
<td>1.50</td>
</tr>
<tr>
<td></td>
<td>DFT+$D^2$Grimme</td>
<td>1.32</td>
</tr>
<tr>
<td>4H</td>
<td>DFT</td>
<td>1.30</td>
</tr>
<tr>
<td></td>
<td>DFT+$D^2$Grimme</td>
<td>1.05</td>
</tr>
</tbody>
</table>
Figure 7.4: Band diagrams of SnS$_2$ 2H and 4H polytypes, with and without dispersion correction. Comparison of PBE and HSE method results.

As can be expected HSE corrects the PBE band-gap. The effect of vdW correction in HSE calculations is similar to what happens in PBE calculations. We found a
Table 7.3: Indirect energy gap ($E_{g,\text{ind}}$) in SnS$_2$ 2H and 4H polytypes in HSE respectively calculated from $\Gamma$-L and $\Gamma$-M transition for 2H and 4H (experimental value in parentheses).

<table>
<thead>
<tr>
<th>SnS$_2$</th>
<th>Method</th>
<th>$E_{g,\text{ind}}$ HSE (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2H</td>
<td>DFT</td>
<td>2.37(2.18 [174])</td>
</tr>
<tr>
<td></td>
<td>DFT+D$_{2\text{Grimme}}$</td>
<td>2.20(2.18)</td>
</tr>
<tr>
<td>4H</td>
<td>DFT</td>
<td>2.28(1.89 [174])</td>
</tr>
<tr>
<td></td>
<td>DFT+D$_{2\text{Grimme}}$</td>
<td>1.97(1.89)</td>
</tr>
</tbody>
</table>

Table 7.4: Direct energy gap ($E_{g,\text{dir}}$) in SnS$_2$ 2H and 4H polytypes in HSE.

<table>
<thead>
<tr>
<th>SnS$_2$</th>
<th>Method</th>
<th>$E_{g,\text{dir}}$ HSE (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2H</td>
<td>DFT</td>
<td>3.17(2.56 [175])</td>
</tr>
<tr>
<td></td>
<td>DFT+D$_{2\text{Grimme}}$</td>
<td>2.80(2.56)</td>
</tr>
<tr>
<td>4H</td>
<td>DFT</td>
<td>3.04(2.43 [175])</td>
</tr>
<tr>
<td></td>
<td>DFT+D$_{2\text{Grimme}}$</td>
<td>2.73(2.43)</td>
</tr>
</tbody>
</table>

decrease in band energies and the shape of the bands remains the same. This results can be seen in Fig. 7.4. An interesting observation relates to the dispersion curves in the segment between the $\Gamma$ point and point A, which is the direction perpendicular to the layers. In this segment the bands are not flat (as would be expected for a purely 2D system without electronic overlap between layers) even in the GGA-optimized geometry which yields a large interlayer separation, implying that also in this latter case there is significant electronic interaction between layers. As could be expected, the band dispersion in this segment increases significantly when the layers approach due to the inclusion of the Van der Waals effect. All these results can be seen in Fig. 7.4.

In Tables 7.2, 7.3 and 7.4 we show the obtained direct and indirect band-gaps ($E_{g,\text{dir}}$ and $E_{g,\text{ind}}$) for the 2H and 4H SnS$_2$ polytypes with the PBE and HSE
functionals and with and without applying the Grimme method. Theoretical band-gaps are compared with experimental results. As is expected PBE results underestimate the band-gaps in both systems and this problem is not solved with a dispersion correction which allow us to obtain good geometrical results. HSE calculations correct band-gaps but the obtained results are overestimated in comparison to the experiment due to the lack of dispersion correction which correct the stacking distance. If we combine both HSE and vdW dispersion correction (HSE+D2), theoretical band-gaps agree quite well with experimental data.

7.1.2 vdW-DF for weak interactions in SnS$_2$

While the calculated equilibrium geometries can be assessed by comparison with experimental data some other works are focussed in the solely comparison of interlayer binding energies [176]. Specifically in this work [176] the authors are focussed in the testing of several methods to be implemented for the treatment of Van der Waals forces while they compare the interlayer binding energy using RPA (Random-Phase Approximation) calculations for the acknowledgement of a quasi-experimental result for this end. Even though they use a wide spectrum of compounds we decide to accurately test the non-local functional results for our layered materials.

While some of the versions of the vdw-DF functionals are roughly tested [28, 98, 176] for the specific situation of the SnS$_2$ the results remain unravelled. That was the motive for us to test this layered material which was basic for our subsequent work.

The stress matrix in VASP was tested when the vdW-DF functional was applied [28, 29] through independent calculations for the obtainment of the corrected lattice parameters $a$ and $c$ in SnS$_2$. The RE-named calculations correspond with the former Lundqvist and Langreth [29] functional, while those named BO correspond with the Michaelides et al [28] implementation.

The obtained equilibrium total energy correspond with an accurate fitting that allows the comparison of the results with and without stress.

In Tables 7.5, 7.6, 7.7, 7.8 the calculated data show the obtained $a$ and $c$ parameters. The cutt-off (ENCUT) energy and the error value (EDIFF) for the total energy in each auto-consistent cycle were increased and the relative energy to that of the smaller value, $E_{rel}$, was obtained. The data obtained with stress was
Table 7.5: Comparison with and without stress of SnS$_2$ 2H polytype using the optB88 functional (BO Functional)

<table>
<thead>
<tr>
<th></th>
<th>ENCUT 400</th>
<th>ENCUT 500</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>with stress</td>
<td></td>
<td></td>
</tr>
<tr>
<td>EDIFF 1E-4</td>
<td>a(Å) 3.711</td>
<td>a(Å) 3.711</td>
</tr>
<tr>
<td></td>
<td>c(Å) 11.821</td>
<td>c(Å) 11.810</td>
</tr>
<tr>
<td>E$_{rel}$(eV)</td>
<td>0.0084</td>
<td>0</td>
</tr>
<tr>
<td>without stress</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(Iterations)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>EDIFF 1E-7</td>
<td>a(Å) 3.711</td>
<td>a(Å) 3.711</td>
</tr>
<tr>
<td></td>
<td>c(Å) 11.814</td>
<td>c(Å) 11.814</td>
</tr>
<tr>
<td>E$_{rel}$(eV)</td>
<td>0.0056</td>
<td>0</td>
</tr>
</tbody>
</table>

Table 7.6: Comparison with and without stress of SnS$_2$ 4H polytype using the optB88 functional (BO Functional)

<table>
<thead>
<tr>
<th></th>
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<tbody>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>with stress</td>
<td></td>
<td></td>
</tr>
<tr>
<td>EDIFF 1E-4</td>
<td>a(Å) 3.7096</td>
<td>a(Å) 3.7096</td>
</tr>
<tr>
<td></td>
<td>c(Å) 11.8368</td>
<td>c(Å) 11.8418</td>
</tr>
<tr>
<td>E$_{rel}$(eV)</td>
<td>0.0084</td>
<td>0</td>
</tr>
<tr>
<td>without stress</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(Iterations)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>EDIFF 1E-7</td>
<td>a(Å) 3.7106</td>
<td>a(Å) 3.7106</td>
</tr>
<tr>
<td></td>
<td>c(Å) 11.8575</td>
<td>c(Å) 11.8575</td>
</tr>
<tr>
<td>E$_{rel}$(eV)</td>
<td>0.0054</td>
<td>0</td>
</tr>
</tbody>
</table>

compared with that independent calculations without stress. Fig. 7.5 show the calculated data for the later and the equilibration energy associated with the equilibration $a$ and $c$ lattice parameters.

These results demonstrated the suitability of the stress implementation for the layered semiconductor SnS$_2$ 2H and 4H polytypes and corroborates that the implemented subroutines for this end in VASP is well tested through our rigorous
Table 7.7: Comparison with and without stress of SnS$_2$ 2H polytype using the revPBE functional (RE Functional)

<table>
<thead>
<tr>
<th>with stress</th>
<th>ENCUT 400</th>
<th>a(Å)</th>
<th>3.7664</th>
<th>$E_{\text{rel}}$ (eV)</th>
<th>0.0078</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>ENCUT 500</td>
<td>a(Å)</td>
<td>3.7661</td>
<td>$E_{\text{rel}}$ (eV)</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>EDIFF 1E-7</td>
<td>c(Å)</td>
<td>12.4567</td>
<td></td>
<td></td>
</tr>
<tr>
<td>without stress</td>
<td>ENCUT 400</td>
<td>a(Å)</td>
<td>3.7663</td>
<td>$E_{\text{rel}}$ (eV)</td>
<td>0.0087</td>
</tr>
<tr>
<td>(Iterations)</td>
<td>EDIFF 1E-4</td>
<td>c(Å)</td>
<td>12.5585</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 7.8: Comparison with and without stress of SnS$_2$ 4H polytype using the revPBE functional (RE Functional)

<table>
<thead>
<tr>
<th>with stress</th>
<th>ENCUT 400</th>
<th>a(Å)</th>
<th>3.7659</th>
<th>$E_{\text{rel}}$ (eV)</th>
<th>0.0078</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>ENCUT 500</td>
<td>a(Å)</td>
<td>3.7658</td>
<td>$E_{\text{rel}}$ (eV)</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>EDIFF 1E-7</td>
<td>c(Å)</td>
<td>12.5899</td>
<td></td>
<td></td>
</tr>
<tr>
<td>without stress</td>
<td>ENCUT 400</td>
<td>a(Å)</td>
<td>3.7694</td>
<td>$E_{\text{rel}}$ (eV)</td>
<td>0.0086</td>
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<tr>
<td>(Iterations)</td>
<td>EDIFF 1E-4</td>
<td>c(Å)</td>
<td>12.5854</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

analysis.

7.1.3 Optical properties of SnS$_2$ polytypes

In Fig. 7.6 the calculation of the optical properties are shown. The comparison of the results of 2H and 4H SnS$_2$ polytypes demonstrated that the optical absorption
depends not only on the band-gaps of these layered semiconductors but also on the arrangement of the sandwiched layers. The 2H polytype, as expected, demonstrated that starts absorbing energy at a higher value comparing with that absorption of SnS$_2$ 4H polytype which absorbs at a lower value of energy. This is because of the band-gaps which is higher for the 2H polytype compared with the 4H if we compares these results with that of the reported experimental band-gaps [174].

7.2 SnS$_2$ doped with V

7.2.1 The SnS$_2$ and VS$_2$ former compounds

SnS$_2$-VS$_2$ solid solution is formed when a great amount of V atoms is thoroughly introduced in SnS$_2$. In the VS$_2$ limit is also a layered material with the same P$_{3m1}$ structure of SnS$_2$ 2$H$-polytype. However, even though these two structures share the same crystalline lattice, VS$_2$ is metallic and magnetic and its cell parameters are smaller [177] than that of SnS$_2$ [67].

Figure 7.7 show the study of the former compounds. The other end of the SnS$_2$-VS$_2$ solid solution, that of small concentration of Sn in VS$_2$ might also be studied but in
Figure 7.6: (a) Optical reflectance and (b) optical absorption of SnS$_2$ 2H and 4H polytypes. Results obtained from the HSE calculation.
Figure 7.7: (a) Scheme of the displacement of the layers, showing the distance $d_L$. PBE (Dotted line) and PBE-D (Solid line) approach were compared with the experimental equilibrium value of parent semiconductors (b) SnS$_2$ and (c) VS$_2$.

In our case we are interested in the correlation of the structural behaviour of the SnS$_2$ material when vanadium is inserted and for this reason no other way to introduce to this compound system is taken into account.

In order to better describe the behaviour of the Grimme’s dispersion correction in this compound system, we applied a displacement of the layers $d_L$, either to bring closer or move away the atomic layers with a width $\Delta$ (Fig 7.7(a)). In this case, the calculations were done in a way that these layers conserved the bond distance within $\Delta$ and applying the displacement $d_L$ just between the layers where the vdw interactions play the major role.

### 7.2.2 Isolated V atom introduced in SnS$_2$

The electronic structures of Sn$_{12}$S$_{24}$ and VSn$_{11}$S$_{24}$ were obtained and the total and atomic projected DOS are shown in Fig. 7.8. Grimme’s dispersion correction gives
a corrected geometry in the direction of the layer stacking when used to obtain the ground-state of the SnS\(_2\)-2\(H\) and 4\(H\)-polytypes, as was previously shown. Therefore, if the correction dispersions containing V atoms are also applied in the structures we assume that the distance between the layers, in the direction of the vdW interactions, will also be improved.

In the host SnS\(_2\)-2\(H\) polytype (Fig. 7.8 (a)) the PDOS of the Sn and S atomic contributions demonstrate that both the VB and CB are mainly made up of S orbitals with \(p\) symmetry. The S orbital contributions with \(s\) symmetry are also located around 5 eV below (and above) \(E_F\). The obtained band-gap of the SnS\(_2\) 2\(H\)-polytype was 1.33 eV.

Figure 7.8 : Total densities of states (DOS) and atomic projected densities of states (PDOS) for (a) SnS\(_2\) 2\(H\)-polytype (Sn\(_{12}\)S\(_{24}\)) and (b) one V atom substituting Sn in SnS\(_2\) 2\(H\)-polytype, V\(_x\)Sn\(_{1-x}\)S\(_2\) with \(x=8.33\%\) (VSn\(_{11}\)S\(_{24}\))
In Fig. 7.8 (b) PDOS of V-atom contribution to the total densities of states (DOS) in VSn$_{11}$S$_{24}$ shows that the $Vd$-orbitals are mainly located between the VB and CB of the host SnS$_2$ band-gap. The $e_g$ - $t_{2g}$ splitting of these $Vd$-orbitals is shown. The $t_{2g}$ triplet is part of the spin-up while the $e_g$ doublet is located in the spin-down. Spin-up $t_{2g}$ orbitals are interacting with the VB forming a non-isolated intermediate-band while spin-down $e_g$ orbitals are empty and bound to the CB. Vanadium 4$s$ orbital-contributions are above in the CB and far from the host’s main band-gap.

However, in this VSn$_{11}$S$_{24}$ case one V atom is further away from the other V atoms (7.30 Å distance) in the same layer. Under these conditions, the non-isolated intermediate-band is formed through a distortion which is not enough to separate the dopant $d$-orbital contributions from the host semiconductor orbitals. Therefore, in order to separate the intermediate-band using lattice distortion we need to study the configuration space of several V atoms and their interactions.

### 7.2.3 Optical properties of SnS$_2$ doped with V, comparison with experimental results.

Spin-polarized DFT with the GGA approximation and the Perdew-Wang 1991 functional [90] was used. Considered valence electron respectively are 5$s$5$p$, 3$s$3$p$, and 4$s$3$d$ electron shells for Sn, S and V atoms. Plane-wave cutoff was 280 eV, and Brillouin zone sampling was a (8 x 8 x 8) Monkhorst-Pack grid. Errors in total lattice energy were corrected within 1 meV/atom. Relaxations of ions (including volume relaxation) with a convergence tolerance of 0.01 eV Å for atomic forces were made for all systems. In the optical calculations were considered only direct transitions. To get accurately converged electronic properties and the frequency dependent dielectric tensor, a 364 eV energy cutoff for the basis set and 200 empty bands were used. A 17 x 17 x 17 grid was needed to sample the Brillouin zone.

With these calculations, optical properties were computed. A scissors operator correction to compensate the gap underestimation typical of GGA was not applied. It is still not clear how the shift should be applied in the case of an IB material, and our aim here is to see what could be the effect of the vanadium insertion on the photon absorption spectrum. Results are displayed in Fig. 7.9 (a), the V-containing material is compared to that obtained for the undoped semiconductor. The closely related imaginary part of the dielectric constant is decomposed in the contributions of the different interband transitions and this is shown in Fig. 7.9 (b). There is a signal appearing at lower energies, approximately around 0.7 eV. This signal
Configurational Study of V in SnS$_2$: V-V interactions

Corresponds with the transitions within the partially filled IB. Transitions between IB and CB or IB and VB significantly increase the overall absorption coefficient. In addition these transitions in the doped material cover a substantial range of sub-bandgap photon energies, which undoped SnS$_2$ is unable to cover. Therefore, a wider range of the sunlight spectrum might be utilized for the photovoltaic process. The theoretical results were compared with the experimental ones which also demonstrated the enhancement of the photon absorption when V is inserted in SnS$_2$ (See Fig. 7.9 (c))

7.3 Configurational Study of V in SnS$_2$: V-V interactions

Layered SnS$_2$ 2H and 4H-polytypes substituted with V atoms in Sn positions were studied through thermodynamic and electronic calculations. Specifically we described the VSn$_{11}$S$_{24}$, V$_2$Sn$_{16}$S$_{36}$ and V$_2$Sn$_{10}$S$_{24}$ structures of the corresponding 8.33%, 11.11% and 16.67% vanadium concentrations. Different geometrical and magnetic configurations in addition to the vanadium concentrations were used and in the case of V$_2$Sn$_{16}$S$_{36}$ we compared the results of the 2H-polytype with that of the 4H-polytype.

All the electronic structures were calculated through DFT. The systems were obtained using spin-density-dependent exchange-correlation energy functional of a GGA (PBE) form, as implemented in VASP [151, 152]. However, a Grimme’s dispersion-correction, D2 (DFT-D2) [27, 101–103] applied after each auto-consistent cycle allowed the calculation of vdW weak interactions in the geometry optimization, which corrects the geometric parameters of the V-doped SnS$_2$. The interactions between the ionic cores and the valence electrons were introduced using the PAW [154]. In this, non-spherical contributions were included in the gradient corrections inside the PAW spheres, which is essential for the accurate total energies of compounds containing atoms with valence $d$ orbitals. Geometry optimizations were accurately obtained with errors of less than 1 meV/atom and the energy cut-off for the plane wave basis set and the k-point grid for the integration into the Brillouin zone of the lattices were selected as 400 eV and 4x4x4 $\Gamma$-centered respectively.

Moreover, the spin polarized calculations allows the description of the different magnetic configurations that are formed in each case and upon this; vanadium antiparallel-spins (APS) and parallel-spins (PS) magnetic configurations were calculated.
Figure 7.9: (a) Theoretical absorption coefficient, (b) partial contributions of the optical transitions and (c) experimental results of the optical absorptions obtained through UV-vis spectroscopy for the comparison with our theoretical calculations [18].
The dopant interactions were also analyzed through a symmetry-adapted space of configurations. This was obtained using the Site Occupancy Disorder (SOD) method [33, 34]. Using SOD there is the possibility of describing not only the dopant interactions in different non-equivalent configurations, but also the probabilities of these configurations.

### 7.3.1 Symmetry-adapted space of configurations for intermediate-band materials

Structures with two SnS$_2$ layers were selected to add up to two V atoms in each layer. Particularly 3x2x2 (36 atoms) and 3x3x2 (54 atoms) supercells, which are expansions of the unit cell and contain two layers of SnS$_2$ were calculated. In the 3x2x2 expansion one and two V atoms in Sn positions in 36-atom supercells resulted in 8.33% and 16.67% vanadium concentrations. In the 3x3x2 expansion this dopant concentration was 11.11%, where two V atoms are in Sn positions in the SnS$_2$-2H and 4H polytypes.

The SOD method [33] allows the reduction of the defective occupied sites by considering the lattice parameters, atom positions and SnS$_2$ structural symmetry. Hence the symmetry of the defect-arrangement configurations is also information obtained from the symmetry-adapted space created in the supercells. We used the number of symmetry elements, the degeneracy and the relative positions of the V atoms (two V atoms in the same layer or two V atoms in different layers) in each non-equivalent configuration in order to compare the geometry of each configuration.

**V$_2$Sn$_{10}$S$_{24}$**

The symmetry-adapted configurational space obtained with SOD for two V atoms in Sn positions in a 3x2x2 expansion of SnS$_2$ unit cell (V$_2$Sn$_{10}$S$_{24}$) show the formation of seven non-equivalent configurations (Fig. 7.10) in this non-isotropic supercell size. The cell parameters of the starting unit cell a= 3.65 Å and c=5.89 Å give a starting cell volume of 942.43 Å$^3$ (78.53 Å$^3$ per unit formula). Degeneracy ($\Lambda$), and initial V atom distances (d$_{VV}^{ini}$) for each configuration in this set are also shown (Table 7.10).

For the sake of clarity, two subsets of structures, related to the degeneracy were labeled: the c01-c03 subset and the c04-c07 subset. Within each subset the degeneracy and the total number of symmetry elements are identical. Hence, the
resulting symmetry of the c01-c03 subset, which has a smaller degeneracy, is higher than that of the latter. These iso-degenerated defect-occupied sites led to c01-c03 and c04-c07 configurations in which electronic structures were
Configurational Study of V in SnS₂: V-V interactions

Figure 7.11: Configurations of two V atoms in Sn positions in SnS₂ 2H-polytype (V₂Sn₁₆S₃₆) obtained through site-occupancy-disorder. Similarly as in 7.10 the axes are considered a(x),b(y),c(z).

comparable, unless the V atoms are located in different layers.

SnS₂ shows a structural anisotropy in all their polytypes, therefore the electronic characteristics of disordered sites will be dependent on the direction in which V atoms are located in the SnS₂, e.g. V atoms in the same layer and V atoms in different layers. If we take this into account, the c01-c03 and c04-c07 subsets of two-disordered-site configurations, should be sub-divided in accordance with these criteria.

V₂Sn₁₆S₃₆: 2H and 4H-polytypes.

In order to obtain a narrow intermediate-band a smaller concentration of V atoms was included in a greater supercell size (V₂Sn₁₆S₃₆). The isotropic 3x3x2 and
Results III: Layered Materials: SnS\textsubscript{2} and SnS\textsubscript{2}:V

Figure 7.12: Configurations of two V atoms in Sn positions in SnS\textsubscript{2} 4H-polytype (V\textsubscript{2}Sn\textsubscript{16}S\textsubscript{36}) obtained through site-occupancy-disorder. Similarly as in 7.10 the axes are considered a(x), b(y), c(z).

3x3x1 supercell sizes for the SnS\textsubscript{2}-2\textit{H} and 4\textit{H} polytypes were obtained respectively and their structures were compared. In these supercells the vanadium concentration was 11.11\% which is near the experimental result. In the comparison of the 2\textit{H} and 4\textit{H}-polytypes, it is demonstrated that both have the same amount of non-symmetrical (and total) configurations at this supercell size. The total number of combinatorial structures is 153 while the symmetry-adapted configuration spaces reduce this total amount to five (Fig. 7.11 and 7.12). In the 4\textit{H} case the parameters used are similar but slightly different from the 2\textit{H} case and yet the doubled \( c \) is also present in this case. The layer stacking in the 4\textit{H}-polytype is displaced which generates a symmetry breaking which allows a lesser amount of symmetry elements in the structure. Nevertheless even including this displacement among the layers the non-equivalent configurations obtained in the 4\textit{H}-polytype are
Configurational Study of $V$ in $SnS_2$: $V$-$V$ interactions

Table 7.9: Total number and reduced number of cation configurations by symmetry for each composition in the bulk models for the vanadium substitution in $SnS_2$ 2H and 4H polytypes.

<table>
<thead>
<tr>
<th>$x$ in $V_xSn_{1-x}S_2$</th>
<th>$n$ in $V_nSn_{1-n}S_{36}$</th>
<th>Total number of configurations</th>
<th>Number of inequivalent configurations (bulk)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.05</td>
<td>1</td>
<td>18</td>
<td>1</td>
</tr>
<tr>
<td>0.11</td>
<td>2</td>
<td>153</td>
<td>5</td>
</tr>
</tbody>
</table>

similar to those of the 2H structure. Degeneracy ($\Lambda$) and initial $V$ atom distances for each configuration are also shown (Tables 7.11 and 7.12).

For the sake of clarity, two subsets of structures related to the $V$ atom positions were labeled: the c01-c02 with $V$ atoms in one layer and the c03-c05 subsets with $V$ atoms in different layers. Despite the higher symmetry that appears in 2H, in 4H case the c01-c02 subset shows two $V$ atoms located in the same layer resulting in rather similar 2H and 4H structures. In addition, degeneracy in both cases also supports this equal local environment for $V$ atoms in these different supercells. Nevertheless, as expected, it was found that the amount of symmetry elements are doubled in c01 and c02 configurations of 2H compared with that of the 4H-polytype.

Furthermore c03-c05 subset includes $V$ atoms in different layers in both the 2H and 4H-polytypes. Within this subset in the 2H-polytype, each configuration has a different degeneracy from the others. As was previously mentioned the electronic characteristics of the disordered sites will be dependent on the direction in which $V$ atoms are located, as well as on the number of symmetry elements (degeneracy). In the 2H-polytype (Table 7.11), degeneracy of c01 and c03 as well as that of c02 and c05 are the same. Nevertheless in these cases the localization of the dopants are different, therefore each configuration will present independent electronic characteristics.

Another situation is found in the 4H structure in which the displaced layers give the same geometry for all of the iso-degenerated configurations in the c03-c05 subset. In accordance to these criteria, we also should subdivide the c01-c02 and c03-c05 subsets. Therefore, in the 2H-polytype each configuration will show independent...
Table 7.10: Characteristics of $V_2Sn_{10}S_{24}$ 2$H$-polytype configurations: Degeneracy ($\Lambda$), initial ($d_{VV}^{ini}$) and final ($d_{VV}^{fin}$) $V$ atom distances in the geometry optimization, final cell volume (Vol.), (in parentheses is the volume of a cell with one formula unit), energy difference between magnetic configurations ($E_{PS-APS}$)

<table>
<thead>
<tr>
<th>$\Lambda$</th>
<th>$d_{VV}^{ini}$ (Å)</th>
<th>$d_{VV}^{fin}$ (Å)</th>
<th>Vol. (Å$^3$)</th>
<th>$E_{PS-APS}$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>c01</td>
<td>6</td>
<td>5.89</td>
<td>5.78</td>
<td>799.75(66.65)</td>
</tr>
<tr>
<td>c02</td>
<td>6</td>
<td>3.65</td>
<td>3.63</td>
<td>805.73(67.14)</td>
</tr>
<tr>
<td>c03</td>
<td>6</td>
<td>6.93</td>
<td>6.84</td>
<td>800.61(66.72)</td>
</tr>
<tr>
<td>c04</td>
<td>12</td>
<td>3.65</td>
<td>3.22</td>
<td>804.66(67.10)</td>
</tr>
<tr>
<td>c05</td>
<td>12</td>
<td>6.93</td>
<td>6.33</td>
<td>806.35(67.20)</td>
</tr>
<tr>
<td>c06</td>
<td>12</td>
<td>3.65</td>
<td>3.19</td>
<td>804.67(67.10)</td>
</tr>
<tr>
<td>c07</td>
<td>12</td>
<td>6.93</td>
<td>6.72</td>
<td>807.19(67.27)</td>
</tr>
</tbody>
</table>

electronic characteristics while in the $4H$-polytype c03-c05 they will be identical. From each vanadium concentration, those cases in which $V$ atoms are located in the same layer and those in the other layer remaining without substitution are considered unlikely in the experimental conditions. This is because, this vanadium concentration is high enough to substitute the $V$ atom in the Sn positions of each $SnS_2$ layer and an extended amount of a layer should not be pure $SnS_2$ under these conditions. Therefore, those configurations with disordered-sites in each layer are more realistic.

7.3.2 Electronic structures and probabilities of $V_2Sn_{10}S_{24}$ and $V_2Sn_{16}S_{36}$

DOS obtained for the configurations of $V_2Sn_{10}S_{24}$ (Fig. 7.13) and the data resulting from these calculations (Table 7.10) are shown. In all the structures calculated the extra electron in each vanadium atom (with valence $V^{5+}$) substituting Sn (with valence $Sn^{4+}$) are located in the $Vd$-orbitals. We obtained the formation of metallic compounds in cases with $V$ atoms in different layers while the formation of non-metallic compounds appears in those with the atoms in the same layer. The non-metallic structures having $V$ atoms in the same layer are not shown, because they are unlikely to be formed.
Table 7.11: Characteristics of V$_2$Sn$_{16}$S$_{36}$ 2H-polytype configurations: Degeneracy ($\Lambda$), initial ($d_{VV}^{ini}$) and final ($d_{VV}^{fin}$) V atom distances in the geometry optimization, final cell volume (Vol.), (in parentheses is the volume of a cell with one formula unit), energy difference between magnetic configurations ($E_{PS-APS}$)

<table>
<thead>
<tr>
<th>( \Lambda )</th>
<th>( d_{VV}^{ini} ) (Å)</th>
<th>( d_{VV}^{fin} ) (Å)</th>
<th>Vol. (Å$^3$)</th>
<th>( E_{PS-APS} ) (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>c01</td>
<td>54</td>
<td>3.65</td>
<td>3.18</td>
<td>1221(67.83)</td>
</tr>
<tr>
<td>c02</td>
<td>18</td>
<td>6.32</td>
<td>6.43</td>
<td>1217(67.61)</td>
</tr>
<tr>
<td>c03</td>
<td>54</td>
<td>6.93</td>
<td>6.89</td>
<td>1220(67.78)</td>
</tr>
<tr>
<td>c04</td>
<td>9</td>
<td>5.89</td>
<td>5.84</td>
<td>1220(67.78)</td>
</tr>
<tr>
<td>c05</td>
<td>18</td>
<td>8.64</td>
<td>8.21</td>
<td>1222(67.89)</td>
</tr>
</tbody>
</table>

Furthermore, the energy difference between magnetic configurations ($E_{PS-APS}$) obtained for those structures with V atoms in the same layer (c02, c04 and c06) are greater than those of these in different layers (c01, c03, c05 and c07). However, the great $E_{PS-APS}$ energy difference found in the c06 structure compared with that of the others, demonstrates that a strong spin-coupling appears in c06 case compared with the c02 and c04 cases. We found that there is a relationship between the
magnetic behavior and the symmetry of the system. Those cases with V atoms in different layers are less affected by the magnetic coupling. In the experimental findings [18], the formation of a compound of V-doped SnS$_2$ 2H showed the formation of an IB material with paramagnetic behavior. In the configurations with V atoms located in different layers the magnetic behaviour is consistent with the formation of a paramagnetic material. In the cases with V atoms in the same layer the PS configuration defines the ground-state energy of the structure. Furthermore, the metallic structures formed in the c01 and c03 cases have the vanadium energy bands interacting with the VB while in c05 and c07 a wide metallic intermediate-band is formed. In these c01 and c03 structures the weak spin-coupling that appears might be related to an interaction with the surrounding host orbitals which lowers the energies around the V-S bonds, binding the intermediate-band to the VB. Therefore, the formation of a wide intermediate-band is only allowed when the system is independent of the spin configuration: in the c05 and c07 cases in which the symmetry is less than that of c01 and c03. Hence, there is a dependency of the structure properties on the symmetry of the V-atom

Figure 7.13: DOS and V(PDOS) of non-equivalent configurations of two V in Sn positions in V$_2$Sn$_{10}$S$_{24}$. Iso-degenerated configurations with V atoms in different layers in (a) c01-c03 subset, c01 and c03, and (b) c04-c07 subset, c05 and c07.
configuration and magnetic behavior.

Geometrical parameters are obtained after relaxation in which a contraction of supercells is shown (Table 7.10). It is known that a smaller cell appears in former VS$_2$ even though the two VS$_2$ and SnS$_2$ have the same structure. These former compounds should result in a V$_x$Sn$_{1-x}$S$_2$ solid solution with the same $P_{3m1}$ symmetry of the host systems. Using this, we infer that the resulting contraction of V$_x$Sn$_{1-x}$S$_2$ supercells is a consequence of this small VS$_2$ lattice when compared with the SnS$_2$ in the form of the 2H-polytype. However, the c01 configuration in V$_2$Sn$_{10}$S$_{24}$ cases appears with stronger reduction of the cell which is a consequence of the location of each V atom in the same position but different layers (which is exactly the direction of the layer stacking).

According to crystal field theory transition-metal $d$ orbitals lead to a distortion of the metal surrounding bonds either located in octahedral or tetrahedral positions. Nevertheless, despite the great deformation of bonds in all the doped structures, a wide intermediate-band is only formed in the c05 and c07 configurations in V$_2$Sn$_{10}$S$_{24}$, which demonstrates that not only is the distortion of the lattice necessary but also certain spin coupling and geometric configurations of the V dopant.

**V$_2$Sn$_{16}$S$_{36}$, 2H and 4H-polytypes.**

DOS obtained for the configurations of V$_2$Sn$_{16}$S$_{36}$ (Fig. 7.14) and the data resulting from these calculations (Tables 7.11 and 7.12) are shown. The 2H and 4H-polytypes are compared under the same conditions and certain situations are also similar to those of 36-atom supercells shown before. Specifically, for the c03 and c04 configurations in 2H-polytype (Fig. 7.14 (a) and (b)) the results are akin those c01 and c03 structures of the V$_2$Sn$_{10}$S$_{24}$ supercells (Fig. 7.13 (a)) while the c05 configuration in the V$_2$Sn$_{16}$S$_{36}$ 2H-polytype (Fig. 7.14 (c)) shows a narrow intermediate-band which supports the results found experimentally [18]. However, for the 4H-polytype the intermediate-band is not completely formed in the c03-c05 subset (Fig. 7.14 (d)). Instead, in these cases the geometric displacement of layers influences the formation of two isolated signals around the Fermi energy level in the electronic structures. This is not a characteristic of a conventional IB but might work as a ratchet IB [178], in which the system is composed by two narrow and very near bands in the middle of the host semiconductor band-gap in which one is empty (the ratched band) and the other one is filled.
Figure 7.14: DOS and V(PDOS) of configurations of two V in Sn positions obtained in $V_2Sn_{16}S_{36}$ for 2H and 4H-polytypes.
The geometrical anisotropy of the lattice of SnS$_2$ layered materials is what determines the direction of the V-atoms arrangement in order to obtain the IB. The lattice is distorted by the dopant repulsions and the V atoms are in the layer stacking direction in a long-range interaction. Hence, no magnetic coupling appears and the energy of the system is independent of the magnetic configurations.

Furthermore, we demonstrated that the inherent weak vdW interactions in SnS$_2$ and the type of layer stacking influences the way in which the IB is obtained, e.g. see the differences between Fig. 7.14 (a) (b) and (c) when these are compared with Fig. 7.14 (d). Therefore, the IB formation will not only be dependent on the number of symmetry elements (degeneracy) of the disordered-site arrangements in the lattice but also on the host SnS$_2$ symmetry.

7.3.3 Statistical Analysis of the Results

In addition, thermodynamic probabilities associated with each position were obtained from the resulting SOD data. Probabilities of each configuration in 16.67% and 11.11% vanadium concentrations were obtained under equilibrium conditions using several temperatures, and also non-equilibrium conditions (Tables 7.10, 7.11 and 7.12). In the V$_2$Sn$_{10}$S$_{24}$ cases the highest probability is found for the c06 configuration under thermodynamic equilibrium. Therefore, if the temperature is raised, c04 is the second most probable configuration at 900 K while in the total disordered situation the c04-c07 subset has the same probability as expected. This implies that the metallic IB (c05 and c07 configurations) might be synthesized using synthesis routes that include a greater disorder, but it should be noted that under these conditions the other configurations in the c04-c07 subset will also be present.

Nevertheless, structures with close V atoms in the same layer (c02, c04 and c06), leaving one unsubstituted SnS$_2$ layer, are not formed in great proportions in experimental synthesis. A low diffusion mechanism might also be involved avoiding the formation of V-S-V aggregates. Hence a synthesis route carried out under non-equilibrium conditions only allows the formation of c05 and c07 configurations.

On the other hand, Tables 7.11 and 7.12 show the probabilities that result from the symmetry-adapted configuration space in the V$_2$Sn$_{16}$S$_{36}$ supercell sets for 2H and 4H-polytypes. In the c03-c05 subset under thermodynamic equilibrium at 900K,
Results III: Layered Materials: SnS₂ and SnS₂:V

Table 7.13: Characteristics of V₂Sn₁₀S₂₄ 2H-polytype configurations: thermodynamic probabilities of each non-symmetrical configuration at 300K \( (p_{300K}) \) and 900K \( (p_{900K}) \) and the probabilities in the non-equilibrium conditions \( (p^\infty) \)

<table>
<thead>
<tr>
<th>( c )</th>
<th>( p_{300K} )</th>
<th>( p_{900K} )</th>
<th>( p^\infty )</th>
</tr>
</thead>
<tbody>
<tr>
<td>c01</td>
<td>0</td>
<td>0.0004</td>
<td>0.0909</td>
</tr>
<tr>
<td>c02</td>
<td>0</td>
<td>0.0068</td>
<td>0.0909</td>
</tr>
<tr>
<td>c03</td>
<td>0</td>
<td>0.0003</td>
<td>0.0909</td>
</tr>
<tr>
<td>c04</td>
<td>0.0364</td>
<td>0.2465</td>
<td>0.1818</td>
</tr>
<tr>
<td>c05</td>
<td>0</td>
<td>0.0054</td>
<td>0.1818</td>
</tr>
<tr>
<td>c06</td>
<td>0.9636</td>
<td>0.7347</td>
<td>0.1818</td>
</tr>
<tr>
<td>c07</td>
<td>0</td>
<td>0.0058</td>
<td>0.1818</td>
</tr>
</tbody>
</table>

The c05 configuration shows the higher probability, while under non-equilibrium conditions, the c03 configuration competes with it.

Our theoretical results support the formation of the IB material in the experimental conditions outside thermodynamic equilibrium.

Table 7.14: Characteristics of V₂Sn₁₆S₃₆ 2H-polytype configurations: thermodynamic probabilities of each non-symmetrical configuration at 300K \( (p_{300K}) \) and 900K \( (p_{900K}) \) and the probabilities in the non-equilibrium conditions \( (p^\infty) \)

<table>
<thead>
<tr>
<th>( c )</th>
<th>( p_{300K} )</th>
<th>( p_{900K} )</th>
<th>( p^\infty )</th>
</tr>
</thead>
<tbody>
<tr>
<td>c01</td>
<td>0.9744</td>
<td>0.8571</td>
<td>0.3529</td>
</tr>
<tr>
<td>c02</td>
<td>0.0255</td>
<td>0.1224</td>
<td>0.1176</td>
</tr>
<tr>
<td>c03</td>
<td>0.0000</td>
<td>0.0050</td>
<td>0.3529</td>
</tr>
<tr>
<td>c04</td>
<td>0.0000</td>
<td>0.0010</td>
<td>0.0588</td>
</tr>
<tr>
<td>c05</td>
<td>0.0000</td>
<td>0.0144</td>
<td>0.1176</td>
</tr>
</tbody>
</table>
Configurational Study of $V$ in SnS$_2$: $V$-$V$ interactions

Table 7.15: Characteristics of V$_2$Sn$_{16}$S$_{36}$ 4H-polytype configurations: thermodynamic probabilities of each non-symmetrical configuration at 300K ($p^{300K}$) and 900K ($p^{900K}$) and the probabilities in the non-equilibrium conditions ($p^\infty$)

<table>
<thead>
<tr>
<th></th>
<th>$p^{300K}$</th>
<th>$p^{900K}$</th>
<th>$p^\infty$</th>
</tr>
</thead>
<tbody>
<tr>
<td>c01</td>
<td>0.9863</td>
<td>0.8568</td>
<td>0.3529</td>
</tr>
<tr>
<td>c02</td>
<td>0.0136</td>
<td>0.0989</td>
<td>0.1176</td>
</tr>
<tr>
<td>c03</td>
<td>0</td>
<td>0.0163</td>
<td>0.1765</td>
</tr>
<tr>
<td>c04</td>
<td>0</td>
<td>0.0122</td>
<td>0.1765</td>
</tr>
<tr>
<td>c05</td>
<td>0</td>
<td>0.0159</td>
<td>0.1765</td>
</tr>
</tbody>
</table>

7.3.4 Thermodynamic of V doped SnS$_2$

Isolated vanadium dopants in SnS$_2$

$$E_{sol} = E[VSn_{17}S_{36}] - \frac{17}{18}E[Sn_{18}S_{36}] - \frac{1}{18}E[V_{18}S_{36}]$$  \hspace{1cm} (7.1)

The solution energy of the vanadium dopant into SnS$_2$ can be obtained from the result of the total energy considering the Eq. 7.1. The results given for SnS$_2$-2H:V and SnS$_2$-4H:V are $E_{sol}$=97.63 kJ/mol and $E_{sol}$=107.13 kJ/mol which are high values and determine that the solubility of this dopant into the SnS$_2$ layered semiconductors is not as simple as using standard synthesis method of temperature and pressure. Other synthesis method (inducing the formation of dopant outside the equilibrium) should then taken into account, in this case it is important to mention the solvothermal synthesis, which have been used before to obtain this material but in a disordered distribution. For obtaining accurate values of solution energy was analized the solid solution in the same scale of supercell size but increasing the V composition.
Vanadium-Vanadium interactions in SnS$_2$

\[ E_{VV} = E[V_2Sn_{16}S_{36}] + E[Sn_{18}S_{36}] - 2E[VSn_{17}S_{36}] \] (7.2)

Figure 7.15: Interaction energy between vanadium dopants in the ferromagnetic with V parallel spins (PS) states, the V-V interaction in one layer are separated of those in two layers for SnS$_2$-2H (open symbol) and SnS$_2$-4H (black symbol) polytypes.

The interaction energies between vanadiums $E_{VV}$ were calculated (Eq.7.2) and the resulting values for each of the configurations demonstrate that these can be related with the distance between dopants, in a way that those with a smaller distance between vanadiums correspond with structures of higher stabilization. The stabilization is the consequence of the interaction between dopants and that there is a tendency to form aggregates. The structures where the smaller distance among defects allow the spin coupling correspond with parallel spin configurations for the vanadiums which contribute to the stabilization of the system. In experimental synthesis the segregation of the dopant zones that can be formed in this system allows the formation of atomic clusters where a high dopant concentration appears. The result is an inhomogeneous doping and also an anisotropy of some physical
properties highly dependent on electronic and configurational structure. The solution energy is favoured in any of the magnetic configurations that can exists, e.g. the named APS or PS even when the coupling interaction between dopants allows only the formation of the parallel spin configurations, if a small distance appears between vanadium dopants in SnS₂. The fact that the total energy of these system do not depends on the magnetic solutions in a long range interaction can result in a macroscopical paramagnetic behaviour.

\[ \Delta H_{\text{mix}} = E[V_xSn_{1-x}S_2] - (1-x)E[SnS_2] - xE[VS_2] \]  
(7.3)

\[ \Delta H_{\text{mix}} = Wx(1-x) \]  
(7.4)

The solution enthalpy was obtained at different vanadium concentrations (Eq. 7.3). The resulting slope W values W=108.6 kJ/mol and W=101.0 kJ/mol were obtained respectively for SnS₂-2H:V and SnS₂-4H:V polytypes by fitting (Eq. 7.4). These higher values demonstrate that these configurations are not favoured in terms of thermodynamical stability. The saturation composition (Xs) was also calculated for SnS₂-4H:V and the limit of this value was obtained for different temperatures (Fig. 7.17), using 1200K the Xs=0.004% which is a small value.

**Specific geometrical characteristics for the 3x3x2 supercell**

The a and c geometrical parameters optimized (Fig. 7.18) for SnS₂-2H and SnS₂-4H polytypes at different compositions of vanadium show a reduction when the concentration of this atom is increased. The relationship of electronegativity and Van der Waals radius with the cell constriction can be observed. Electronegativity in Sn atom is slightly higher than the value of V atom but if we compare the Van der Waals radius of Sn atom with that of V atom there is a great difference. Therefore, Sn atom is bigger than V atom and this induced to a smaller cell formation for the upper values of this solid solution.

The set of obtained configurations for the SnS₂:2V 2H and 4H polytypes showed two configurations in which the vanadiums are located in the same layer and other 3 configurations with vanadiums in different layers and with different vanadiums distances. The most stable configuration of these sets are those where the two vanadiums are located in the same layer with less distance. Fig. 7.15 shows the relative energy of configurations to the most stable one. The disorder when the V
pair appears in different layers is less favoured and the V in this material has a tendency to form aggregates because a defect interaction takes place, as showed before. Furthermore, the cation-sulphur bond distances (M-S) can be observed in Table 7.16 and can be compared with the experimental values for SnS$_2$ and VS$_2$ parent structures. The values obtained with the Grimme’s dispersion correction applied for solid in PBE-D (D2) version are very close to the experimental values. In addition, the obtained structure with one vanadium in SnS$_2$, in the 2H polytype, showed identical V-S bond distances demonstrating that the distortion is not present when the vanadium is inserted in the cell. In SnS$_2$ 4H polytype, 3 bond distances appear near VS$_2$ bond distances while the other 3 bond distances are near SnS$_2$ one. This distortion is a result of the displacement of the two layers in SnS$_2$ 4H polytype in its parent structure. Moreover, these results from the cells having two vanadiums inserted in Sn positions show different bond distances. Nevertheless, the long range interaction in SnS$_2$:V with V atomic pairs in the 2H polytype, demonstrated that the relative energy is lowered if we compared these results with which are obtained in the same conditions.
7.4 Summary of this chapter

Dispersion corrections were applied for the $2H$ and $4H$ SnS$_2$ layered polytypes. The resulting lattice parameters and the indirect and direct band-gap were obtained using PBE and HSE06 functionals. Interlaying spacing results are in good agreement with experimental values when dispersion force corrections are applied, including both this effect and the HSE06 functional give the best agreement of the computed band gap with experiment. Band dispersions along the main directions for the different functionals are compared with results adding a vdW correction. The shape and width of the bands remain nearly unchanged and we found a decrease in energy for the corrected bands relative to the valence band upper edge.

Theoretical optical properties of the V substituted SnS$_2$ compared with that of the
Table 7.16: Bond distance in the two extreme of the solid solution and the V dopant in SnS$_2$-2H and SnS$_2$-4H polytypes.

<table>
<thead>
<tr>
<th>Polytype</th>
<th>$M_{\text{theo}}$ (Å)</th>
<th>$M_{\text{exp}}$ (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sn$<em>{18}$S$</em>{36}$ 2H</td>
<td>6x2.59</td>
<td>6x2.60</td>
</tr>
<tr>
<td>Sn$<em>{18}$S$</em>{36}$ 4H</td>
<td>6x2.59</td>
<td>6x2.57</td>
</tr>
<tr>
<td>V$<em>{18}$S$</em>{36}$   -</td>
<td>6x2.35</td>
<td>6x2.35</td>
</tr>
<tr>
<td>VSn$<em>{17}$S$</em>{36}$ 2H</td>
<td>6x2.43</td>
<td>-</td>
</tr>
<tr>
<td>VSn$<em>{17}$S$</em>{36}$ 4H</td>
<td>3x2.56 3x2.31</td>
<td>-</td>
</tr>
</tbody>
</table>

SnS$_2$ host semiconductor demonstrated that an enhanced photon absorption appears when V is inserted in this semiconductor. In addition, the theoretical results were compared with similar experimental findings.

We obtained symmetry-adapted configurations of V atoms at disordered-sites in SnS$_2$. The number of symmetry elements, degeneracy and positions of the dopants (e.g. two V atoms in one layer or two V atoms in different layers) were compared and correlated with the electronic results. We demonstrated that these configurations with same degeneracy and disordered sites in the same direction have an equivalent electronic structure. We established that while in the 2H-polytype at 16.67% V concentration c05 and c07 cases (Fig. 7.13) show a wide metallic IB, in the same polytype at 11.11% V concentration, c05 structure (Fig. 7.14) shows characteristics of a narrow, isolated and partially filled IB.

Specifically, intermediate-band structure with a V metal concentration of 11.11% has a similar concentration as achieved in the experimental results in SnS$_2$ 2H-polytype [18]. In this configuration the distance between the V atoms is the highest obtained in all the structures with two V atoms substituting Sn, 8.21 Å. The zero energy difference between the PS and APS spin-configurations of V atoms is consistent with a ground-state independent of the spin-configurations. Therefore, all these theoretical characteristics are coherent with the experimental results that report a paramagnetic material [18].

Moreover, the spin coupling that appears when V atoms have a small $d_{VV}$ avoids the formation of the IB. Therefore, V atoms should have a certain distance between them in order to obtain non-interacting V extra electrons delocalized throughout
Figure 7.18: Geometrical parameters obtained with PBE-D functional after relaxation in function of Vanadium composition for SnS$_2$-2H (open square) and SnS$_2$-4H (black square) polytypes.

non-bonded $d$ orbitals.
The probabilities from the symmetry-adapted configurations showed that V atoms in different layers are likely in the non-equilibrium conditions while at 900K the configuration with the intermediate-band prevails in the lower concentration that was calculated. In this work we have demonstrated that the intermediate-band
material obtained under these conditions not only depends on the symmetry of the host SnS$_2$ but also on the symmetry of the dopant arrangement in the lattice. In addition, the formation of the V-doped SnS$_2$ was studied based in some thermodynamic parameters of the system. These results demonstrated that SnS$_2$:V solid solution can be formed only under non-equilibrium conditions e.g. by using a synthesis method that tends to increase disorder. We also observed a tendency to form VS$_2$ aggregates in SnS$_2$ lattice and the feasibility to obtain SnS$_2$:V in an ordered way is not supported by a spontaneous process. The most stable configuration corresponds with that of the nearest distance between vanadiums. Still, if the vanadiums interacting in the same layer are inhibited by certain mechanism in SnS$_2$:V then the configuration that allows the long range interaction with the resulting distortion is the most favoured one. Therefore, theoretically an intermediate band can be obtained while these results are similar of that experimental findings.
Results IV: Bi in Cadmium Telluride
Chapter 8

Results IV- Bi in Cadmium Telluride

8.1 CdTe structure

The CdTe has gradually attracted attention on the scientific community following its successful role as a solar cell material. Previously, experimental results demonstrated that CdTe doped with Bi enhance at certain concentration level the photon absorption of the incident solar radiation [24, 25]. The structure of the defect formations in Bi doped CdTe have been studied both theoretically [179], and experimentally [25]. Nevertheless in our work we intend to obtain an accurate explanation of the particular characteristics of this doped material.

CdTe structure is proposed as one of the most used semiconductors of the photovoltaic materials nowadays. The atomic structure and electronegativity of the atoms in this material allows the formation of a neither-ionic nor-covalent bond that yields a direct band-gap not far from the optimum band-gap for the conversion efficiency [3]. A CdTe zinc blende structure consists of two face centered cubic sublattices (fcc) [180] interconnected along the <111> direction. The cubic fcc unit cell is characterized by the space group Td (F43m) and contains four formula units. In III-V and II-VI fcc structures one sublattice is occupied by the cations and
the other by the anions. This has 3 interstitial sites in the $\langle 111 \rangle$ direction: 2 tetrahedral and 1 octahedral the $\langle 111 \rangle$ is the preferential direction of the interstitial defect movement (Fig. 8.1). Each atom site is tetrahedrally coordinated with near neighbours.

Figure 8.1 : CdTe with fcc structure zinc blende type exhibiting tetrahedra with Cd in the center points.

We obtained a band structure of CdTe through VASP code and using the Perdew-Burke-Ernzerhof [89] parametrization of the generalized gradient approximation [88]. The atomic structure is a expansion of the primitive cell in CdTe which actually have one formula unit. Therefore, a $2 \times 2 \times 2$ expansion of this primitive cell was a supercell containing 16 atoms.

The band structure of CdTe is shown (Fig. 8.2). The obtained direct band-gap is around 0.7 eV. Further calculation using HSE06 screened hybrid functional was used to actually obtain a band gap which is near the experimental value, 1.45 eV. Nevertheless the band dispersion in this HSE06 diagram was identical to that of the PBE calculation CdTe.

The contribution of the atomic orbitals can also be observed. The valence band and the conduction band are mainly formed by Te $p$-orbitals and Cd $s$-orbitals respectively while the Cd $d$-orbitals are deep below the Fermi energy level. In CdTe there is an interaction of the localized semicore $d$-electrons with the valence $sp$-electrons. A large portion of their properties is directly related to this characteristic which is different from that of other II-VI semiconductors.

This PBE-GGA calculation exhibits conduction levels about 1.3 eV below the correct values. The Cd localized $4d$-orbitals are about 1.5 eV too high. The
experimental value is around 9.5 eV in $\Gamma$ [181] while we obtained these levels around 8.5 eV below Fermi energy level. Other authors [182] had calculated the band structures of CdTe simply avoiding Cd $d$-orbitals. In principle this is fair enough but a corrected description of the system is only done including the Cd $d$-orbitals.

Figure 8.2: CdTe band diagram showing the partial Cd and Te orbital contributions in the PAW spheres. It should be noticed that Cd $d$-orbitals appears in a localized band deeper below the Fermi energy level. The orbital contributions are depicted using different colors for each type of orbitals in Cd and Te atoms. The $s$-orbitals (Green), the $p$-orbitals (blue) and the $d$-orbitals (pink).
8.2 Bi doped CdTe

Bi doped CdTe has shown enhanced photon absorption of the incident solar radiation at certain concentration through experimental results [24, 25]. With the growth of CdTe cadmium vacancies $V_{Cd}$ [183] appear to act like acceptor centres, which are the predominant defects under Te rich conditions. The $V_{Cd}$ in the Te and Bi rich condition has been experimentally found negatively and double negatively charged at $E_V + 0.14\text{eV}$ and $E_V + 0.38\text{eV}$ respectively [24] and with a concentration ranging from around $10^{17} - 10^{18}\text{cm}^{-3}$ (where $E_v$ is the energy that corresponds with the valence band maximum). In addition, in the undoped CdTe it is demonstrated that interstitial Cd, $\text{Cd}_i$, is the dominant defects in the Cd rich condition [184, 185].

$Bi$ with a metal behaviour, high carrier mobility and low effective masses is a widely used dopant. When $Bi$ is inserted into a CdTe semiconductor, a deep level at $E_V + 0.71\text{eV}$ is reported [24]. Different hypotheses have been proposed to explain this deep level in CdTe:Bi. Saucedo et al [25] states that the insertion of $Bi$ in a Cd position ($\text{Bi}_{Cd}$) compensates the $V_{Cd}$ and forms the semi-insulating CdTe when a tetrahedral to octahedral distortion is induced, and consequently Te atoms are displaced forming two Te-Te dimers around the $\text{Bi}_{Cd}$.

We calculated using DFT the formation energy of a modeled supercell containing two Te-Te dimers around $\text{Bi}_{Cd}$ [186]. The results of this simulation demonstrated that the Te-Te configurational equilibration position is far from a dimer formation in these conditions and instead a simple $\text{Bi}_{Cd}$ substitution without structural distortion appears. This theoretical result is different from the prediction of Saucedo et al [25] but a tetrahedral to octahedral distortion is in fact what should happen in CdTe:Bi.

M. H. Du [179] points out that Bi in CdTe located at Cd position and interacting with $O$ substituting Te ($\text{Bi}_{Cd} + \text{O}_{Te}$) adopts a $C_3\nu$ symmetry that is coherent with a Jahn Teller distortion [187]. This result implies a high oxygen co-doping. However, these aforementioned experiments [24, 25] are made restricting $O$ concentration range to the $10^{14}-10^{15}\text{cm}^{-3}$ level [180]. Therefore this cannot be the explanation.

Furthermore, it is predictable under the Te and Bi rich condition that the dominant defects are the interstitial bismuth atoms $\text{Bi}_i$ and $V_{Cd}$ with the possibility of defect compensation in a long range interaction. The probability of $\text{Bi}_i$ as a dominant defect is predicted analogue to the case of a Cd rich condition in undoped CdTe where $\text{Cd}_i$ is the dominant defect.

In previous works it was demonstrated that Bi spontaneously diffuses throughout
Bi doped CdTe

the CdTe lattice [24, 25] despite the fact that Bi is a big atom to be placed in the interstices. The diffusion coefficient of Bi in CdTe cannot be determined. The explanation of this phenomenon by Hage-Ali et al [188] is consistent with a complex defect formation in which V_{Cd} and Bi should be addressed. These authors also compared the diffusion mechanism in CdTe:Bi with that of the Cu doped Ge [189]. Thus the existence of Bi inside CdTe in the Cd position or displaced to an interstitial site and interacting with V_{Cd} depends on the concentration of V_{Cd}.

We studied the CdTe structure in order to characterize in which positions its atomic contributions should be located. The different possibilities of the predicted dominant defects that can appear in CdTe:Bi under Te and Bi rich conditions were calculated. Bi located in either Cd or Te positions were analysed. Moreover, Bi atom interacting with other Bi atoms were also considered. Finally complex defects as Bi interstitial with a long-range interaction with V_{Cd} or oxygen co-doping (O_{Te}) interacting with Bi_{Cd} were evaluated in the created models.

The calculations were made with VASP code and using the Perdew-Burke-Ernzerhof [89] parametrization of the generalized gradient approximation [88]. All the parameters were tested to obtain accurate convergence in each case. The electronic calculations were made by increasing the k-points grid in order to obtain accurate results. The method used after relaxation was the linear tetrahedron as implemented in the VASP code.

8.2.1 Electronic structures of Bi doped CdTe

In this work several different possibilities have been taken into account to overcome the problem of the CdTe:Bi modelling. The previous bibliographic survey gave us the keys to formulate either substitutional or interstitial defective sites of the Bi dopant. Bi substituting Cd Bi_{Cd} or Bi in Te position Bi_{Te} are indistinctly allowed since Bi exhibits amphoteric behaviour.

While Bi in Te position is well described experimentally [25], Bi_{Cd} is still under study since might be related with the deep level directly associated with the enhancement in the photo-response. We obtained the electronic structure of both Bi_{Cd} and Bi_{Te} defects structures. Despite the possibility to obtain the actual position of Bi_{Te} level this is observed near the valence band and it is experimentally described through photo-luminescence spectra that this defect is located at 0.30 eV above the valence band [24]. Therefore our calculations are
Figure 8.3: Total densities of states (DOS) and atomic projected densities of states (PDOS) for (a) CdTe (Cd$_{32}$Te$_{32}$) and (b) one Bi atom substituting Cd in CdTe, Bi$_x$Cd$_{1-x}$Te with $x=3.1$ % (BiCd$_{31}$Te$_{32}$)

coherent with that result.

### 8.2.2 Configurational Study of Bi in CdTe

Similar to SnS$_2$:V in which structures with two SnS$_2$ layers were selected to add up to two V atoms in each layer, we calculated two Bi atoms configurations from the site-occupancy-disorder. Particularly 64 atom supercells, which are 2x2x2 expansions of the unit cell were calculated. In these, two Bi atoms in Cd positions resulted in a 6.26% vanadium concentration.

The symmetry-adapted configurational space obtained with SOD for two Bi atoms in Cd positions (Bi$_2$Cd$_{30}$Te$_{32}$) show the formation of five non-equivalent
configurations (Fig. 8.4) in these cubic supercells. Degeneracy ($\Lambda$), and initial $Bi$ atom distances ($d_{Bi-Bi}^{ini}$) for each configuration in this set are shown in Table 8.1.

DOS obtained for the configurations (Fig. 8.5) and the geometric data resulting from these calculations (Table 8.1) are shown. It is clear that, different from the layered SnS$_2$, in this case the degeneracy is not related with the DOS. In the first configuration, which has the smallest possible Bi distance, (Fig. 8.4 a)) the Bi repulsion is such that the distortion separate the Bi energy bands from the host semiconductor bands. These isolated bands form a completely-filled intermediate-band. In addition, the analysis of the thermodynamic probabilities (Fig. 8.2) demonstrates that this configuration, which forms the completely-filled intermediate-band, is the most stable one.
Table 8.1: Characteristics of Bi₂Cd₃₀Te₃₂ configurations: Degeneracy ($\Lambda$), Bi atom distances initial ($d_{Bi}^{ini}$) and final ($d_{Bi}^{fin}$) in geometry optimization, initial and final distance differences ($\delta d_{Bi}$), relative energy difference between $E_0$ and the other energies ($E-E_0$), final cell volume (Vol.)

<table>
<thead>
<tr>
<th></th>
<th>$\Lambda$</th>
<th>$d_{Bi}^{ini}$ (Å)</th>
<th>$d_{Bi}^{fin}$ (Å)</th>
<th>$\delta d_{Bi}$ (Å)</th>
<th>$E-E_0$ (eV)</th>
<th>Vol. (Å³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>c01</td>
<td>192</td>
<td>4.579</td>
<td>5.872</td>
<td>1.29</td>
<td>0.00</td>
<td>2342.89(73.22)</td>
</tr>
<tr>
<td>c02</td>
<td>48</td>
<td>6.476</td>
<td>6.686</td>
<td>0.21</td>
<td>0.56</td>
<td>2363.82(73.87)</td>
</tr>
<tr>
<td>c03</td>
<td>192</td>
<td>7.931</td>
<td>8.224</td>
<td>0.29</td>
<td>0.48</td>
<td>2355.61(73.61)</td>
</tr>
<tr>
<td>c04</td>
<td>48</td>
<td>9.158</td>
<td>9.420</td>
<td>0.26</td>
<td>0.40</td>
<td>2361.70(73.80)</td>
</tr>
<tr>
<td>c05</td>
<td>16</td>
<td>11.217</td>
<td>11.533</td>
<td>0.32</td>
<td>0.50</td>
<td>2361.89(73.81)</td>
</tr>
</tbody>
</table>

Table 8.2: Thermodynamic probabilities of each non-symmetrical configuration at 300K ($p^{300K}$) and 900K ($p^{900K}$) and the probabilities in the non-equilibrium conditions ($p^\infty$)

<table>
<thead>
<tr>
<th></th>
<th>$p^{300K}$</th>
<th>$p^{900K}$</th>
<th>$p^\infty$</th>
</tr>
</thead>
<tbody>
<tr>
<td>c01</td>
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</tr>
<tr>
<td>c02</td>
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<td>0.0002</td>
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<tr>
<td>c03</td>
<td>0</td>
<td>0.0021</td>
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</tr>
<tr>
<td>c04</td>
<td>0</td>
<td>0.0015</td>
<td>0.0968</td>
</tr>
<tr>
<td>c05</td>
<td>0</td>
<td>0.0001</td>
<td>0.0323</td>
</tr>
</tbody>
</table>

### 8.2.3 Complex defects: Bi⁺+V₉⁻ and Bi₉⁺+O₈⁻

Using *ab initio* calculations, a defect interaction between some important defects in CdTe demonstrates a distortion that breaks the symmetry of the orbitals and separates some states in the middle of the gap which can be related to the deep level previously found experimentally (Fig. 8.6). These interacting defects are Bi₉⁺+O₈⁻, two interacting Bi₉⁺ and finally Bi⁺+V₉⁻ which are compared with the simple Bi₉⁺.
Figure 8.5: The densities of states associated with the configuration space of two Bi doped CdTe in a 2x2x2 supercell. The illustration of each non-equivalent configuration and the partial Bi densities of states can also be seen.
Figure 8.6: DOS of (a) the host semiconductor CdTe. (b)-(e) CdTe:Bi in different situations: (b) Bi$_{Cd}$, (c) Bi$_{Cd}$+O$_{Te}$, (d) 2Bi$_{Cd}$, (e) Bi$_i$+V$_{Cd}$. PDOS in PAW spheres and in arbitrary units qualitatively demonstrate the position of the Bi orbital contribution.

The resulting DOS and PDOS of Bi in all of the doped cases (and O in Bi$_{Cd}$+O$_{Te}$ case) were obtained (Fig 8.6). The dopant levels can be seen in the band-gap
vicinity if we compare the DOS of the doped supercells with that of the host CdTe semiconductor. When Bi substitutes the Cd in the CdTe structure (Fig 8.6 (b)) the excess electron added by Bi raises the Fermi energy level to the conduction band, resulting in a n-type doping which is not consistent with the formation of a semi-insulating material found experimentally. Then if an stoichiometric amount of oxygen O is added (Fig 8.6 (c)) a Jahn Teller distortion appears as expected [179]. The O electronegativity being higher than that of Te stabilizes the Bi levels producing new states below the Te-related conduction band, and at the same time the O imposes an attraction to the neighboring Bi atom. Therefore, a distorted structure with a semi-occupied Bi level, having the excess electron band separated from the conduction band can be obtained. In the interacting 2Bi$_{Cd}$ (Fig
Results IV: Bi in Cadmium Telluride

<table>
<thead>
<tr>
<th>Defect type</th>
<th>(d_{\text{Bi-Te}}) (Å)</th>
<th>(d_{\text{Bi-O}}) (Å)</th>
<th>(\angle\text{Te:Bi:Te}) (°)</th>
<th>(\angle\text{Te:Bi:O}) (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{Bi}_{\text{Cd}})</td>
<td>3.07</td>
<td>-</td>
<td>109.6</td>
<td>-</td>
</tr>
<tr>
<td>(\text{Bi}<em>{\text{Cd}}+\text{O}</em>{\text{Te}})</td>
<td>3.01</td>
<td>2.49</td>
<td>93.6</td>
<td>128.4</td>
</tr>
<tr>
<td>(2\text{Bi}_{\text{Cd}})</td>
<td>3.04-3.25</td>
<td>-</td>
<td>90.4-121.3</td>
<td>-</td>
</tr>
<tr>
<td>(\text{Bi}<em>{\text{i}}+\text{V}</em>{\text{Cd}})</td>
<td>2.94-3.47</td>
<td>-</td>
<td>118.2</td>
<td>-</td>
</tr>
</tbody>
</table>

8.6 (d)) a deformation product of a Bi atom repulsed by steric hindrance appears. The resulting deformed structure has the Bi DOS separated from the rest and containing the excess two electrons. Finally the \(\text{Bi}_{\text{i}}\) interacting with \(\text{V}_{\text{Cd}}\) (Fig. 8.6 (e)) also deforms the structure when the two are in a long-range interaction, the resulting DOS forms an isolated partially-filled intermediate-band having the excess electron. The Bi PDOS in the cases of the interacting defects demonstrated that the Jahn Teller distortion breaks the symmetry of the contribution of 6\(p\) Bi orbitals and separates part of the hybridized levels in the formed structure, but the separation of the Bi levels in Bi PDOS of the \(\text{Bi}_{\text{Cd}}\) case cannot be seen. Table 8.3 contains the obtained Bi-Te distances (and Bi-O distance in \(\text{Bi}_{\text{Cd}}+\text{O}_{\text{Te}}\) case) and Te:Bi:Te angles (and Te:Bi:O angles in \(\text{Bi}_{\text{Cd}}+\text{O}_{\text{Te}}\) case). The CdTe bond distance is approximately 2.8 Å and a relaxation to higher values can be seen in all cases. All the Bi-Te distances in the \(\text{Bi}_{\text{Cd}}\) case are higher but identical and this does not lead to a distortion in the cell because the Te:Bi:Te angle in this case remains identical to that of the former structure. The distorted final structures around the Bi in \(\text{Bi}_{\text{Cd}}+\text{O}_{\text{Te}}, 2\text{Bi}_{\text{Cd}}\) and \(\text{Bi}_{\text{i}}+\text{V}_{\text{Cd}}\) also goes to higher but different values and the tetrahedral angles go from 109.4 ° to different values by the distortion provoked by defect interactions. The Bi-O distances are lower than those of the CdTe host lattice, which is coherent with the attraction that appears among the Bi and O atoms. Also the Bi-O bond is stronger than the Bi-Te or O-Cd bonds of the surrounding structure, which is inferred due to the fact that the vdW radius of O is smaller than that of Te (the electronegativity of O is higher than that of Te) In addition in our results we found that the Bi-O bond distance is the smallest (Fig. 8.3). The case of \(\text{Bi}_{\text{i}}+\text{V}_{\text{Cd}}\) that forms the intermediate-band presents a defect
compensation that occurs along the $<111>$ in the $C_3v$ axis. In Fig. 8.7 the PBE band diagram along the direction of maximum symmetry k-points of the corresponding CdTe 216 spatial group can be observed. In this figure the Bi $6p$ orbital projections over the PAW spheres can also be observed. The intermediate-band is made up of one delocalized electron in the Bi $6p$ outer shell orbital.

The Fermi energy level is located in the intermediate-band but the $\Gamma$ point has an energy which is the lowest in the IB. This is because the host band-gap is direct and has a great dispersion at the $\Gamma$ point that forms a deep minimum in the conduction band. The Bi levels included also form a same band dispersion in the IB due to the interaction with $V_{Cd}$.

The surrounding Te atoms have non-compensated bonds near the $V_{Cd}$ zone and the Bi atom with $6p^3$ outer shell compensates the Te bonds, probably hybridized with the Te $5p$ outer shell orbitals. This forms a bonding band which is located deeper within the valence band that also has the anti-bonding part around 3 eV over the Fermi level (Fig. 8.7).

A resulting Jahn Teller distortion occurs but only when the Bi atom is located in the interstitial site $Bi_i$ in a long range interaction instead of the substitutional case $Bi_{Cd}$. The deformed obtained structure still has a trigonal symmetry, having a $C_3v$ axis along the $<111>$ direction. It is demonstrated that a $Bi_{X}Te_{Y}$ spontaneously appears when CdTe is doped with Bi [179]. The three Te that are near the Bi atom form a 118.2$^\circ$ angle near the 120$^\circ$ trigonal angles, preventing the adoption of the correct geometry configuration that forms a $Bi_{X}Te_{Y}$. A subsequent calculation using the HSE06 [26, 96] screened hybrid functional was applied after the PBE geometry optimization to obtain more accurate subband-gaps. The resulting valence-intermediate (VB-IB) and intermediate-conduction (IB-CB) subband-gaps at the $\Gamma$ point obtained were 0.42 eV and 1.29 eV respectively.

In Fig. 8.10 (a) it can be observed that the optical absorption $\alpha$ of CdTe:Bi having the $Bi_i+V_{Cd}$ interaction, is higher than the $\alpha$ of the CdTe host semiconductor. The $\alpha$ of the intermediate-band is obtained by applying a corresponding scissor shift [10, 15] using the subband-gaps that we obtained from the HSE06 calculation at the $\Gamma$ point. This shift was applied to the VB-IB and IB-CB transitions. In the case of VB-CB transitions the scissor shift applied corresponds to the band-gap obtained after an HSE06 calculation of the CdTe host. The gained photon absorption can also be observed with the increase in the partial contributions to the optical absorption in Fig 8.10 (b).
Figure 8.8: A 2x2x2 expansion of the structure obtained in (a) a 32 atoms supercell along the direction of the defect line, the positions of cadmium vacancy, $V_{Cd}$ are also observed and (b) a 16 atom supercell with romboedric axis, the $V_{Cd}$ is represented by the trigonal area along the surrounding Bi atoms.

The experimental conditions that could favour the Bi complex in the synthesis of CdTe:Bi includes the formation of an extended concentration of cadmium vacancies. As has been theoretically described in Table 8.4, Bi in Cd position is more favoured than Bi in interstitial sites. The stabilization of $V_{Cd}$ defects with low formation energy [190] greatly favours the stabilization of Bi in an interstice of CdTe lattice and the consequent intermediate-band formation.

The experimental findings on the position of Bi in CdTe are not completely understood yet. In fact, it is not clear that Bi is actually located in Cd positions and
Table 8.4: CdTe:Bi energetics. Relative energy $E_{\text{rel}}$ of Bi displaced from Cd position forming a Bi-complex $\text{Bi}_i + V_{\text{Cd}}$ in relation with the corresponding energy of Bi in Cd position, $\text{Bi}_{\text{Cd}}$

<table>
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<th>$E_{\text{rel}}$ (eV)</th>
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<tr>
<td>$\text{Bi}_{\text{Cd}}$</td>
</tr>
<tr>
<td>$\text{Bi}<em>i + V</em>{\text{Cd}}$</td>
</tr>
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</table>

that the deep level identified at Ev+0.71 eV, that is related to the enhanced photon absorption cannot be explained as a hole trap. Instead, an intermediate-band theory might be applied for discussing the enhanced photon absorption that appears in this case. An intermediate-band through the delocalization of electrons avoids rapid recombination and/or a hole trap formation.

Furthermore, Bi is a big atom and steric hindrance can appears after stabilization of Bi in Cd position. The valence of Bi (3) different from that of Cd (2) is an added argument to produce a new material with a different symmetrical order (Fig. 8.8). The extended Bi 6p orbital forms a "disconnected" delocalized band that contains one electron per Bi atom filling this orbital by the half and giving space to the excitation of the new electrons. This delocalized band, extended into a different symmetrical order, avoids losses through its partial dispersion and perfect isolation from the other bands.

A CdTe lattice with $V_{\text{Cd}}$ and having Bi impurity forms a stable compound in a distorted cell which should correspond to the experimental findings. A structure containing Bi in a Cd position does not have distortion and a simple n-type doping is the result. Bi interacting with O demonstrates a distortion that inserts in the gap states separated from the conduction band minimum. The Bi states appear semi-filled in the middle of the host semiconductor band-gap. $2\text{Bi}_{\text{Cd}}$ presents a repulsion among the Bi atoms and the resulting distortion breaks the symmetry of the $p$-orbitals and the excess electron appears in separated densities of states, forming a completely-filled IB. The mechanism of one or the other defect interactions in the CdTe is dependent on $V_{\text{Cd}}$, $\text{Bi}_i$, $O_{\text{Te}}$ and $\text{Bi}_{\text{Cd}}$ concentrations and the distances between them. A partially filled and isolated intermediate-band in the mid-gap of the host CdTe is formed when a complex defect $\text{Bi}_i + V_{\text{Cd}}$
appears. The experimental deep level found at Ev+0.71 eV corresponds to the formation of this partially delocalized and partially dispersed band that is located in the middle of the band gap of the host semiconductor resulting from the Bi$_i$+V$_{Cd}$ complex defect formation.

### 8.3 Optical properties

![Optical absorption coefficient of CdTe:Bi where Bi is in Cd or Te positions.](image)

Figure 8.9 : Optical absorption coefficient of CdTe:Bi where Bi is in Cd or Te positions.

The optical properties of CdTe and Bi-doped CdTe were obtained and the results are shown in Fig. 8.9. The partial contributions to the optical absorption were obtained through the product of weighted imaginary part $\varepsilon_2$ of the total dielectric function and the energy of the different direct transitions in each band. The dielectric function is multiplied by the energy giving a weighted result that allows the comparison of the partial contribution of the different direct transitions in each band. The separation of the occupancies by bands permits the obtainment of the optical absorption in
Figure 8.10: a) Corresponding optical absorption and b) weighted imaginary part $\varepsilon_2$ of the total dielectric function and the partial contribution of the different direct transitions to it.

In order to compare with the experimental one, despite the subestimation of the band-gap in the GGA method. We used the HSE06 screened hybrid functional [26, 96]
to obtain each gap, from valence band (VB) to the IB and from IB to conduction band CB. The results were used to apply a scissor shift to the result of the weighted imaginary part $\varepsilon_2$ of total dielectric function and partial contribution of the different direct transitions in each band. [15] This scissor shift permits the correct absorption coefficient related with gaps in CdTe:Bi to be obtained. The cells used are unit cells of CdTe in which a Bi atom substitutes Cd or Te in each case. Bi presenting amphoteric behaviour substitutes Cd or Te in CdTe. Nevertheless the relative comparison of these substitutions demonstrates that while Bi actually is in Cd positions an enhance of the optical absorption appears, meanwhile Bi in Te positions exhibits a low gaining of optical absorption.

8.4 Defect Compensation

Defect compensation in CdTe is very common. Shallow levels from intrinsic defects can be found compensating the deep levels of the dopants, forming a semi-insulating material [180]. In addition, the control of n-type doping in CdTe is difficult due to the p-type conductivity of undoped CdTe to the predominant concentration of $V_{Cd}$ in Te-rich growth conditions. General features result from the formation of defect complexes between $V_{Cd}$ and the dopants which are the so-called A centers. Dopants of the III and VII groups are commonly employed for the n-type doping in CdTe, by substituting for Cd and Te sites, respectively. Besides, in general terms, this defect interaction that appears when two defects are located in a semiconductor at certain distance results in a rather distorted structure. When an impurity is included in a semiconductor the overall symmetry of the geometrical system is changed and the resulting distortion might separate some impurity energy levels from the host CdTe, forming an intermediate-band at certain dopant concentration. Therefore, this phenomenon that appears in CdTe can also be applied to intermediate-band materials that might be formed in a long-range defect interaction.
Results V: GaN doped with Cr
Chapter 9

Results V- GaN doped with Cr

9.1 GaN doped with Chromium

GaN crystallizes in a wurzite-type structure, in normal environmental conditions of temperature and pressure, but in some situations a formation of a zinc-blende structure with greater order occurs [191]. Therefore GaN exists in both wurzite and zinc-blende phases. Varying temperature and pressure parameters and growth restriction through use of Si or GaAs substrates the zinc-blende-type GaN is readily obtained. The band gap of GaN is reported 3.28 eV for zinc-blende structure while in wurzite this value is 3.47 eV [192].

In order to obtain enhanced magnetic properties, Cr doped wurzite type GaN has been earlier theoretically studied [70, 71, 73, 78, 79, 193]. This promising diluted magnetic material was successfully synthesized in the last decade [194]. The feasibility of the clustering formation in this doped semiconductor was also obtained [74–76]. In addition, its electronic structure has also been obtained from first principles [80]. The results showed that this system is ferromagnetic and the clustering formation is favored, where what is formed is Cr-N-Cr clusters. When Cr atom is doping GaN, it goes to the Ga substitutional site as Cr$^{3+}$. Therefore the
extra three electrons of Cr are located in its $d$-orbital. This magnetic impurity contributes to the hole formations (p-type doping) to the GaN semiconductor [70].

9.2 The Premises for an IB in GaN:Cr

GaN have a wide band-gap, therefore there is a possibility to obtain an intermediate-band material while doping GaN with a transition metal as Cr. The photovoltaic properties of the resulting material in GaN:Cr system were experimentally characterized demonstrating the formation of an intermediate band [40]. The band structure of sputtered GaN:Cr films was investigated using optical absorption and charge transport measurements, among others techniques. It was found that an additional energy band is formed in the intrinsic band gap of GaN upon Cr doping, and also that charge carriers in the material move in this additional band. In addition, the proposed IB was validated by studying the I-V characteristics under light irradiation. Prototype solar cells showed enhanced short-circuit current and open-circuit voltage in the n-GaN/GaCrN/p-GaN structure compared to the GaCrN/p-GaN structure, which validates the concept of an IBSC. Nevertheless, in the theoretical results that have been carried out, this is not satisfactorily exposed while using this level of theories. Some studies [70, 71, 73–76] have been performed without taking into account the strong correlation in the Cr $3d$-orbitals by using plain GGA. Therefore, for better describing this system, GGA+U method should be satisfactorily in the calculation of this electronic system [77, 79, 193].

In addition, in Ref. [71], that uses plain GGA-DFT method, the authors showed an association of the experimental photo-response with Ga $4s$-orbital. The assumption of Ga $4s$-orbital as the cause of the enhance photo response is rather unlikely. These authors considered a theoretical intermediate-band which is bounded with the conduction band. These $4s$ orbitals are forming empty states within the conduction band and non-real transition might occur within this level. If transitions considering the intermediate-band are in fact which enhance the photo-response in Cr-doped GaN, then Cr $3d$-orbitals are the keystone in this improved response.

Moreover, while some studies about GaN:Cr have been performed using the GGA+$U$ method using $U = 3$ eV [78], it was demonstrated that those results of some zinc-blende type semiconductors doped with Cr are not sensitive with the change of the $U$ value [195]. The effective $U=4$ eV has been also used [77] and they satisfactorily obtained an intermediate-band for a Cr doped (wurtzite-type)
GaN without N-vacancies in a 32 atoms supercell. The structure, with this rather small supercell, contains 6.25 % Cr composition which is a high dopant proportion.

In this work we studied the possibility of an intermediate-band formation in Cr doped GaN, in a clustered system using the GGA+U method. First, we performed the comparison of GGA and GGA+U results in a zinc-blende type GaN doped with Cr. Then, using symmetry-adapted configurations, the electronic structures of Cr-doped GaN (wurztite-type) were obtained. This study was performed in the wurztite-type because is that, the structure that showed the intermediate-band in the experimental results. In addition, the associated thermodynamic probabilities in the configurational study was also analysed.

9.3  GGA vs. GGA+U for Cr:GaN zinc-blende system

The electronic structure of one Cr in (zinc-blende type) GaN was obtained and the comparison of GGA and GGA+U results was included. For these calculations a 64 atoms, 2x2x2 supercell from the GaN unit was used. In this, one Ga was substituted by one Cr in order to obtain the doped material with a total Cr composition of 3.1%. We used the effective $U=4$ eV (See section 3.2.1) This characteristic makes that Cr $3d$-orbitals are strongly localized and the correlation in the GGA calculation needs to be corrected for these orbitals, and this is done including the $U$ Hubbard term. The comparison of GGA or GGA+U methods was obtained using PBE-sol [91] as GGA type method which enhance the resulting geometric parameters in the lattice. The results are shown in 9.1 where (a) and (c) densities of states have their respective (b) and (d) projected densities of states of d-orbitals of the Cr substituting Ga in GaN. The Fig. 9.1 (a) and (b) show the GGA results while Fig. 9.1 (c) and (d) shows the GGA+U calculations. The Cr $d$-orbitals are better described when GGA+U method is used, as is shown. This cubic structure demonstrates the formation of a rather narrow intermediate-band in this case. Besides, in 9.1 the projected densities of states respectively shown for the (b) GGA and (d) GGA+U methods, demonstrated the orbital splitting that occurs between the $t_{2g}$ and $e_g$ symmetry of the orbitals. While indeed in the GGA+U this differentiation is accurately reproduced in the GGA the $d$-orbitals are poorly described. Therefore for all the statements previously exposed we can assume that the GGA+U method is better for describing the GaN doped systems and particularly Cr $3d$-orbitals which are the cause of the intermediate-band formation.
Figure 9.1: The DOS and PDOS of one Cr in GaN using GGA or GGA+U (a) and (c) respectively are the total DOS using GGA or GGA+U, and (b) and (c) respectively are the PDOS of the particular Cr d-orbitals in each method.

9.4 The Cr in wurztite-type GaN

The electronic structures of Ga$_{36}$N$_{36}$ and CrGa$_{35}$N$_{36}$ were obtained (Fig. 9.2). GGA+U gives a corrected correlation for the d-orbitals when used to obtain the ground-state of the Cr doped GaN, as was previously shown.

In the host GaN (Fig. 9.2 (a)) the projected densities of states (PDOS) of the Ga and N atomic contributions are also shown. These are formed from atomic orbital contributions of Ga and N atoms with s and p symmetry. The obtained band-gap of the GaN was 1.72 eV.

In Fig. 9.2 (b) PDOS of Cr-atom contribution to the DOS in CrGa$_{35}$N$_{36}$ shows that the Cr d-orbitals are mainly located between the VB and CB of the host GaN band-gap. The $e_g$ - $t_{2g}$ splitting of these Cr d-orbitals is shown. The $t_{2g}$ triplet is part of the spin-up while the $e_g$ doublet is located in two parts, one in the spin-up and the other in the spin-down. Spin-up $t_{2g}$ orbitals are isolated and forming an empty intermediate-band while $e_g$ orbitals are showing one part filled and the other empty but bound to the CB. Chromium 4s orbital-contributions might be the signal located
Figure 9.2: DOS and Cr(PDOS) for (a) GaN (Ga_{36}N_{36}) and (b) one Cr atom substituting Ga in GaN, Cr_{x}Ga_{1-x}N_{2} with x=2.78 % (CrGa_{35}N_{36})

below the Fermi energy level inside the host main band-gap. However, in this CrGa_{35}N_{36} case one Cr atom is further away from the other Cr atoms. Under these conditions, the corresponding distortion is not enough to separate the dopant d-orbital contributions from the host semiconductor orbitals. Therefore, in order to separate the intermediate-band using lattice distortion we need to study the configuration space of several Cr atoms and their interactions.

9.5 Configurational Study of Cr in wurztite-type GaN

In order to better describe the Cr-doped wurztite-type GaN a set of several configurations in a statistic way was performed. Symmetry-adapted configurations allowed the description of the electronic structures of Cr-doped GaN. The Cr_{2}Ga_{34}N_{36} supercells were used. In accordance with the previous findings that demonstrated that this system is predominantly ferromagnetic, the magnetic behaviour of this diluted-magnetic material was considered as spin parallel (PS). In Table 9.2 the relative energy difference between E_0, the energy of the most stable
Figure 9.3: Configurations of two Cr atoms (blue) in Ga positions in wurtzite type GaN (Cr$_2$Ga$_{34}$N$_{36}$) obtained through site-occupancy-disorder. Configuration, and the other energies (E-E$_0$) are shown. The structure that is the most stable in the conjunct is the c04 while the others have relative energy values.
Table 9.1: Characteristics of Cr$_2$Ga$_{34}$N$_{36}$ configurations: Degeneracy ($\Lambda$), Cr atom distances initial ($d_{Cr}^{ini}$) and final ($d_{Cr}^{fin}$) in geometry optimization and initial and final distance differences ($\delta d_{Bi}$)

<table>
<thead>
<tr>
<th></th>
<th>$\Lambda$</th>
<th>$d_{Cr}^{ini}$ (Å)</th>
<th>$d_{Cr}^{fin}$ (Å)</th>
<th>$\delta d_{Cr}$ (Å)</th>
<th>E-E$_0$ (eV)</th>
</tr>
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<tbody>
<tr>
<td>c01</td>
<td>18</td>
<td>5.176</td>
<td>5.248</td>
<td>0.072</td>
<td>0.69</td>
</tr>
<tr>
<td>c02</td>
<td>36</td>
<td>5.518</td>
<td>5.609</td>
<td>0.091</td>
<td>0.70</td>
</tr>
<tr>
<td>c03</td>
<td>36</td>
<td>7.566</td>
<td>7.681</td>
<td>0.115</td>
<td>0.88</td>
</tr>
<tr>
<td>c04</td>
<td>108</td>
<td>3.186</td>
<td>3.166</td>
<td>-0.02</td>
<td>0.00</td>
</tr>
<tr>
<td>c05</td>
<td>108</td>
<td>6.078</td>
<td>6.165</td>
<td>0.087</td>
<td>1.87</td>
</tr>
<tr>
<td>c06</td>
<td>108</td>
<td>3.175</td>
<td>3.184</td>
<td>0.009</td>
<td>0.14</td>
</tr>
<tr>
<td>c07</td>
<td>108</td>
<td>5.512</td>
<td>5.609</td>
<td>0.097</td>
<td>1.05</td>
</tr>
<tr>
<td>c08</td>
<td>108</td>
<td>4.498</td>
<td>4.653</td>
<td>0.155</td>
<td>0.22</td>
</tr>
</tbody>
</table>

that are higher than c04 configuration. The higher relative energy is found for the c05 and c07 configurations.

Table 9.2: Characteristics of Cr$_2$Ga$_{34}$N$_{36}$ configurations: Relative energy difference between E$_0$ and the other energies (E-E$_0$)

<table>
<thead>
<tr>
<th></th>
<th>E-E$_0$ (eV)</th>
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<tbody>
<tr>
<td>c01</td>
<td>0.69</td>
</tr>
<tr>
<td>c02</td>
<td>0.70</td>
</tr>
<tr>
<td>c03</td>
<td>0.88</td>
</tr>
<tr>
<td>c04</td>
<td>0.00</td>
</tr>
<tr>
<td>c05</td>
<td>1.87</td>
</tr>
<tr>
<td>c06</td>
<td>0.14</td>
</tr>
<tr>
<td>c07</td>
<td>1.05</td>
</tr>
<tr>
<td>c08</td>
<td>0.22</td>
</tr>
</tbody>
</table>
The intermediate-band is observed in the c01, c02 and c03 situations, where smaller thermodynamic probabilities are associated in these cases (Table 9.3). These parameters demonstrated that c04 and c06 structures are more stable at 300K ($p^{300K}$) and also in the total disordered situation $p^\infty$. These are the configurations with smaller distance between Cr atoms. As expected [74] it is confirmed a strong tendency of this magnetic ion, occupying Ga sites, to form embedded clusters. Furthermore, the distances between Cr atoms $d_{Cr}^{ini}$ before and $d_{Cr}^{fin}$ after the relaxation was performed, which demonstrated that there is a mutual repulsive interaction between Cr atoms. The GGA+$U$ method was applied in order to correct the correlation energy of the
Table 9.3: Thermodynamic probabilities of each non-symmetrical configuration at 300K \((p^{300K})\) and 900K \((p^{900K})\) and the probabilities in the non-equilibrium conditions \((p^{\infty})\)

<table>
<thead>
<tr>
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<th>(p^{300K})</th>
<th>(p^{900K})</th>
<th>(p^{\infty})</th>
</tr>
</thead>
<tbody>
<tr>
<td>c01</td>
<td>0</td>
<td>0</td>
<td>0.0286</td>
</tr>
<tr>
<td>c02</td>
<td>0</td>
<td>0</td>
<td>0.0571</td>
</tr>
<tr>
<td>c03</td>
<td>0</td>
<td>0</td>
<td>0.0571</td>
</tr>
<tr>
<td>c04</td>
<td>0.9948</td>
<td>0.8148</td>
<td>0.1714</td>
</tr>
<tr>
<td>c05</td>
<td>0</td>
<td>0</td>
<td>0.1714</td>
</tr>
<tr>
<td>c06</td>
<td>0.0051</td>
<td>0.1402</td>
<td>0.1714</td>
</tr>
<tr>
<td>c07</td>
<td>0</td>
<td>0</td>
<td>0.1714</td>
</tr>
<tr>
<td>c08</td>
<td>0.0002</td>
<td>0.0449</td>
<td>0.1714</td>
</tr>
</tbody>
</table>

d-orbital contributions. This allowed to obtain the theoretical characterization that is coherent with the experimental findings which are reported in literature [40, 71] and where an increased photon absorption is shown while GaN is thoroughly doped with Cr transition metal. Particularly, in Ref. [40] an intermediate-band formation is associated with the enhancement in the photon absorption of the Cr:GaN obtained material. We theoretically calculated this intermediate-band material while an GGA+\(U\) method is applied using an effective \(U\) parameter of 4 eV. While in one-Cr-doped GaN structure, this intermediate-band material was not obtained, in those calculated cases in which more-than-one Cr atom is inserted, therefore we obtain a distortion that separates this dopant energy levels and forms an intermediate-band, which is coherent with the experimental findings. In addition, the statistical thermodynamics associated with the symmetry-adapted space of configurations while GaN is doped with two Cr atoms, was analyzed in order to obtain the feasibility of the formation of Cr-atom aggregates in the experimental conditions. The results demonstrates that only in the non-equilibrium situation is when this intermediate-band configurations are formed, while all the other possible cases are also present. This is expected due to the fact that those configurations with pairs of Cr-atoms forming aggregates show higher degrees of distortion, and the total energy of the system should demonstrate an stabilization.
While the aggregate formation allows the rearrangement of the atom distribution in the local defect environment, this result in a better stabilization, therefore this local distortion allow that lower energy characterize the whole configuration.
Summary and Conclusions
Summary and Conclusions

Summary

The assessment of the feasibility for the formation of potential intermediate band materials has been carried out under a theoretical approach in which thermodynamic, electronic and optical characteristics of these materials and their precursor host semiconductors have been studied. Whenever possible, the obtained theoretical results were corroborated with the experimental findings in order to demonstrate the reliability of each of the applied theoretical procedures. The complexity of the precursors of the intermediate band materials was elucidated in some cases as e.g. in CdIn$_2$S$_4$ and MgIn$_2$S$_4$ octahedral spinels or SnS$_2$ 2H and 4H polytypes. In addition, the characteristics of the electronic structures related to the position of the dopants and the interaction between them were also analyzed. Dopant substances were introduced in the different materials. The crystal symmetry was employed to determine the different configurations of dopants. Each symmetrically independent structure has particular theoretical characteristics. In addition, the electronic structures related to the position of the dopants and the interaction between dopants was also analyzed. The summary of results is listed
Summary and Conclusions

Results I- \( Mn_2S_4 \) Spinel type materials

- In \( Mn_2S_4 \) and \( CdIn_2S_4 \) spinels our theoretical calculations corroborated the experimental findings in which the inversion degree is of around 0.20 for the \( CdIn_2S_4 \) and 0.82 for the \( MgIn_2S_4 \). From a generalized point of view our theoretical calculations can be therefore considered as a new approach for the calculation of inversion degree in spinels, in which the order-disorder transition takes place through the exchange between octahedral and tetrahedral cations.

- The \( CdIn_2S_4 \) is found to be an almost direct spinel, this gave us the possibility to propose the band-gap control that might be used when this spinel type is synthesized. The modeled temperatures under which the \( CdIn_2S_4 \) might be obtained and its synthesis might be controlled allows the tuning of the inversion degree in order to obtain the desired band-gap.

- In addition, the \( CdIn_2S_4 \) spinel has been studied under a range of pressure and results demonstrated that the inversion degree of this structure is not as variable under high external pressure as appear under normal conditions. Under these extreme conditions the range of inversion degree is narrowed compared with that obtained under normal conditions. The geometrical volumes and also the electronic band-gaps obtained under a range of pressures were accurately alike the experimental values while the indirect and direct theoretical band-gaps are in between the two extremes found in the experimental Urbach’rule.

- The thermodynamic parameters associated with the inversion degree were obtained under 3GPa. This pressure, in addition to the temperature effect is acting upon the inversion degree. A synergy of both, pressure and temperature arises in a wider variation of inversion degrees when different temperatures are considered at 3GPa, in comparison with these under normal pressure.

- Particularly in \( MgIn_2S_4 \) almost-inverse spinel, the inversion degree value is considered within a cation exchange which is an equilibrium process. The
range of all the possible inversion degrees that can be obtained demonstrated the formation of a nearly zero value for the configuration energy of inversion and therefore demonstrating that even though 0.82 is the turning point for the inversion degree (in which this energy is exactly zero) all the other values around this are very small. Thus a different inversion degree might be found when using another synthesis route.

• Intermediate-band material are formed when calculating the electronic properties of the V doped MgIn$_2$S$_4$ and also V doped CdIn$_2$S$_4$ while using inversion degrees of $x=1$ and $x=0$ respectively and in the partially inverted materials with $x=0.75$ for MgIn$_2$S$_4$ and $x=0.25$ for CdIn$_2$S$_4$. This demonstrates the lack of influence of the inversion degree in the intermediate band material formation.

Results II- Zn band-gap modulator in Chalcopyrites with Ti

• We demonstrated that Zn insertion with different dilutions in Ti:CuGaS$_2$ modulates the band-gap width and separates the energy levels of the intermediate-band from the conduction band.

• We confirmed the previous experimental findings in which the Zn in CuGaS$_2$ reduced the band-gap of this wide gap chalcopyrite.

• The feasibility of Zn insertion in CuGaS$_2$:Ti through different proposals of spontaneous decomposition of $(Zn_yTi_{1-y})_xCuGa_{1-x}S_2$ system. The results demonstrated that these reaction schemes were spontaneous. Therefore, it is thermodynamically unfavorable to obtain the Zn and Ti substituted CuGaS$_2$ but this does not exclude that the material might be obtained using kinetically controlled methods.

• The formation of an intermediate-band in CuGaS$_2$:Ti:Zn is still not suitable to be proposed as an intermediate-band material. The width of this intermediate band is too large which is far from the theoretically proposed intermediate band, which should be slightly dispersed but narrower than those in CuGaS$_2$:Ti:Zn.
Summary and Conclusions

Results III-Layered Materials: SnS\textsubscript{2} and SnS\textsubscript{2}:V

- Interlaying spacing results are in good agreement with experimental values when dispersion force corrections are applied in the 2\textit{H} and 4\textit{H} SnS\textsubscript{2} layered polytypes. In addition, including the HSE06 functional we obtained the best agreement of the computed band-gap with experiment.

- When applying the vdW dispersion correction the shape and width of the bands remain nearly unchanged but we found a slightly lower energy for the corrected bands.

- We demonstrated that symmetry-adapted configurations of \textit{V} atoms at disordered-sites in SnS\textsubscript{2} with same degeneracy and disordered sites in the same direction have an equivalent electronic structure.

- The configuration which has a narrow, isolated and partially filled intermediate-band was identified at 11.11\% vanadium concentration while a wide metallic intermediate-band appears at 16.67\% vanadium concentration. While at higher concentration the structure show a wide metallic intermediate-band which is far from the theoretical predictions, the smaller concentration show similar characteristics of the experimental findings in which a 10\% V concentration was included in SnS\textsubscript{2} \cite{18}.

- Calculations with V parallel spin and also with V anti-parallel spin were obtained. The zero energy difference between different spin configurations of V atoms is consistent with a ground-state which can be considered paramagnetic and comparable with the experimental findings.

- In addition, it was demonstrated that the intermediate-band material in V doped SnS\textsubscript{2} not only depends on the symmetry of the host SnS\textsubscript{2} but also on the symmetry of the dopant arrangement in the lattice.

- This system exists outside thermodynamic equilibrium. While the probabilities from the symmetry-adapted configurations showed that V atoms in different layers are likely in the non-equilibrium conditions, at 900K the configuration with the intermediate-band prevails at 11.11\%.

- The most stable configuration corresponds with that of the nearest distance between vanadiums. Nevertheless if the formation of interacting vanadiums,
those located in the same layer, are inhibited by certain mechanism in V doped SnS$_2$ then the configuration with the long range interaction is the most favored one.

\textit{Results IV- Bi in Cadmium Telluride}

- A CdTe lattice with a V$_{Cd}$ and a Bi impurity forms a stable compound in a distorted cell. In these conditions the CdTe:Bi lattice form an intermediate-band as a result from the long-range interaction that appears between V$_{Cd}$ intrinsic defect and Bi impurity in an interstitial site (a Bi$_i$+V$_{Cd}$ complex defect formation). These theoretical results are coherent with the experimental findings in which the Bi insertion in CdTe gives an enhanced photoresponse associated with a level found in the middle of the band-gap.

- Bismuth interacting with oxygen demonstrates a distortion which inserts states in the gap of the host semiconductor and these are separated from the conduction band minimum, which results in a possibility of isolation of the levels while the concentration of the dopants is strictly controlled.

- 2Bi$_{Cd}$ bonded to the same Te atom shows a repulsion among the Bi atoms and the resulting distortion breaks the symmetry of the p-orbitals. The excess electron appears in separated densities of states forming a completely-filled intermediate-band. This structure which has two Bi at the lower distance and forms a completely filled intermediate-band, shows a higher stability when compared with different configurations of Bi atoms inside CdTe.

- The mechanism of formation one or the other defect interactions in the CdTe is dependent on V$_{Cd}$, Bi$_i$, O$_{Te}$ and Bi$_{Cd}$ concentrations and the distances between them.
The electronic structures obtained for the zinc-blende structure of Cr doped GaN when comparing GGA and GGA+U methods demonstrated that GGA+U method is better for describing the GaN doped systems. The correlation energies of Cr 3d-orbitals are enhanced using the GGA+U method. Cr 3d-orbitals are the cause of the intermediate-band formation.

Our theoretical results of electronic structures for GaN doped with Cr, in which an intermediate band material is obtained in the Cr doped GaN, are coherent with the experimental findings.

The configurational space of two Cr atoms in the wurzite-type GaN shows a formation of an intermediate band in the Cr doped GaN in certain configuration where the distance between Cr atoms is small and therefore these atoms are interacting. Nevertheless, the formation of an intermediate band in this wide-gap semiconductor still needs a co-dopant that modulates the band-gap for obtaining an enhanced photon-absorption.

Using the configurational study, the results demonstrated that the most stable configuration do not correspond with those of the intermediate band formation. This is because in the experimental conditions the formation of an intermediate-band structure in this system is obtained through a synthesis operating through non-equilibrium thermodynamics. Therefore, the conjunct of all the structures will appear at the same time under these conditions.
Appendix I: Configuration statistics in canonical ensembles
Configuration statistics in canonical ensembles

A.1 General formulation

The equations for probabilistic statistics are normally within the canonical ensemble [34]. Using these equations, those from the reduced space of inequivalent configurations are slightly adapted. Each independent configuration $k$ ($k = 1, \ldots, K$), has an energy ($E_k$) and no degeneracy is accounted. The probability of each of them will be:

$$P_k = \frac{1}{Z} e^{-\frac{E_k}{k_B T}} \quad (A.1)$$

where the partition function is:

$$Z = \sum_{k=1}^{K} e^{-\frac{E_k}{k_B T}} \quad (A.2)$$

where $k_B$ is the Boltzmann constant, and $T$, temperature. Any magnitude theoretically obtained for each ordered configuration within the configurational
ensemble has an average value from each independent configuration which is the effective value in the disordered solid:

$$A = \sum_{k=1}^{K} P_k A_k$$  \hspace{1cm} (A.3)

and in the same manner is obtained the average energies, by using those from the independent configurations:

$$E = \sum_{k=1}^{K} P_k E_k$$  \hspace{1cm} (A.4)

One of the tasks that should be accomplished when using this statistical approach is to obtain the configurational free energy. This magnitude is important for evaluating the thermodynamic stability of the disordered solid at a given temperature. Not only the energy but also the configurational multiplicity of the system should be taken into account in the calculation of this magnitude:

$$F = -k_B T \ln Z = -k_B T \sum_{k=1}^{K} e^{-E_k/k_B T}$$  \hspace{1cm} (A.5)

Furthermore, in any thermodynamic approach not only internal energy, but also configurational entropy should be obtained, in order to determine the feasibility of the system in study. The difference per temperature unit between the average and total free energies determines this magnitude, and this is also expressed in terms of the probabilities $P_k$:

$$S = \frac{E - F}{T} = -k_B \sum_{k=1}^{K} P_k \ln P_k$$  \hspace{1cm} (A.6)

While obtaining configurational entropy we should acknowledge which type of system is involved. If this is going toward the perfect orderly situation or if instead this is going toward the perfect disordered situation. This can be identified through
the following statements:

- If configuration \( k = 1 \) is more stable than the others, which means that its energy is separated (and lower) from the others, by an energy difference \( \Delta E > k_B T \), then \( P_1 = 1 \) while \( P_k = 0 \) for \( k \neq 1 \). The configurational entropy in the system is zero (toward orderly situation).

- If the energies of all the configurations are very similar \( (\Delta E \leq k_B T) \) or formally in the limit \( T \to \infty \), then \( P_k = 1/K \) and the configurational entropy reaches its maximum possible value (toward disorderly situation):

\[
S_{\text{max}} = k_B \ln K = k_B \ln \frac{N!}{[N(1-x)]! [Nx]!} \tag{A.7}
\]

which, in the limit of an infinitely large supercell \( (N \to \infty \) at constant composition \( x \)) is:

\[
S_{\text{ideal}} = -k_B N (x \ln x + (1-x) \ln (1-x)) \tag{A.8}
\]

Varying degrees of ordering, in between, give temperature-dependent values of entropy, free and internal energies using Eq. A.4. Nevertheless the main drawback is that any finite supercell is unable to describe exactly the perfect disorder limit. Therefore is better to describe the free energy (Eq. A.5) as follow [196]:

\[
F = -k_B T \ln K - k_B T \ln \left( \frac{1}{K} \sum_{k=1}^{K} e^{(-E_k/k_B T)} \right) \tag{A.9}
\]

The entropy contribution of the disorder is in the ideal limit, this is the contribution of the energy and the correction of the contribution of entropy due to the partial ordering. The first term can also be adjusted as:

\[
F = -k_B T N (x \ln x + (1-x) \ln (1-x)) - k_B T \ln \left( \frac{1}{K} \sum_{k=1}^{K} e^{(-E_k/k_B T)} \right) \tag{A.10}
\]
A.2 Including vibrational contributions

The previous formulation was made excluding vibrational terms, in order to only account the magnitudes associated with the configurational space [34]. The addition the vibrational contributions is important in certain systems that have vibration modes with large frequencies which means that the overall vibrational energy cannot be neglected. Nevertheless in certain situations, the calculations that includes the vibrational terms might be neglected, simplifying the calculations when only including configurational terms. The vibrational energies are evaluated as explained in Chapter 3 within the harmonic approximation and the related partition function is as follow:

\[
Z = \sum_{k=1}^{K} \sum_{\nu} e^{-\left(\frac{E_{k,\nu}}{k_B T}\right)}
\]  

(A.11)

In terms of the vibrational partition function \(Z_{k}^{(vib)}\) and the vibrational free energy \(-F_{k}^{(vib)}\) of each configuration, this becomes:

\[
Z = \sum_{k=1}^{K} Z_{k}^{(vib)} = \sum_{k=1}^{K} e^{-\left(\frac{F_{k}^{(vib)}}{k_B T}\right)}
\]  

(A.12)
Appendix II: VASP code and its characteristics
The VASP code and its implementation

The Vienna Ab-initio Simulation Package, VASP\textsuperscript{i} code is a plane-wave DFT code that uses pseudopotentials as a regular electronic implementation. Other codes: Quantum-Espresso \textsuperscript{ii}, Abinit\textsuperscript{iii} also perform DFT calculations.

In this thesis all the calculations were made using (VASP) [152,153] code, in different parametrizations of the exchange-correlation potential and using projector augmented waves (PAW) [154,156].

B.1 General aspects

The wide spreaded method combining DFT plus pseudopotential plus plane-wave method is adscribed to Car and Parrinello [197], through \textit{ab initio} molecular dynamic simulations on condensed matter, and now is widely used. Using this method, for a given ion the selfconsistent ground state and its energy are determined by minimizing the total energy functional with respect to the plane-wave coefficients.

\begin{itemize}
  \item \textsuperscript{i}http://vasp.at
  \item \textsuperscript{ii}http://www.quantum-espresso.org/
  \item \textsuperscript{iii}http://www.abinit.org/
\end{itemize}
The calculated forces on the nuclei are then used with equation of motion to
generate the trajectories of all the nuclei. The equation of motion might be used
through different methods to "relax" the atomic positions: quasi-Newton’s
equations or a conjugate-gradient algorithm [198]. The quasi-Newton’s equation
are used to obtain an accurate ground-state total energy, but this is only possible if
first we had previously relaxed the system. This is because this algorithm fails if
the initial atomic positions are a bad guess. To achieve this, finite steps of time are
used within discrete intervals. The selfconsistent ground state and the forces are
recomputed at each step.

In addition, k-point sampling and plane-wave cut-off are two important key aspects
that have to be controlled in a plane-wave DFT code using pseudopotentials.

B.2 The reciprocal lattice and the Brillouin Zone

The first Brillouin Zone is described as the Wigner-Seitz-type primitive unit cell of
the reciprocal lattice. This can be represented by including planes in the mid-point
between atoms of the unit cell. Therefore, the result is the smaller representation of
a system. This is very useful, because allows the correct description of the whole
system, while including the smallest amount of raw data, in order to save computing
time.

B.2.1 The Bloch’s Theorem of periodicity in crystalline systems

The Bloch’s Theorem [83] of periodicity in crystalline systems allows the
extrapolation of the results, that where obtained locally, to the whole bulk system
through its implementation.

Bloch’s theorem states that a wavefunction of an electron \( \psi_{j,k} \) within a periodic
system of potentials, is constituted by a product of an element representing the
lattice periodicity \( u_j(r) \) and another element representing the “local” wave-function
of the electron \( e^{i k \cdot r} \)

\[
\psi_{j,k}(r) = u_j(r) e^{i k \cdot r},
\]

where \( k \) is the wavevector in the band of \( j \)
The term \( u_j(r) \) has the same periodicity as the direct lattice, it can be expressed
in terms of a discrete plane-wave basis set with wavevectors \( G \) that are reciprocal
lattice vectors of the crystal

\[ u_j(r) = \sum_G c_{jG} e^{G \cdot r} \]  

(B.2)

The reciprocal lattice and the Brillouin Zone

The periodic boundary conditions allow to describe extended system using as a representation a portion of this array of atoms. In other words, the collection of atomic cores and electrons in the used cell or supercell is surrounded by periodic images of itself.

B.2.2 The \( k \)-points sampling in the Brillouin Zone

Partial occupancies help to decrease the number of \( k \)-points necessary to calculate an accurate band-structure energy.

The integral over the filled bands is:

\[ \sum_n \frac{1}{\Omega_{BZ}} \int_{\Omega_{BZ}} \epsilon_{nk} \Theta(\epsilon_{nk} - \mu) \, dk, \]  

(B.3)

Due to our finite computer resources this integral has to be evaluated using a discrete set of \( k \)-points

\[ \frac{1}{\Omega_{BZ}} \int_{\Omega_{BZ}} \rightarrow \sum_k w_k. \]  

(B.4)

Keeping the step function we get a sum:

\[ \sum_k w_k \epsilon_{nk} \Theta(\epsilon_{nk} - \mu), \]  

(B.5)

After fully relaxation of the forces with a finite temperature method, the linear tetrahedron method \([156]\) implemented in VASP allows the calculation of accurate total energies and densities of states. The main drawback in this method is that the Blöchl method is not variational with respect to the partial occupancies. The partial occupancies within the framework of the linear tetrahedron method are
straghtforward calculated because the linear tetrahedron method is outside the finite temperature density-functional theory. Within the linear tetrahedron method, the one-electron energies are interpolated linearly between the k-points, and the integral for the band-structure energy is performed analytically within each tetrahedron [153].

In this method a k-mesh which allows to construct tetrahedra should be included because the terms are interpolated linearly between two k-points. Therefore high symmetry k-point paths are not suitable.

### B.3 The pseudopotentials.

The pseudopotentials are potentials that mimic the movement of the electrons inside each atom in a way that the localized ones, that lie in the core levels are considered using an average potential, that contains them. This is done, in order to minimize the computational cost. The valence electrons are those that participate in the bonds, therefore their actual potential cannot be neglected. In the pseudopotential approach the electrons are divided into two classes: core electrons and valence electrons. The core electrons are exactly assumed to be in the same state as in the free atom. Which are the distinctive characteristics of the pseudopotential is that in the core region the resulting wave-like functions, either describe the atomic density as a whole and lack the rapid oscillations possessed by the true wave functions. In an ab initio pseudopotential, the interaction potential, that has almost exactly the same scattering properties, is replaced by an effective potential (pseudopotential) between valence electrons and atomic cores. This avoid describing the core electrons expliciterly and also avoid the rapid oscillations of the wavefunction near the nucleus, which normally require either complicated or large basis sets [199]. This "smoothness" allows the wave-like functions to be represented with rather simple mathematical basis functions. The normal procedure is to use as a basis free-electron wavefunctions, or plane waves.

#### B.3.1 The projector augmented waves (PAW) for the pseudopotentials and other types of pseudopotentials.

The Projector Augmented Waves (PAW) [154, 156] are a type of pseudopotential that gives reliable results. These pseudopotentials are a combination of the ultrasoft pseudopotentials (USPP) and LAPW method (Linear Augmented Plane
Implementation of vdW-DF functional

Waves) [200, 201]. The USPP [202] were proposed as an alternative method for the Norm-Conserving Pseudopotentials (NCP) that are hard potentials, that require an increased amount of Fourier components, especially for elements with valence $d$-orbitals. PAW pseudopotentials involve less parameters while include elements of the all-electron calculations. Nevertheless, the computational cost is rather small, so they use less plane-waves. Despite that PAW potentials are usually slightly harder than USPP, the results demonstrate an improved accuracy of PAW in same cases as, for example, magnetic material calculations.

In VASP the implemented pseudopotentials are USPP and Projector Augmented Waves (PAW). The USPP are generated through atomic levels (electronic configuration) and orbitals within DFT. This is done assuming a spherically symmetric self-consistent Hamiltonian [203]. The electronic configurations are obtained by solving a radial Schrödinger-like (Kohn-Sham) equation. Therefore, the generation of the correct USPP through a trial-error test should overcome different and rather profound issues for each situation. PAW potentials work reliably and accurately at the provided energy cutoff as they were tested. Therefore, in VASP wherever possible we have used PAW potentials. VASP includes a database of optimized PAW pseudopotentials and these have been used in this thesis for all calculations.

B.4 Implementation of vdW-DF functional

In VASP the vdW-DF method use the precalculated kernel which is distributed in the VASP package. Currently the evaluation of the vdW energy term is not fully done within the PAW method but the sum of the pseudo-valence density and partial core density is used. The implementations of this functional in VASP are a result of Michaelides et al [28, 98] work. In VASP manual there is an explanation for spin polarized calculations, but strictly speaking the non-local vdW correlation is not defined for spin-polarized systems. In our experience this functional only gives good results in semiconductor systems, while in transition-metal-doped semiconductors this is not suitable to be applied due to the lack of implementation in spin polarization. Further testing of these functionals both in the former version

\footnote{http://www.vasp.at/vasp-workshop/slides/pseudoppdatabase.pdf}
and also in that of the optimized one used for the SnS$_2$ polytypes was applied in this thesis.
Publications regarding this thesis
Refereed Journal Publications


7. Y. Seminovski, P. Palacios, and P. Wahnon. *Configurational Analysis of SnS<sub>2</sub> Doped with Vanadium Proposed as an Intermediate-Band Material In preparation*

8. Y. Seminovski, P. Palacios, P. Wahnon and R. Grau-Crespo Thermodynamic analysis of SnS<sub>2</sub> Doped with Vanadium. *In preparation*

9. Y. Seminovski, P. Palacios, P. Wahnon and R. Grau-Crespo High pressure analysis on CdIn<sub>2</sub>S<sub>4</sub> inversion degree. *In preparation*
Proceedings
Photovoltaic Meetings


5. J.C. Conesa, R. Lucena, Y. Seminovski, P. Palacios, P. Wahnon Metal-substituted octahedral sulphides for more efficient PV: theoretical modeling and experimental verification of sub-bandgap photon use *E-MRS 2013 Spring Meeting, Strasbourg* Symposium D Advanced inorganic materials and structures for photovoltaics


9. R. Lucena, F. Fresno, J. C. Conesa; P. Palacios, I. Aguilera, Y. Seminovski, P. Wahnon In$_2$S$_3$ and SnS$_2$, with or without doping, as visible light photocatalysts *E-MRS 2011 Spring Meeting, Strasbourg* Symposium S Novel materials for heterogeneous catalysis

Nanotechnology Meetings


Patents


Conference Presentations

Talks


Posters

1. Y. Seminóvski, P. Palacios, P. Wahnón "New Intermediate Band Based in CdTe. A defect interaction between a Cd Vacancy and Bi impurity and Other Defects." E-MRS 2013 Spring Meeting, Strasbourg.


7. Y. Seminovski, P. Palacios, P. Wahnon Description of Bi evolution in CdTe lattice using First Principles Calculations in VIII Seminars of Advanced Studies on Molecular Design (SEADIM8), La Habana, Cuba, Julio 2011

8. R. Lucena, F. Fresno, J. C. Conesa; P. Palacios, I. Aguilera, Y. Seminovski, P. Wahnon "In\textsubscript{2}S\textsubscript{3} and SnS\textsubscript{2}, with or without doping, as visible light photocatalysts" EMRS 27-31 May, 2013 Spring Meeting, Strasbourg, France.


13. P. Wahnon, J.C. Conesa, P. Palacios, R. Lucena, I. Aguilera, Y. Seminovski and F. Fresno. New generation of intermediate band materials for better use of


Bibliography


[8] L. Cuadra, A. Marti, and A. Luque, “Type II broken band heterostructure quantum dot to obtain a material for the intermediate band solar cell,” *Physica...*


