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Modélisation *ab initio* des défauts ponctuels chargés et de leur impact sur les propriétés opto-électroniques de matériaux semiconducteurs cristallins

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Abbreviations

BCC	Body-Centred Cubic
BSE	Bethe-Salpeter equation
CBD	Chemical Bath Deposition
CBM	Conduction Band Minimum
CIGS	$\text{CuIn}_{1-x}\text{Ga}_x(\text{S}_y\text{Se}_{1-y})_2$
CZTS	$\text{Cu}_2\text{ZnSnS}_4$
DFPT	Density Functional Perturbation Theory
DFT	Density Functional Theory
DGF	Defect Green's Function
DLS	Defect Localised State
DLTS	Deep Level Transient Spectroscopy
DOS	Density of States
DTL	Defect Transition Levels
EDX	Energy-dispersive X-ray spectroscopy
EHT	Extended Hückel Theory
EPR	Electron Paramagnetic Resonance
EXAFS	Extended X-ray Absorption Fine Structure
FERE	Fitted Elemental-phase Reference Energies
FTO	Fluorine-doped Tin Oxide $\text{SnO}_2\text{:F}$
GD3-BJ	Grimme's semi-empirical dispersion scheme of pair-wise corrections with Becke-Johnson damping
GGA	Generalized Gradient Approximation
LDA	Localized Density Approximation
NMR	Nuclear Magnetic Resonance
PA	Potential Alignment
PAS	Positron Annihilation Spectroscopy
PAW	Plane Augmented Waves
PBC	Periodic Boundary Conditions

PBE	Perdew Berke and Ernzerhof electronic density functional
PHS	Perturbed Host State
PL	Photoluminescence
PV	Photovoltaics
PVD	Physical Vapour Deposition
RPA	Random Phase Approximation
SC	Semiconductor
SCAN	Strongly Constrained and Appropriately Normed semilocal density functional
SCF	Self-Consistent Field
SEM	Scanning Electron Microscopy
SIMS	Secondary Ion Mass Spectroscopy
SM	Semi-Metal
SOC	Spin-Orbit Coupling
STM	Scanning Tunneling Microscopy
TB	Tight-Binding
TEM	Transmission Electronic Microscopy
TMD	Transition Metal Dichalcogenides
V_{OC}	Open-Circuit Voltage
VASP	Vienna Ab Initio Simulation Package
VBM	Valence Band Maximum
XRD	X-Ray Diffraction

Introduction

Context

The long-range periodic arrangement of atoms in crystalline materials has been proven since the beginning of the 20th century by the observation of the diffraction of a X-ray beam by a crystal.[1, 2] Several features of the diffraction patterns obtained, such as the number and spacing of spots¹, can be correlated to those of the atomic lattice encountered by the beam, in this case symmetry and cell parameters. This technique has been extensively developed to determine the crystal structure of solids. It yields an ideal description of the arrangement of matter at the microscopic scale as the periodic repetition in the three directions in space of an irreducible pattern, the unit cell.

The impact of the microscopic arrangement of atoms on the macroscopic properties of crystalline materials was highlighted early on.[1] For instance, the occurrence of cleavage planes when breaking a crystal is a direct manifestation at the macroscopic scale of the microscopic organisation of matter. Given this very strong structure-property link and the observation by early mineralogists of many macroscopic imperfections in natural samples, such as, among others, inclusions and cracks, it had soon been imagined that defects may exist at the microscopic level as well. The real microscopic structure is well described by the ideal model on average but local disorders exist, as illustrated in Figure 1.[3, 4] The first and most obvious ones are the surfaces delimiting the finite-size monocrystal, in opposition to the infinite ideal solid. Note that for the thermodynamic reasons exposed in Chapter 1, the equilibrium state of the material includes a non-zero intrinsic defect concentration related to the synthesis process. Defects appear from the early stages and throughout crystal growth. Of course in real materials which may not be in equilibrium conditions, they may evolve in time depending on the environment it is subjected to (temperature, corrosion, radiations, external solicitations such as electric fields and mechanical constraints, etc).

Large discrepancies between theoretical predictions based on the ideal crystal model and measurements of several mechanical (crack propagation, plastic deformations, etc), optical (color, luminescence, etc), ionic and electronic transport (electron/hole conductivities, carrier recombinations, thermal conductivities, etc) properties could only be explained *via* the presence of defects and their propagation. A synthesis of the different works leading to the acceptance of the concept of crystalline point defects is given hereafter. Such an importance of defects on the properties makes them of vital importance in applicative materials. Metallurgists have long been studying dislocations for their impact on the mechanical properties of metals, most notably to explain the transition from reversible deformation in the elastic regime to plastic deformations[5–8] and in the study of crack propagations and fractures.[9–12] The use of precipita-

1. in the case of diffraction by a monocrystal, peaks by a powder

tion hardening has allowed the development of ultrahard light alloys for the aeronautic industry.[13, 14] Since the early days of the development of the semiconductor industry, engineers and scientists have highlighted the importance of the control of impurities and dopants in semiconducting materials onto the electronic properties (hole/electron conductivity, hole-electron recombination rates, etc) of the different layers within a device.[15–17] The importance of defects in this field is illustrated in Figure 2. The process of aliovalent doping of silicon, the base material of the semiconductor industry, developed since its rise in the 1960s is one of the most educative examples for this. Hole (electron) doping is typically obtained by boron (phosphorus) substitutions of silicon atoms.[18, 19] The importance of point defects is not limited to silicon. Bulk point defects are still under extensive investigations in chalcopyrite and related 2nd generation photovoltaic (PV) thin-film materials.[20–24] Defect-related transport mechanisms are of paramount importance for battery materials.[25, 26] Crystal defects appear ubiquitous in applicative materials² thus their study and understanding appears as a field of both fundamental and technological importance.

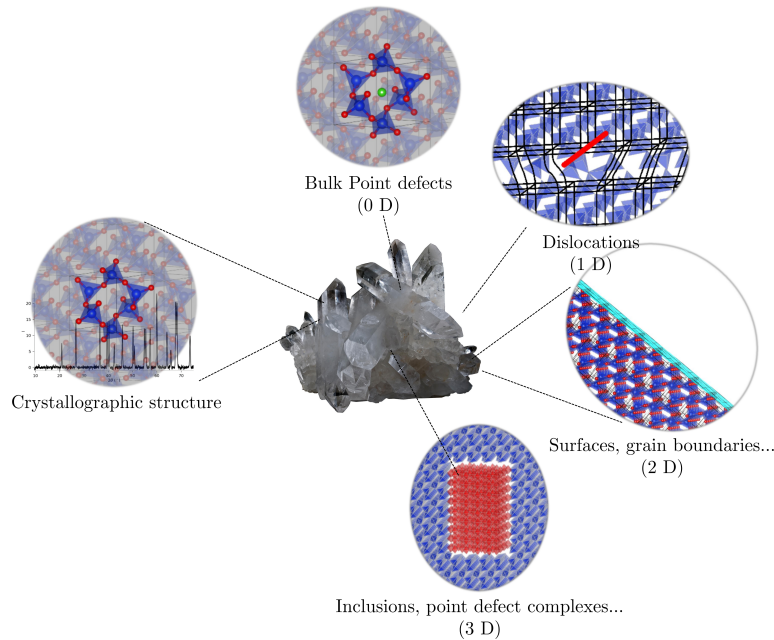


Figure 1: Different deviations from the crystallographic structure: from point to volume defects.

Different types of crystal defects exist and can be classified on a geometric argument. The “most elementary” defects are point defects (0D) involving a single atom. They are the most local lattice disorders. They are traditionally classified into three types, namely vacancies, interstitials and substitutions. Vacancies are atoms missing from their crystallographic position within the ideal structure as illustrated in Figure 3a. The notation employed throughout the manuscript for a vacancy of X is V_X . Interstitials are atoms sitting in a position normally unoccupied within the ideal host lattice, as shown in Figure 3b and noted X_i . Last, in compounds involving two or more atomic species, substitutions consist in atoms of a given chemical species occupying the crystallographic position of another species. The substitution of X by Y is noted Y_X herein. The association of several point defects within a few interatomic distances is referred to as a defect complex. It can be envisioned as a 3D defect (an inclusion) when so many point

2. with the exception of amorphous materials

defects aggregate that another structure appears locally. When involving extrinsic defects, it can be viewed as a sort of “pseudo-inclusion” to some respect. Defects involving only the chemical species of the compounds are intrinsic point defects and inherent to the material. Impurities and other voluntarily added species (dopants) may form extrinsic point defects. Fundamentally, substitutions can be viewed as the result of two primary operations on the lattice. Indeed, there are only two such operations possible on the lattice, that are either removing (creating a vacancy) or adding an atom. The substitution can be viewed conceptually as the result of the creation of a vacancy and the addition of an atom onto the vacant site. The insertion of an additional atom onto a vacancy also seems the most energetically favourable process for substitution formation. The typical point defect concentrations in non-degenerate semiconductors is 10-100 ppm[18]³.

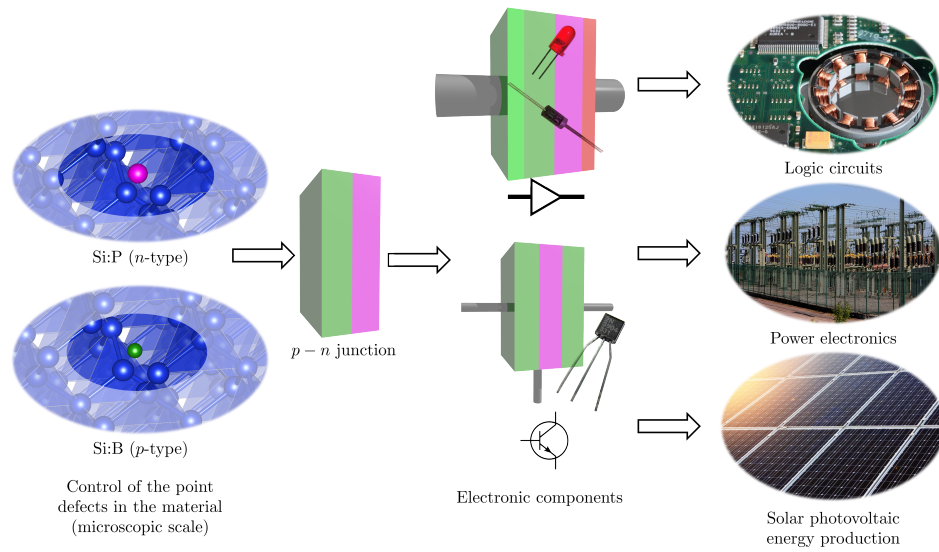


Figure 2: From defect control at the scale of the material to the engineering application.

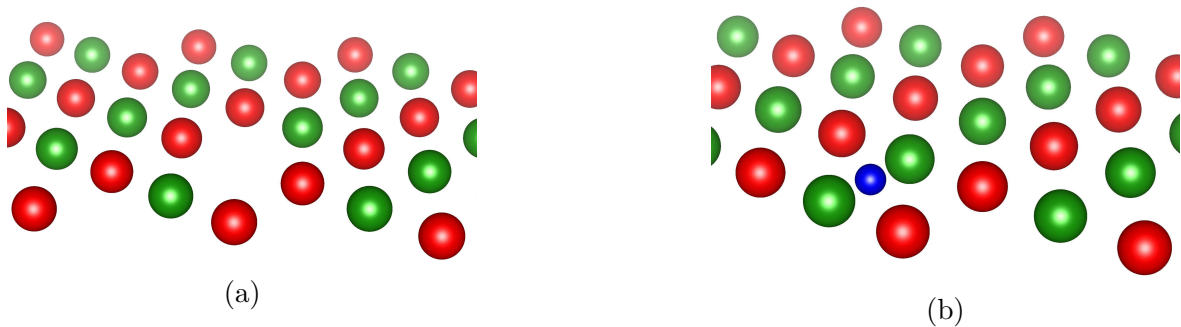


Figure 3: Illustration of point defects in a hypothetical lattice containing two types of atoms: a) a vacancy (a green atom is missing from the perfect lattice) b) an interstitial (an additional blue atom is added to the ideal atomic arrangement).

Line (1D) defects are called dislocations and can be separated into two types: screw- and edge-dislocations, both represented in Figure 4.[3] An edge dislocation can be regarded as an additional atomic plane. The screw dislocation can be described as

3. Part per million. For instance, a 10 ppm defect concentration in silicon, with a crystallographic cell of $20 \text{ \AA}$ containing 8 atoms, corresponds to a $5 \times 10^{17} \text{ cm}^{-3}$ volume defect concentration.

one block of atoms ripping onto another by one or more interatomic distance(s), for instance due to shear stress.

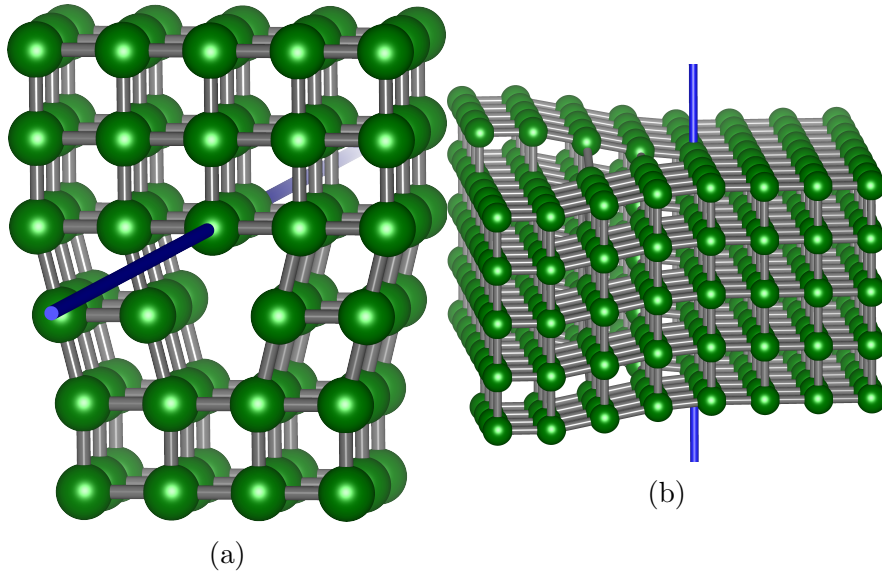


Figure 4: Line defects, *i.e.* dislocations. The axis is drawn in blue. a) Edge-dislocation can be seen as an extra atomic plane, here in the upper half of the figure. b) Screw dislocation can be seen as the result of shear stress on the lattice.

Planar defects (2D), such as stacking faults, crystal surfaces, twinning and grain boundaries⁴ also exist. One example of the latter is drawn in Figure 5. Finally, volume defects such as inclusions have also been studied by material scientists. As mentioned earlier, point defect complexes involving a very large number of defects can also be viewed as 3D defects.

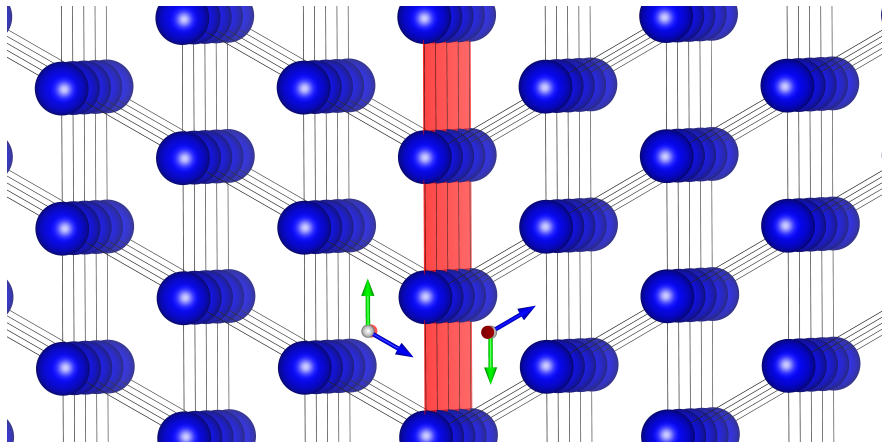


Figure 5: An example of surface defect: a twinning defect (red plane) in a hexagonal lattice. Blue spheres represent atoms.

Our research group focuses on optical and electronic properties of inorganic and hybrid materials and has a strong interest in structure-property relationship. Point

4. There is an underlying ambiguity behind the term “grain boundary”, as it can mean for some communities the surface separating two crystallites (regions of homogeneous lattice orientations) and for others the region between two grains (coherent entities). We accept the first and most stringent definition.

defects are known to play a major role in many physical phenomena involved in the field of optics, for instance as optical centres in luminescence mechanisms[27, 28] or electron/hole donors in optoelectronic devices.[3] Thus, of all the different types of defects presented beforehand, the field of point defect is of main interest for the group and is the object of this work. Of course, defects of higher dimensions exist in the materials investigated but are not studied herein, as the opto-electronic properties of interest are first driven by point defects. Given the fact that metals reflect most of the incoming light and insulators have a bandgap too large to absorb sunlight, the materials investigated in the present manuscript are all semiconductors. A particular emphasis was put on materials related to the PV field, *i.e.* generation of electricity from sunlight absorption. Indeed, in addition to the current need for more sustainable ways of generating electricity, they provide interesting technical and scientific challenges. Systems studied were not limited to this application and materials of fundamental scientific interest were also studied.

The idea of the existence of point defects dates back from the beginning of the previous century, when Frenkel measured a lower ionic conductivity than theoretically expected and imagined pre-existing vacancies to explain the easier than predicted displacement of ions.[29] Schottky and Wagner among others further investigated the possible types of point defects within a crystal.[30, 31] Koch and Wagner pioneered the experimental control of defect concentrations *via* doping on AgBr and CdBr₂. [32] The following decade saw the application of these scientific discoveries to the development of the semiconductor industry.[33–35] By the beginning of the 1960s, defect chemistry had become an important field in the area of material growth.[36–39] The existence of a forbidden band in the electronic structure of semiconductors and insulators implies that point defects may be charged. Conceptually, the emphasis was then put on charge balance by compensating defects. In particular, the idea of Schottky and Frenkel defects were widely used. A Schottky defect is a neutral defect complex involving cationic and anionic vacancies, such as $V_{Cd}^{-2} + V_S^{+2}$ in PV buffer material CdIn₂S₄. A Frenkel defect is an atom displaced from its crystallographic position in the host cell to a neighbouring interstitial site, such as $V_{Cd}^{-2} + Cd_i^{+2}$ in the same material. Literature from this period most probably employs the notation introduced by Kroger and Vink ($V_S^{+2} = V_S^{\bullet\bullet}$ and $V_{Cd}^{-2} = V_{Cd}''$).[40]

The importance of point defects in the design of an electronic device has been illustrated in Figure 2. Let us now cover the physical mechanisms at stake through the well-known example of silicon, the historical material of the semiconducting industry. As mentioned previously, the first step to master is the elaboration of hole (electron) doped semiconductors. It is obtained *via* the incorporation of acceptor (donor) dopants, such as boron (phosphorus), as represented in the lower half of Figure 6. The boron atom represented by the green sphere in the bottom-left corner ($q=0$) has three valence electrons ($2s^2 2p^1$ electronic configuration), one less than silicon constituting the host lattice ($3s^2 3p^2$). In silicon, the formation of four covalent bonds ensures the stabilising filling of the outer 3p orbitals of Si in a tetrahedral conformation. The boron atom sitting in place of a silicon atom can also form four covalent bonds with the neighbouring silicons. However, it has one less valence electron than silicon. Thus, it can be ionised by the thermal kinetic energy to accept one electron from the host lattice ($q=-1$). The corresponding charge is represented in yellow. It is localised and fixed on the defect. The electron excited from the Valence Band of the host leaves an empty electronic state, a “hole” quasi-particle, represented in cyan. It is delocalised and may leave the defect site. It acts as a free positive charge carrier. The defect ionisation energy

positions the “defect level” in the bandgap, represented by a solid black line on the band structure of Figure 6. This micro-process involving one defect and one electron can be apprehended from a global point of view using concepts of statistical physics. At very low temperatures, the chemical potential of the electrons, *i.e.* the Fermi level μ_{E_F} , lies halfway between the defect level and the Valence Band Maximum (VBM). The defect bears no charge ($q=0$) at low temperature.⁵ As stated in semiconductor textbooks, the Fermi level in this *p*-doped material increases with temperature to stabilise mid-gap once the entire acceptor defect population is ionised. Electron doping, for instance thanks to substitution of silicon by phosphorus, works similarly, *mutatis mutandis*.

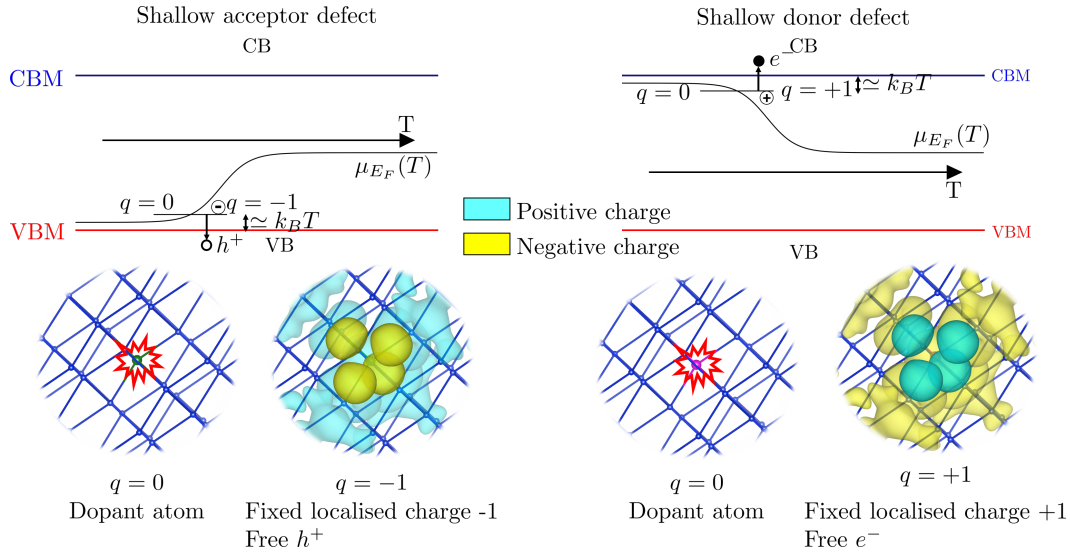


Figure 6: Thermal activation of shallow defects. A schematic electronic band diagram featuring the band extrema is shown in the top half. The Charge Transition Level is represented by the solid line near the VBM (CBM) for the acceptor (donor) defect. Variations of the Fermi level μ_{E_F} with respect to the temperature T are embedded in the bands. The well-known examples of Si:B (0/-1) and Si:P (0/+1) introduced in Figure 2 are kept here. As discussed in Chapter 1, it can be generalised to any acceptor/donor defect in semiconductors. The $q = 0$ (left) and the ionised, $q \neq 0$, (right) states of the defect are illustrated in direct space in the lower half of the Figure. The substitutional dopant atom is visible in darkgreen (acceptor) and pink (donor). Cyan (yellow) symbolises positive (negative) charges.

The next step towards device fabrication consists in the creation of a *p-n* junction, schematically by putting in contact a *p*- with an *n*-doped semiconductor, as illustrated in Figure 7.⁶ Near the junction in the *p*-doped material (darkgreen), the free holes are repelled by the positive fixed charges (cyan) on the *n*-side (pink). Similarly, electrons in the *n*-side are repelled by the fixed negative charges on the other side of the interface. It

5. Four covalent bonds are formed with the neighbouring silicon atoms. The thermal kinetic energy at very low temperature is insufficient to ionise an electron from the host lattice and the system remains in this configuration. The charge of the three valence electrons, one less than in silicon atoms, is exactly compensated by that of the nuclei of the boron atom, hence the neutral charge of the defect.

6. In practice, the two materials are not grown separately and then assembled. For a heterojunction, *i.e.* different *p*- and *n*-type materials, one material is directly grown on top of the other. For a homojunction, *i.e.* same *p*- and *n*-type material, different dopants, it is often more appropriate to implant one dopant in the material already doped with the other. For instance, *p-n* junction in silicon are often obtained by implanting donor dopants in a *p*-doped silicon ingot.

creates a region in the vicinity of the interface depleted in free charge carriers (electrons and holes), the space charge region, inducing a build-in electric field as represented. In terms of band structure, the populations of electrons and holes equilibrate, fixing the Fermi level to a single value within both semiconductors.

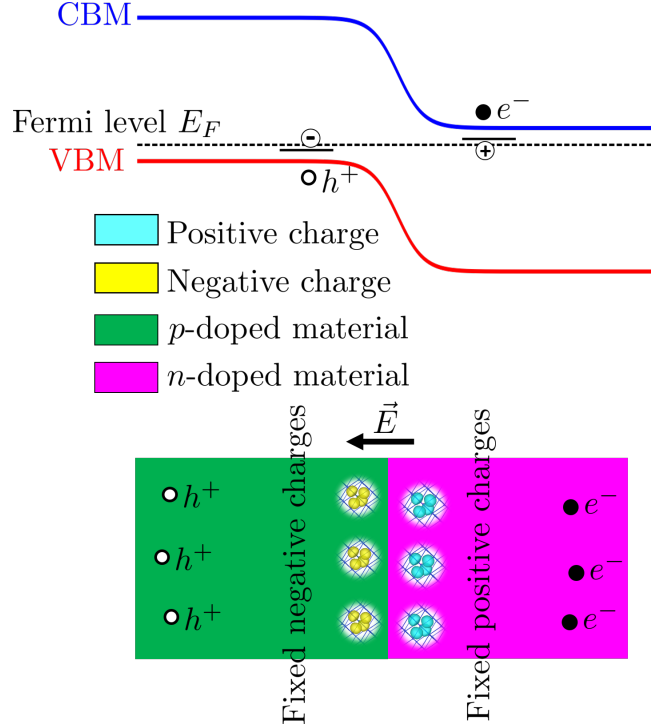


Figure 7: p - n junction at equilibrium. A schematic electronic band diagram featuring the band extrema is shown in the top half. The Fermi level E_F is represented by the dotted line. The spatial distribution of fixed (ionised defects) and free charges (carriers) in the junction is represented in the lower half. The p (n)-doped material is drawn in green (pink). Cyan (yellow) symbolises positive (negative) charges.

Finally, one or more junction(s) is(are) embedded into an electronic component (diode, solar cell, transistor...) by adding some functional layers not described herein and connecting it to an external electric circuit. The focus in the present work is set on solar cells, with most results of interest for other optic, electronic and opto-electronic applications. A simplified solar cell under illumination and its associated schematic band diagram are presented in Figure 8. A photon of energy higher than the bandgap of a semiconductor may excite an electron from the Valence Band (VB) into the Conduction Band (CB), generating an electron-hole pair. This is known as the photoelectric effect and is represented in the left half of Figure 8. It drives the splitting of the Fermi level into two quasi-Fermi levels, E_F^p (E_F^n) for holes (electrons) in the p (n)-side as represented by the two dotted lines of Figure 8, and the rise of an electrostatic potential energy difference V .⁷ The potential in the n -doped region is inferior to the potential in the p -doped side. Due to the presence of the electric field (sum of the build-in field and the one induced by V), the electron-hole pairs separate themselves. Holes (electrons) in the Valence (Conduction) Band of the p (n)-doped material flow to the left

7. The generation of electron-hole pairs under illumination due to the photoelectric effect leads the system out of equilibrium. The free hole (top of VB) and electron (bottom of CB) populations in such case are described not anymore by one but by two independent Fermi distributions centered on two quasi-Fermi levels.

(right) side of the drawing. The charge current may be hindered by different physical processes. Defects at the p/n interface may lead to carriers recombinations.[41] Free electrons at the bottom of the Conduction Band may spontaneously recombine with holes, *i.e.* changing their electronic state to lower their energy to that of the Valence Band. The total conservation of the momentums is guaranteed by the release of some energy to the lattice, often viewed as the creation of a phonon of momentum $\vec{q}_p$. This situation is represented in Figure 8. The recombination may also re-emit a photon (not represented). The propagation of free charge carriers may also be hindered by deep defects in the gap. The defect-assisted electron-hole recombination creates a phonon, as represented in Figure 8. Last, charge carriers may interact with the lattice vibrations (phonons). This phenomena is known as electron-phonon scattering. The related mesoscopic variables are carrier mobility and mean free path, which can be evaluated experimentally.[42, 43] In spite of the different mechanisms listed previously, some free carriers reach the electrodes leading to the formation of an electric current I within the external circuit, as represented in the lower half of the Figure. This demonstrates that different point defects, acceptors, donors, deep defects, intervene at all stages of the material use, from the design of a single semiconductor to its operation within a device.

In order to develop a deeper understanding of the physical mechanisms involved, several experimental techniques were tried out to characterise point defects.[44–47] The reference materials to test new developments soon became diamond, silicon, and to a lower extent GaAs⁸ thanks to the extensive literature accumulated on these compounds. Numerous measurement techniques emerged from decades of trials for the experimental investigation of point defects, listed in the two comprehensive reviews on the matter by Freysoldt *et al.* and Alkauskas *et al.*[48, 49] All have specific constraints on the defects investigated. Extended X-ray Absorption Fine Structure (EXAFS) can potentially be used to study the distortions induced by heavy impurities. Scanning Tunneling Microscopy (STM) may give structural information on the surface as well. Secondary Ion Mass Spectroscopy (SIMS) provides extrinsic defect concentrations with respect to the depth, but is irrelevant for intrinsic defects. The detection threshold varies from one element to the other. Electron Paramagnetic Resonance (EPR) relies on the presence of unpaired electrons and their interaction with an applied magnetic field to give valuable insight on symmetry and chemical species within the environment of a defect. Hall effect measurements yield charge carrier concentrations and mobilities. Photoluminescence (PL) measurements can be used to search for the fingerprints of specific impurities. Deep Level Transient Spectroscopy (DLTS) and Positron Annihilation Spectroscopy (PAS) are among the most used. DLTS[50–54] allows the determination of the concentration of deep level defects (carrier traps) through the measure of transient capacitance of the material. One or more voltage pulses are applied to the material at different temperatures and the rate of the return to equilibrium is measured.[50] It is limited to the study of deep⁹ defects. PAS[55–57] consists in bombarding the sample with positrons, the antiparticle associated to the electron, and measuring their lifetime. When encountering electrons from the ions of the sample, positrons are annihilated. Therefore, any void, and for the present interest, vacancies, increase their lifetime.[56, 57] Each technique will globally sum all detected defects at the scale of the sample. Moreover, most of them do not allow the identification of the defect without any prior knowledge of its nature (DLTS, Hall, PL, PAS) and their practical imple-

8. the III-V semiconductor used in PV panels of space exploration

9. in the electronic sense

mentation may be cumbersome, often involving the use of large and complex apparatus (EXAFS, PAS, STM, EPR). Thus, a complementary method allowing the comprehensive determination of all defects would prove a valuable asset for the community.

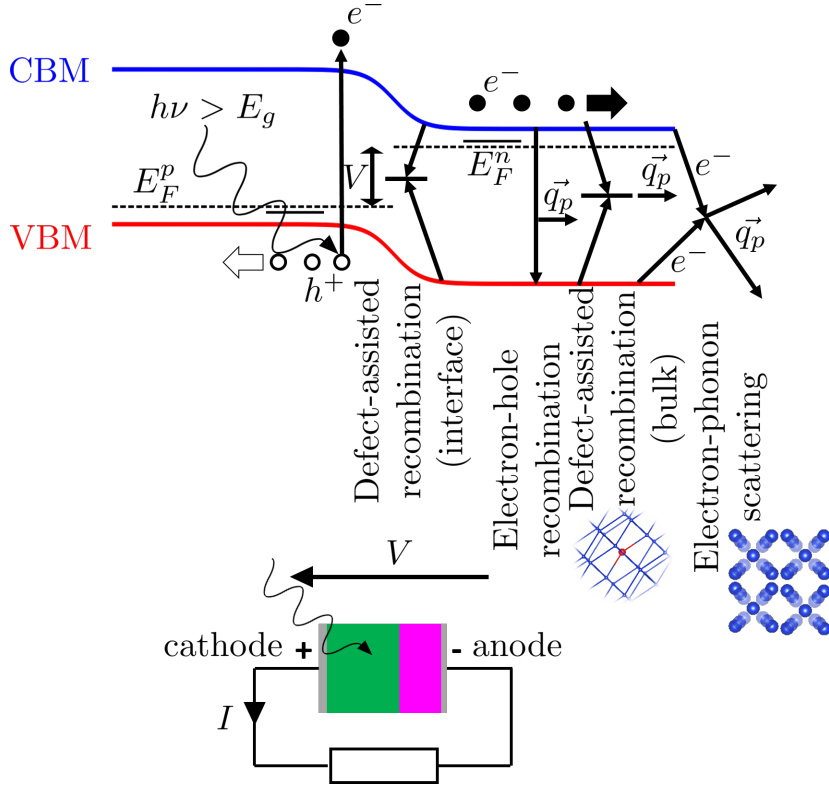


Figure 8: Simplified solar cell under illumination. Photons of energy $h\nu$ higher than the bandgap may transmit their energy to electrons e^- at the top of the VB, generating an electron-hole pair (left). The hole h^+ (electron) quasi-Fermi level E_F^p (E_F^n) is represented in dotted line. The difference constitutes the voltage V . The electric field generated in the space charge zone separates the carriers, giving rise to a hole (electron) current to the left (right) of the Figure towards the anod (cathod) of the device. Some physical processes potentially lowering the carrier lifetime are represented on the right side. $\vec{q}_p$ stands for the phonon momentum. The corresponding electric circuit when the cell is connected to a resistor is drawn in the lower half.

As discussed before, point defects are the smallest lattice imperfections that one can imagine and are objects of atomic scale. The behaviour of matter at this scale, or at least of the electronic cloud, is most appropriately described by quantum mechanics. Theoreticians have developed the physical models and mathematical tools enabling simulations of matter at this scale. Early on, defects have been subjects of interest for theoreticians. Let one draw a quick portrait of the different modeling strategies which were tried out as the joint evolution of simulation techniques and computational power unfolded.

First, Debye-Hückel model for electrolytes[58] introduced in 1923 was generalised to calculate the activity of point defects in solid-state and used throughout the 1960s as a model to calculate defect concentrations semi-empirically.[38, 59–62] As quantum chemistry developed, the Extended Hückel Theory (EHT) for molecular orbitals allowed to compute small clusters in the presence of a defect.[63–65] Dangling bonds at the edges of the cluster were usually passivated by adding additional hydrogen atoms. In spite of being at the state of the art of possible simulations at the time, researchers

wondered whether the model would be close enough to the real system to get physical trends.

The impurity problem continued to puzzle the community and the late 1970s saw the practical application of early ideas of Koster, Slater and others to tackle it. They proposed to consider the point defect problem as a perturbation of the wavefunction of the ideal host lattice and to follow a Green’s function framework to find the wavefunction of the faulted system.[66, 67] This method may be referred to as Defect Green’s Function (DGF) in literature of this period. In more concrete terms, this is the mathematical translation of embedding a defect within the ideal lattice.[68] As for every new development, silicon was the most studied material using these methods.[69–73] In practice, it was either implemented within a Tight-Binding (TB) model or using pseudopotentials, although it was demonstrated later on that the latter was to be preferred.[74] The drawbacks of the DGF method were the use of localised basis sets, with the associated forces and basis set convergence issues, and early implementation not allowing relaxation of the defect geometry.[68]

The following decade took a radically different approach to solve this issue. Density Functional Theory (DFT) had established itself as a valuable tool for solid-state calculations and provided a convenient way to compute total energy and various other properties, including band structure (in spite of the bandgap problem discussed in Chapter 1). Planewave basis set along with Periodic Boundary Conditions (PBC) had been implemented in codes routinely used by a growing community and under constant improvements. In the mid-1980s, the computational power had become sufficient to build supercells of tens of atoms and faulted systems were simulated.[75–78] This new method quickly gained popularity and overtook the DGF method. It has since been constantly evaluated and improved and remains so far the standard approach to model point defects. Its main advantages compared to DGF are the fact that relaxation is taken into account, and on a more practical basis, that it builds upon the strengths of the numerous planewave DFT codes available. Of course, the method is not without its imperfections, discussed in details in Chapter 1, but allowed to gain valuable insights in applicative materials such as, among others, traditional III-V semiconductors (GaN,[79–82] GaAs[83, 84]), oxides (ZnO[85–88]), chalcogenides for PV solar cells (CuInSe₂,[89, 90] CuGaSe₂[91, 92]). This propelled the supercell approach to become a key technique complementary to experiment with a predictive power.

Aim, scope and organisation of the present work

The aim of the present work is to determine the key defects in materials with potential applications for their optical and/or their electronic properties or more broadly with a fundamental interest. The impact of point defects regarding the targeted properties is studied through the supercell approach within the DFT framework.

The present manuscript is organised as follows. The supercell methodology is detailed in Chapter 1 using mainly Sb₂Se₃, a binary chalcogenide with potential application as a PV absorber, as the running example. A detailed computational study on the intrinsic and extrinsic point defects of β -In₂S₃, a buffer material for thin-film chalcogen solar cells, is presented in Chapter 2. Experimental trials are briefly discussed. Then, TiS₂ provides an interesting system to assess the limits of the study on the fundamental question of its semiconducting or semimetallic nature, as detailed in Chapter 3. Selenium, an element at the heart of current research on chalcogenides for PV, is also considered as a potential absorber, and offers the opportunity to tackle

some simulation challenges, as reported in Chapter 4. Finally, a general conclusion closes the present manuscript and brings perspectives for future work on the subject. During the three years of research leading to this manuscript, a portfolio of seven materials investigated for their defect properties was constituted, namely β - In_2S_3 , Sb_2Se_3 , CsCu_5Se_3 , TiS_2 , ZrSe_2 , β - and γ -Se. For the sake of clarity, only β - In_2S_3 , TiS_2 and Se results are discussed in detail herein. Sb_2Se_3 is extensively used as an example to explain the supercell methodology throughout Chapter 1.

Chapter 1

Point defects simulations in solids

1.1 Thermodynamics: from Gibbs' free energy to enthalpy of defect formation

As discussed in the introduction, the microscopic structure of real-life compounds deviates from the (ideal) crystallographic structure due to the presence of defects. They can be classified depending on their dimensionality (0D to 3D) and have a major impact on the properties of materials. The present work focuses on the simulation of point defects, which are defects involving one single atomic site, and their impact on opto-electronic properties. The central question the model presented herein aims to answer is the amount of energy required to create a single point defect. The fictional reaction of defect formation considered for the following thermodynamic reasoning is illustrated in Figure 1.1. The initial state is the ideal lattice and the final state is the lattice after introduction of a single point defect. This is formally the problem we want to simulate. We will see hereafter that the application of periodic boundary conditions on a system of reasonable size for DFT calculations slightly modifies our system.

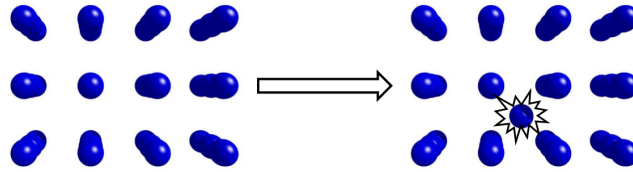


Figure 1.1: Reaction of point defect formation considered illustrated in the case of an interstitial defect. Blue spheres represent the atoms. The initial state (left) is the ideal lattice and the final state (right) is the ideal lattice after introduction of a single point defect.

The process of defect creation stems from the competition between the stability of the ideal crystal on the one hand and the increase in entropy due to defect creation on the other hand. The stability of the periodically-organised system, the ideal crystal, is due to the formation of chemical bonds and the minimisation of electrostatic interactions. The increase in entropy comes from the breaking of symmetry induced by the point defect, the appearance of a disorder.[3, 93] It is due to the thermal kinetic energy. In more conceptual terms, the creation of defects allows to lower the Gibbs' free energy of the system by increasing the entropic contribution. Indeed, entropy is a measure of the microscopic disorder. Formally, the Gibbs' free energy of formation of a defect D in charge state q noted $\Delta G^{D,q}$ is given by equation 1.1 as a function of

pressure P and temperature T .

$$\Delta G_{form}^{D,q}(P, T) = \Delta H^{D,q}(P, T) - T\Delta S_{form}(P, T) \quad (1.1)$$

By using the definition of the enthalpy, it can be stated as in equation 1.2.

$$\Delta G_{form}^{D,q}(P, T) = \Delta E_{form}^{D,q}(P, T) + \Delta(PV(P, T)) - T\Delta S_{form}(P, T) \quad (1.2)$$

Strictly speaking, the direct application of thermodynamics entices us to evaluate $\Delta G^{D,q}(P, T)$, nevertheless, it might prove a challenging task in practice.

DFT, the workhorse of computationally-oriented material scientists, is a ground-state theory well-adapted to total energy computations at absolute zero temperature. Taking into account the internal variables (P and T) does not seem as direct. Despite such obstacle, the weight differences between each contribution might give a valuable help to overcome this difficulty. In order to approach this state function, the quantitative importance of each term should be evaluated to discard negligible terms if appropriate.

Let us start with the importance of the pressure-volume term. The object of the model is diluted point defects. One can view it as one single isolated defect formed in an otherwise ideal crystal. Hence, the variation of volume due to the creation of the defect is negligible in this dilute case. Thus, the formation enthalpy can reasonably be approximated by the internal energy, noted here ΔE . Additionally, the frequently-used Birch-Murnaghan third order equation of state 1.3 allows to assess numerically the weight of the contribution of the $\Delta(PV(P, T))$ term.[94] In equation 1.3, we introduce the volume ratio $r = \frac{V_0}{V}$ where V_0 is the equilibrium volume without any external pressure. We note $B_0 = -V \left(\frac{\partial P}{\partial V} \right) \Big|_{P=0, T}$ the equilibrium bulk modulus and $B'_0 = -V \left(\frac{\partial B_0}{\partial P} \right) \Big|_{P=0, T}$ its derivative with respect to pressure. As highlighted in Figure 1.2, one must apply tremendous pressures of several gigapascals to get a $PV(P)$ -energy significantly higher than a tenth of electronvolt, corresponding to a variation of volume of no more than a few per cent. The “chemical pressure” induced by the introduction of a dilute defect in the ideal lattice is in no way comparable to such pressures. This intuition can be cross-checked against calculation results, as the relaxation of the faulted supercells with periodic boundary conditions yields a pressure value. This value corresponds to a largely overestimated upper-bound for the true pressure induced by the defect, as the ratio of defect in the supercell model is largely higher than the real concentration. In the example case of Sb_2Se_3 , the pressure calculated during geometry optimisation does not exceed 30 kbar= 3 GPa. Figure 1.2b shows that, although the exact value of $\Delta PV(P)$ varies from one material to another, the order of magnitude is the same. So the upper-limit for $\Delta PV(P)$ in Sb_2Se_3 is indeed a few tenth of electronvolts.¹ From these numerical verification, one can conclude that the pressure-volume term can safely be neglected in the expression of $\Delta G^{D,q}$ to tackle the modelling of defects. $\Delta G^{D,q}$ then simplifies to the Helmholtz free energy of formation as expressed in equation 1.4. Note that if one is interested in such properties, as can the metallurgist community be, the effect of point defects on mechanical properties can be assessed through elastic theory from the field of continuum mechanics, as illustrated

1. Note also the practical difficulty to evaluate the variation ΔPV as the optimisation of both atomic positions and cell parameters will yield a pressure of zero and also conflicts with the dilute defect picture, whereas imposing cell parameters constant to the ideal ones during relaxation is equivalent to a constant volume, $\Delta V = 0$. In this case, $P\Delta V = 0$, yielding $\Delta PV = V\Delta P$.

by the works of Varvenne *et al.*[95, 96]. However, in semiconductors this is rarely the main interest of the community.

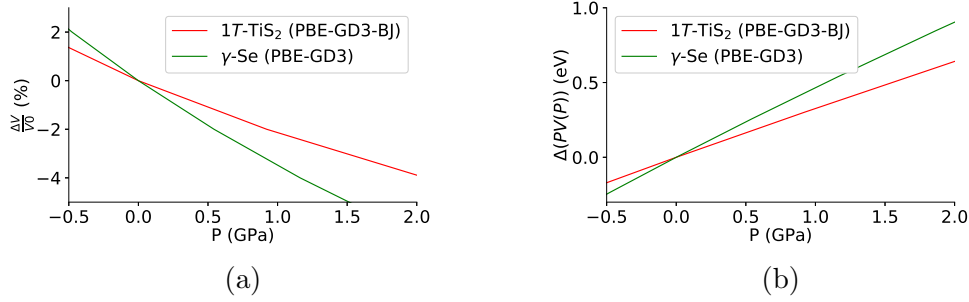


Figure 1.2: a) Relative variations of volume of 1T-TiS₂ (in red) and γ -Se (in green) with respect to pressure calculated by fitting equations 1.3 onto series of dispersed-corrected PBE calculations at different volumes, b) amplitude of the pressure-volume term in the expression of the enthalpy for 1T-TiS₂ (in red) and γ -Se (in green) with respect to pressure calculated by fitting equations 1.3 onto series of dispersed-corrected PBE calculations at different volumes.

$$\left\{ \begin{array}{lcl} r & = & \frac{V_0}{V} \\ B_0 & = & -V \left(\frac{\partial P}{\partial V} \right) \Big|_{P=0, T} \\ B'_0 & = & -V \left(\frac{\partial B_0}{\partial P} \right) \Big|_{P=0, T} \\ E(V) & = & E_0 + \frac{9}{16} B_0 V_0 \left(r^{\frac{2}{3}} - 1 \right)^2 \left(\left(r^{\frac{2}{3}} - 1 \right) B'_0 + 6 - 4r^{\frac{2}{3}} \right) \\ P(V) & = & \frac{3}{2} r^{\frac{5}{3}} \left(r^{\frac{2}{3}} - 1 \right) \left(1 + \frac{3}{4} (B'_0 - 4) \left(r^{\frac{2}{3}} - 1 \right) \right) \end{array} \right. \quad (1.3)$$

$$\Delta F = \Delta E(P, T) - T \Delta S(P, T) \quad (1.4)$$

Then, one should assess the weight of the entropic term. Intuitively, solid-state is a highly organised state of matter and, as stated before, entropy is a measure of disorder. One can foresee that the enthalpy contribution to $\Delta G^{D,q}$ will be predominant. Rigorously from statistical physics, the entropy of a closed system is defined as expressed in equation 1.5, where Ω stands for the microscopic distribution function and k_B , the Boltzmann constant ($\simeq 8.617 \cdot 10^{-5}$ eV.K⁻¹).

$$S = k_B \ln(\Omega) \quad (1.5)$$

In a crystalline solid, the entropic term comes from three contributions ; by decreasing order of magnitude, the configurational entropy, the vibrational entropy and the electronic entropy.[48, 93] Let us address the configurational entropy first. To assess it, one must evaluate the number of microscopic states of the system arising from the different configurations which can be explored by the system. Due to the large number of particles n involved in the system (a crystallite typically), the Stirling approximation² stands. It allows to express the configurational entropy in the form of

2. $\ln(n!) \underset{n \rightarrow +\infty}{\sim} n \ln(n) - n$

equation 1.6 where k_B stands for the Boltzmann constant, $[D^q]$ stands for the concentration of defect D expressed not as a volume concentration as usually is but as the ratio of the number of defects (faulted crystallographic cells) over the total number of cells constituting the system and N_{sites} stands for the degeneracy of the defect, *i.e.* the multiplicity of the available sites for the defect in the structure. Fundamentally, this expression is based on the mathematical function $x \mapsto x(1 - \ln x)$ with $x \in [0, 1]$. The statistical physics behind it are technically valid for any defect concentration (inferior to one to keep a physical meaning), but since the defect model presented is based on the dilute defect assumption, the x ratios will be largely inferior to one (concentrations of a few hundreds ppm).

$$\Delta S_{conf} = k_B([D^q] - [D^q] \ln[D^q] + [D^q] \ln(N_{sites})) \quad (1.6)$$

As shown in Figure 1.3, it weights no more than 0.12 eV at high temperatures, and can thus be safely neglected unless a highly accurate picture is desired.

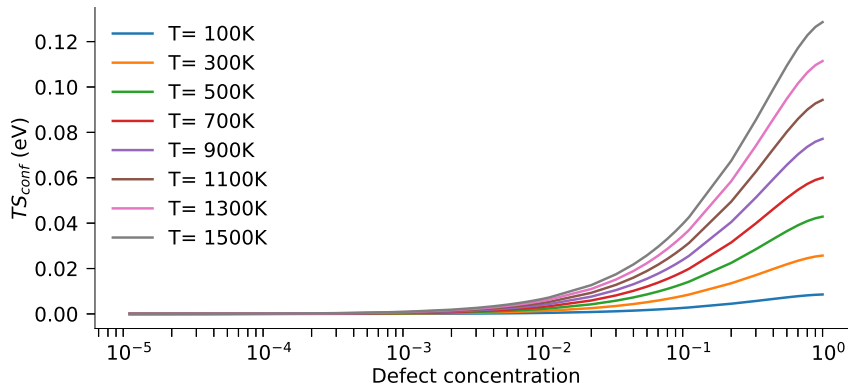


Figure 1.3: Product of configurational entropy and temperature as a function of defect concentration for different synthesis temperatures. The entropy is calculated using equation 1.6. Note that even at high temperatures, it is inferior to 0.12 eV.

In the framework of periodic boundary condition *ab initio* calculations using DFT, the number of particles is fixed, there is no exchange with a particle reservoir, and the temperature is also fixed to zero, as only the equilibrium position of the nuclei is determined in a static picture at $T = 0$ K. It is however, possible to evaluate the increase in energy due to the displacement of the nuclei from the equilibrium position, either using perturbation theory or finite differences. As pointed out by Neugebauer *et al.*, one could compute the vibrational entropy term for a very high, most of the time prohibitive, computational cost.[48, 97] The importance of this term is expected to vary with the class of materials and the physical process leading to defect formation, especially the synthesis temperature. In any case, it is quantitatively even less important than the configurational entropy so can in turn be neglected as well. The electronic contribution to the entropy comes from the additional electronic states available to the system of electrons due to the introduction of the defect. The number of new configurations available to the distribution function Ω in equation 1.5 is small and the logarithmic relationship between S and Ω makes the electronic defect formation entropy negligible.

This quantitative assessment of the weight of the different terms contributing to the Gibbs' free energy of formation of a defect allows us to reasonably simplify the calcu-

lation of this thermodynamic state function to the calculation of the defect formation energy. It will be hereafter referenced either as Defect Formation Energy or Defect Formation Enthalpy (DFE) due to the absence of variations in volume in the case of dilute defects.

So far, the community's efforts focusing on the defect formation energies have already led to qualitative and quantitative results for a wide range of applicative materials, *i.e.* Si,[98–100] GaN,[49, 80, 101, 102] GaAs,[103–106] ZnO,[103, 107] PbTe [108–111] and CIGS derivatives.[112–114]

DFE expression

Now that we have simplified the problem to the determination of an energy, we can come back to our model reaction sketched in Figure 1.1. The process of forming a point defect in a lattice can be seen as the exchange of atoms with an "atomic" reservoir (within the reactor, the source of the chemical species involved in the defect) and electrons with an "electronic" reservoir, as illustrated in Figure 1.4. This electronic reservoir can be envisioned as the result of the reducing/oxidizing power of the synthesis conditions. In the case of solid-state synthesis for instance, it is linked to the atmosphere under which the reaction occurs. Thus it derives from the oxygen partial pressure in the reactor for the synthesis of an oxide, the use of argon, hydrogen or nitrogen atmospheres when relevant for other classes of materials. The defect formation enthalpy $\Delta H_{form}^{D,q}$ is expressed [48, 115] as a linear function of the chemical potential of the electrons (Fermi level), noted in this work μ_{EF} , and of the chemical potentials of the elements involved in the defect D as stated in equation 1.7.

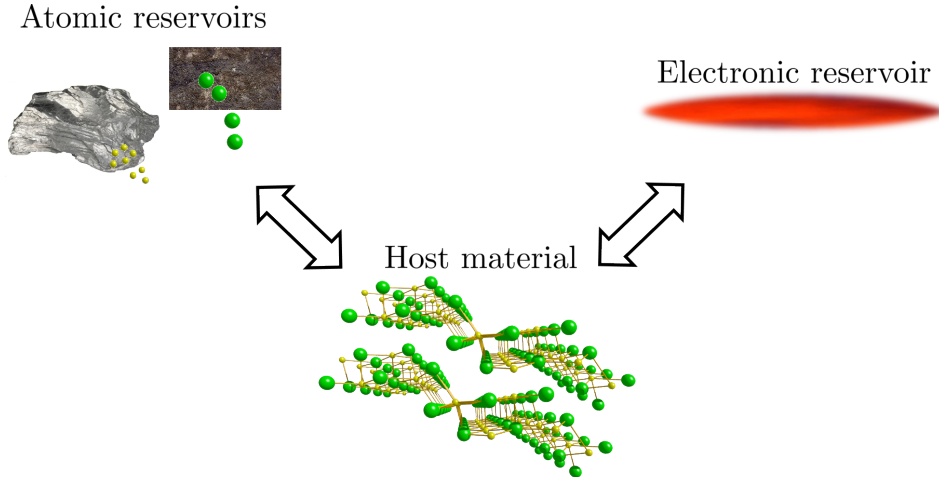


Figure 1.4: Illustration of the concept of reservoirs during the formation of a defect with the example of Sb_2Se_3 .

$$\Delta H_{form}^{D,q}(\mu_{EF}) = E_{total}^{D,q} - E_{total}^{host} + \sum_{X_i} n_{X_i}(\mu_{X_i}^0 + \Delta\mu_{X_i}) + q(E_{VBM}^{host} + \mu_{EF}) + corr(D, q) \quad (1.7)$$

where

- $E_{total}^{D,q}$ is the total energy of the faulted supercell (the supercell containing the defect) after relaxation of the atomic positions at fixed cell parameters³ without symmetry constraints⁴
- E_{total}^{host} is the total energy of the ideal supercell (also referred to as the host cell)
- $\mu_{X_i}^0$ is the chemical potential of element X_i in its standard phase (for instance, crystal α -S₈, indium metal and O_{2(g)} in the case of sulphur, indium and oxygen, respectively)
- $\Delta\mu_{X_i}$ is the variation of the chemical potential of element X_i from its chemical potential in the thermodynamic standard phase ($\Delta\mu_{X_i} < 0$), induced by the crystal growth conditions as detailed in the next paragraph
- n_{X_i} is the number of atoms of species X_i added to the ideal host lattice ($n_{X_i} < 0$), for instance, $n = -1$ in the case of an interstitial or substitutional defect, or removed from the lattice ($n_{X_i} > 0$) in the case of a vacancy
- E_{VBM}^{host} is the energy corresponding to the valence band maximum (VBM). It is the reference energy for μ_{E_F}
- μ_{E_F} is the chemical potential of the electrons, the so-called Fermi level
- $corr(D, q)$ correspond to various corrections to take into account and detailed hereafter in section 1.3.

Possible states of charge

The possible charges for the defect can be determined through the following reasoning. Let us detail the three examples of V_{Sb}, Se_i and I_{Se} in Sb₂Se₃. From an atomic perspective, removing an Sb atom, inserting an Se atom and substituting an Se atom by an I one is charge neutral. This gives us the state of charge $q = 0$ for the defect. The opposite extreme picture of the lattice is the ionic one. In this case, removing an Sb³⁺ ion will create a $q = -3$ vacancy. Inserting an Se²⁻ anion will create an interstitial of charge $q = -2$. Substituting an I⁻ to an Se²⁻ ion results in a $q = -(-2) + (-1) = +1$ charge. As stated before, the substitution can be viewed as the combination of the vacancy V_{Se} and the interstitial I_i on the vacant site. It seems the most probable physical mechanism by the way, as it is energetically easier to fill a vacant site with an interstitial than for the interstitial to “push” the original atom from its equilibrium site to replace it.

Note that the charge q is the charge of the supercell resulting from the number of electrons of the system, it may not be localised only on the defect. To summarise, the atomic and ionic models of the lattice give the most extreme possible charges for the defect. All intermediate charge should also be calculated as a more refined description may be in the middle of those two extremes. In this case, $q = -1$ and $q = -2$ should also be computed for V_{Sb} and $q = -1$ for Se_i. Please also mind that the number of electrons of the $q = 0$ state of charge for a defect may well be different from the one of the supercell as is visible in Table 1.1. In itself, the number of electrons of the pristine supercell is of no use to build the inputs of the calculations, it just gives a clue to the computational cost of the calculation.

Taking explicitly into account the 4s²4p⁴ valence electrons for Se and 5s²5p³ for Sb, respectively, in the 1 × 3 × 1 supercell of 60 atoms, we obtain the values reported in

3. As mentioned beforehand, in the dilute defect limit the change in volume is none so that the supercell parameters are kept identical to those of the host throughout the optimisation.

4. The dilute defect locally breaks the symmetry of the crystal. Keeping the symmetry in the PBC calculation could artificially reduce the degrees of freedom for the defect, especially if the initial defect position is located on a special position of the space group of the host.

Table 1.1 for the example developed beforehand.

Table 1.1: States of charge and associated electronic counts for V_{Sb} , V_{Se} , Se_i and I_{Se} in a 60-atom supercell of Sb_2Se_3 .

Defect	Charge q	Explicit number of e^-
Host	0	336
V_{Sb}	0	331
	-1	332
	-2	333
	-3	334
V_{Se}	0	330
	1	329
	2	328
Se_i	0	342
	-1	343
	-2	344
I_{Se}	0	337
	+1	336

1.2 Choice of chemical potentials

As shown in the expression of the defect formation enthalpy $\Delta H_{\text{form}}^{D,q}$ stated in equation 1.7, one of the most quantitatively important simulation parameters are the values of the chemical potentials. They are needed to compensate the difference in number of atoms between the ideal supercell and the faulted supercell due to the introduction of the defect. This translates as a linear dependence of $\Delta H_{\text{form}}^{D,q}$ in chemical potentials through the $\sum_{X_i} n_{X_i}(\mu_{X_i}^0 + \Delta\mu_{X_i})$ term. For instance, when considering an interstitial defect X_i , one needs to compare the energy of the host cell composed of N atoms with the one of the faulted cell containing $N + 1$ atoms. Before relaxation of the atomic positions, the energy is shifted by the negative value μ_X because of the presence of the additional atom X_i . One compensates such energy difference by adding $-\mu_{X_i}$ to the total energy difference $E_{\text{total}}^{D,q} - E_{\text{total}}^{\text{host}}$. This can also be interpreted as the energy required to retrieve an atom of X from the corresponding atomic reservoir. Such a reasoning extends to vacancies, and naturally substitutional defects and complex defects and justifies the signs of n_{X_i} . It is negative in the case of an added atom, $n_{X_i} < 0$, and positive for an atom removed from the lattice, $n_{X_i} > 0$. This linear relation implies that any change in chemical potential will proportionately affect the defect formation enthalpy $\Delta H_{\text{form}}^{D,q}$. Thus, they must be chosen with care.

The chemical potential μ_X of chemical element X is defined as the variation of Gibbs' free energy of the system when changing the quantity of matter of such element X ($\mu_X = \frac{\partial G}{\partial n_X}$). It is often expressed as the sum of the chemical potential of reference μ_X^0 , taken for the most thermodynamically stable phase of pure X in normal conditions, (*vide supra*) and the deviation from this value in the considered conditions, $\Delta\mu_X$, which leads one to write $\mu_X = \mu_X^0 + \Delta\mu_X$. Stevanovic *et al.* report these values for 50 chemical species assessed by least square minimisation of experimental *vs.* GGA+U formation enthalpy difference for 252 compounds (metals, pnictides, chalcogenides, and halides to cite a few).[116]

The thermodynamically allowed values are given by the stability domain of the host. We proposed the generalized expression 1.8 to describe the stability domain of crystalline material $X_{1,n_1}X_{2,n_2}\dots X_{p,n_p}$. [117] It basically states that the targeted host material is formed, hence satisfying the formation enthalpy equation, to the exception of all other possible compounds within the stability domain (undesired phases). This translates as the inequations in system 1.8.

$$\left\{ \begin{array}{l} \sum_{i=1}^p n_i^{target} \Delta\mu_i = \Delta H_f(target) (\text{constrain due to the formation of } target) \\ \forall i \in [1; N], \Delta\mu_i \leq 0 \\ \forall undesired \in \{\text{competing phases}\}, \sum_{i=1}^p n_i^{undesired} \Delta\mu_i \leq \Delta H_f(undesired) \end{array} \right. \quad (1.8)$$

For instance, when studying intrinsic defects of antimony selenide Sb_2Se_3 , one must write first the formation enthalpy of the host material Sb_2Se_3 , as stated in equation 1.9.

$$H_f(\text{Sb}_2\text{Se}_3) = E_{total}^{\text{Sb}_2\text{Se}_3} - 2\mu_{\text{Sb}} - 3\mu_{\text{Se}} \quad (1.9)$$

Given the expression of the chemical potentials (equation 1.10), where the reference chemical potentials can be calculated as the energy per atom of the reference phase ($\mu_{\text{Sb}}^0 = E_{total}^{\text{Sb(s)}}$ and $\mu_{\text{Se}}^0 = \frac{1}{8}E_{total}^{\text{Se(s)}}$), one can subtract the reference formation enthalpy (equation 1.11) to the formation enthalpy in the conditions considered in equation 1.9 to obtain equation 1.12. It strictly corresponds to the application of equation 1.8 to the example case of Sb_2Se_3 .

$$\left\{ \begin{array}{l} \mu_{\text{Sb}} = \mu_{\text{Sb}}^0 + \Delta\mu_{\text{Sb}} \\ \mu_{\text{Se}} = \mu_{\text{Se}}^0 + \Delta\mu_{\text{Se}} \end{array} \right. \quad (1.10)$$

$$H_f^0(\text{Sb}_2\text{Se}_3) = E_{total}^{\text{Sb}_2\text{Se}_3} - 2\mu_{\text{Sb}}^0 - 3\mu_{\text{Se}}^0 \quad (1.11)$$

$$\Delta H_f(\text{Sb}_2\text{Se}_3) = 2\Delta\mu_{\text{Sb}} + 3\Delta\mu_{\text{Se}} \quad (1.12)$$

Additionally, one must ensure that the other phases which exist in the Sb-Se system do not form. Here, only two such competing compound are thermodynamically stable, namely metallic antimony and crystalline Se (in γ form made of chains of Se atoms). This translates as the two inequation given in expression 1.13.

$$\left\{ \begin{array}{l} \Delta\mu_{\text{Sb}} \leq 0 \\ \Delta\mu_{\text{Se}} \leq 0 \end{array} \right. \quad (1.13)$$

The frontiers defined by such inequations can be plotted in a $(\Delta\mu_{\text{Sb}}, \Delta\mu_{\text{Se}})$ plane as shown in Figure 1.5. Thus, the limits of the stability domain of the host Sb_2Se_3 can be obtained from the total energies of Table 1.2 as reported in Table 1.3. The case of Sb_2Se_3 presents the simplest situation as there is only one thermodynamically stable binary compound in the Sb-Se system. Thus the graph only contains three phases: the two elemental phases and Sb_2Se_3 . In more complex cases, all thermodynamically stable phases within the system ought to be taken into account. One must keep in mind that the only accessible points at the thermodynamic limit within this space lie on one of the three lines. Hence, there is only one independent variable, fixing one of the two $\Delta\mu$ will mechanically fix the other. To summarize the situation, only the extreme cases are used to calculate DFE, nevertheless, the whole stability domain can

be accessed experimentally. Realistic synthesis conditions may be anywhere in the stability domain.

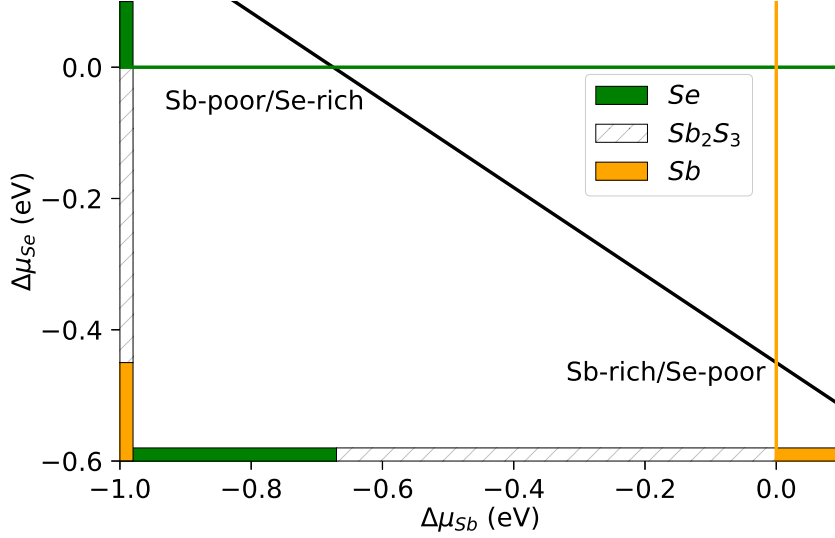


Figure 1.5: Sb_2Se_3 stability domain in a $(\Delta\mu_{Sb}, \Delta\mu_{Se})$ plane.

Table 1.2: Energy per formula unit for each compound (eV) computed with PBE-GD3. Z is the number of formula unit per crystallographic cell.

Phase	E_{tot} (eV/Z)
Sb_2Se_3	-24.95
Sb	-4.40
Se	-3.70

Table 1.3: Limits of Sb_2Se_3 stability domain (eV) calculated using PBE-GD3.

	μ_{Sb} ($\Delta\mu_{Sb}$)	μ_{Se} ($\Delta\mu_{Se}$)
Sb-rich/Se-poor	-4.40 (-0.00)	-4.15 (-0.45)
Sb-poor/Se-rich	-5.06 (-0.67)	-3.70 (-0.00)

Let us now consider a more complex example with the case of $CsCu_5Se_3$, a ternary compound.[118] There are now three chemical potentials to determine ($\mu_{Cs}, \mu_{Cu}, \mu_{Se}$). Let us keep in mind that due to equation 1.14 being satisfied, there are only two independent variables as the third chemical potential is deduced by equation 1.14. The two chemical potentials can be arbitrarily chosen.

$$\Delta H_f(CsCu_5Se_3) = \Delta\mu_{Cs} + 5\Delta\mu_{Cu} + 3\Delta\mu_{Se} \quad (1.14)$$

From a chemical point of view, playing with three chemical species instead of two will combinatorially allow to form much more different phases (elemental solids, binaries and possible competing ternaries). Indeed, in this case, no less than 16 phases were considered. To clarify, only the phases setting the boundaries of $CsCu_5Se_3$ stability domain are discussed.

First, the stability domain can be represented in the 3D chemical potential space, as shown in Figure 1.6. As mentioned previously, it is a 2D polyhedron, because the formation of each compound defines a plane. This representation, although aesthetically gratifying, is difficult to handle. In general, the representation of numerical data in 3D is advised to be avoided. To get a clearer idea of the stability domain, one can work with a 2D projection as presented in Figure 1.7.

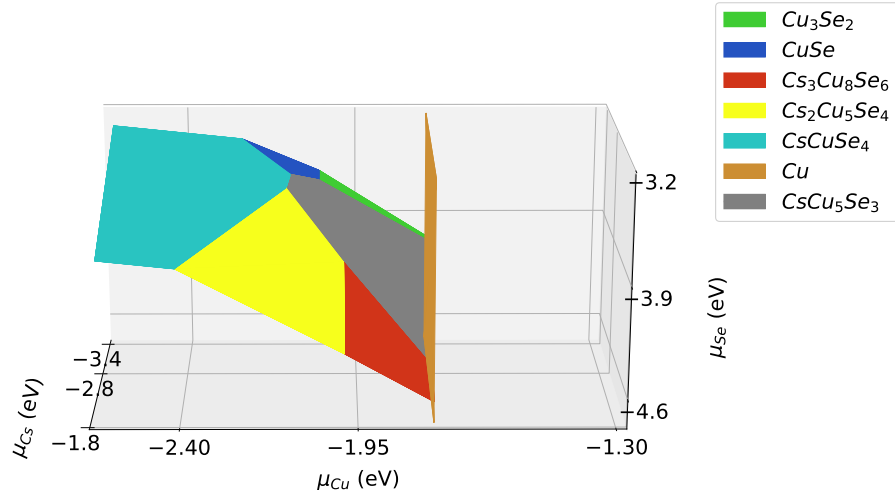


Figure 1.6: CsCu_5Se_3 stability domain in a $(\mu_{\text{Cs}}, \mu_{\text{Cu}}, \mu_{\text{Se}})$ space, calculated using PBE + U ($U = 6$ eV for 3dCu electrons).

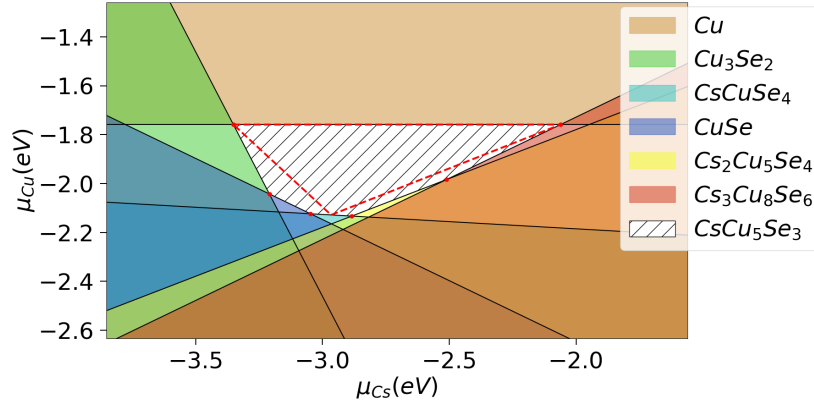
Rigorously, one ought to take into account all the summits of the stability domain as different extremal synthesis conditions in the DFE study, however, Figure 1.7 allow to notice the short chemical potential range separating some summits. It seems appropriate to simplify the shape of the stability domain and consider fewer conditions for the DFE, in this example three. This framework is practically necessary when increasing the dimensionality of the system. For instance, the stability domain of a quaternary compound such as kesterite $\text{Cu}_2\text{ZnSnS}_4$ is a 3D volume. More generally speaking, it is a subset of a hyperplane ($\text{dim} = N - 1$) for a compound involving N chemical species.

$\Delta\mu = \frac{\partial G}{\partial n}$ is rigorously a function of pressure and temperature, macroscopic variables which can be measured experimentally. This appears clearly in the widespread equation 1.15, where a_X is the activity of chemical species X . A lot of efforts has been dedicated in the field of process engineering to develop activity models for the gaseous and liquid states of matter, the most practical to manipulate in industrial processes. The gas form version of equation 1.15 is often used in the case of the synthesis of oxides to draw a link between the chemical potential of oxygen μ_{O} and the oxygen partial pressure $p_{\text{O}_2(g)}$. However, such a definition of the activity lacks in the solid-state. The fundamental reason for this is the intrinsic inhomogeneity of such a medium, contrary to a liquid or gaseous mixture which can be considered at least locally as homogeneous (constituting the basis of all finite-elements methods). Conversely, in solid-state reaction where slow diffusion through site-to-site hopping is the main physical phenomena involved in opposition to convection quickly leading to equilibrium, the chemical potential could only be defined rigorously at a very local scale, *i.e.* in each grain. Chalcopyrites used for 2nd generation photovoltaic solar cells even exhibit differences in composition within the same grain with a gradient between the grain boundary

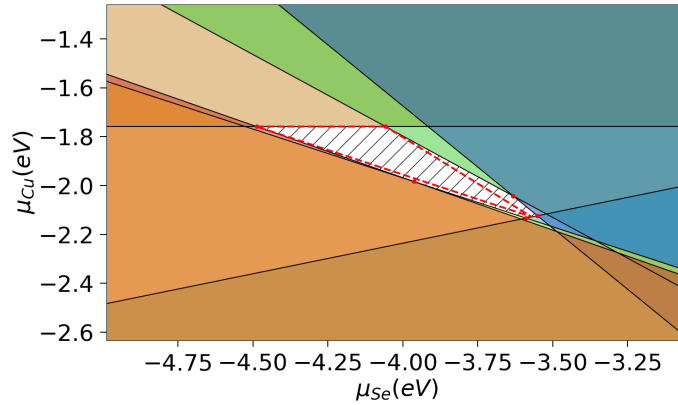
and the bulk. Based on those considerations, it seems very difficult to realistically account for the dependence in pressure and temperature of chemical potentials in the solid state. Besides, we have demonstrated beforehand that these dependencies can satisfactorily be neglected in the case of solid-state synthesis.

$$\begin{cases} \mu_X = \mu_X^0 + RT \ln(a_X) \\ \mu_X = \mu_X^0 + RT \ln(\frac{p_X}{p^0}) & \text{(ideal mixture of gases)} \\ \mu_X = \mu_X^0 + RT \ln(\frac{C_X}{C^0}) & \text{(dilute solution)} \end{cases} \quad (1.15)$$

Freysoldt *et al.* point out that such calculations may yield different results depending on the level of theory used.[119] Thus, performing them using the same methodology as the whole point defect study is compulsory. Interestingly, as reported in [120], this can be applied to extrinsic defects as well, adding the chemical potential of the impurity as an additional dimension.



(a)



(b)

Figure 1.7: CsCu_5Se_3 stability domain calculated using PBE + U ($U_{3d}(\text{Cu})=6$ eV) and a proposed simplification (dotted red triangle) for the different atmospheres to consider within a DFE study. a) Projection onto a $(\mu_{\text{Cs}}, \mu_{\text{Cu}})$ plane. b) Projection onto a $(\mu_{\text{Se}}, \mu_{\text{Cu}})$ plane.

1.3 Formation enthalpy corrections

Following the previous demonstration, we have shown that the defect Gibbs' free energy of formation can be approximated by the defect formation enthalpy (energy as the PV term is negligible). Furthermore, the practical implementation of the calculation of this quantity in itself has limitations which can be quantified and addressed by including various corrections. Basically, these corrections derive from two different limitations.[48, 121] On the one hand, the model describing the underlying physics ruling the behaviour of electrons, *i.e.* Density Functional Theory (DFT), limits the precision of the energy calculation because of the approximations made to the true electron behaviour, in short, the exchange-correlation issue. On the other hand, finite-size supercell construction with periodic boundary conditions gives rise to spurious artefacts detailed hereafter.

1.3.1 Limitations of DFT

Band-edges correction

When using functionals at the LDA or GGA levels of theory, the bandgap is severely underestimated,[122] commonly up to 50%, leading sometimes to a wrongly simulated metallic behaviour, as in the case of CuInSe_2 . [89, 122] Indeed, the GGA is a local (Taylor) expansion of the Fermi electron gas (LDA) where electrons are delocalised, as in a metal. Thus, it tends to overdelocalise the electrons, which translates as empty states composing the conduction band being too low in energy.[123] As the chemical potential of the electrons (Fermi level) μ_{E_F} takes values between the Valence Band Maximum (VBM) and the Conduction Band Minimum (CBM), one needs to correctly assess the bandgap in a point defect study. Besides, we will see further on that the position of the defect levels with respect to the band edges is of capital importance, so that we need to know where the CBM lies in the most accurate way available. To do so and taking advantage of the ideal cell's small size and symmetry, a more refined description can be used to perform an accurate bandgap calculation, such as a hybrid functional, typically HSE06 or PBE0, or leaving DFT for a quasiparticle many-body approach, the so-called GW ansatz. Such methods are described at the end of the paragraph. Nevertheless, the calculations on the faulted cells are performed at lower levels of theory. They can then all be corrected thanks to the position of the VBM in the most refined description. In order to recover the correct description, the VB (CB) of the host in GGA is shifted down (up) by ΔE_V (ΔE_C), as sketched in Figure 1.8. For the rest of the study, this will be referred to as the host band structure. It allows to recover the most precisely calculated bandgap $E_g = E_g^{GGA} + \Delta E_V + \Delta E_C = E_g^{hybrid/GW}$.

As previously said, the Fermi level takes value in the bandgap, *i.e.* the reference $\mu_{E_F} = 0$ corresponds to the Fermi level sitting at the top of the VB. This is captured in equation 1.7 through the $q(E_{VBM}^{host} + \mu_{E_F})$ term. Note that in fact, $E_{VBM}^{host} = E_{VBM}^{host,GGA} - q\Delta E_V$, so that the DFE expression $\Delta H_{form}^{D,q}(\mu_{E_F})$ includes the quantity $q\Delta E_V$. In this way, the correction of the bands (energetic) positions also induces a correction on the DFE by $q\Delta E_V$.

Going beyond GGA: meta-GGA, hybrids and GW

Among the different numerical schemes available to the computationally-oriented chemist or physicist, DFT has emerged as the tool of choice with the best computational

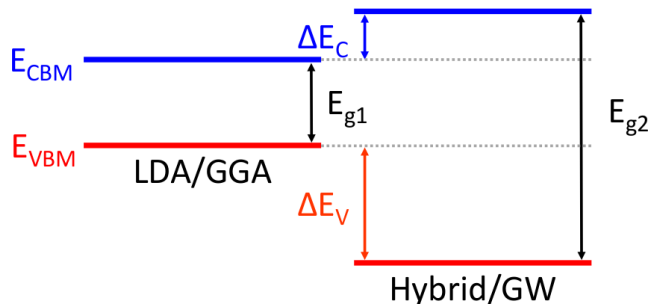


Figure 1.8: Band-edge correction principle. In the present work, we adopt the convention of positive band energy shifts ($\Delta E_V > 0$) so that the final gap is $E_g = E_g^{\text{GGA}} + \Delta E_V + \Delta E_C$.

time over precision ratio.[124, 125] One could add that most other methods used by molecular theoretical chemists (double hybrids, coupled cluster, multi-configurational self-consistent fields...) are often far too demanding for solid-state. Even in DFT, as the exchange-correlation part of the energy functional is unknown, different families of approximations have been developed to approach it, leading to different precisions and computational costs. It ranges from the cheap gas of free electrons description of the Local Density Approximation (LDA) to the much more refined double-hybrids, such as B2PLYP.[126] This progression has been metaphorically described by Perdew [127] as the Jacob’s ladder of *ab initio* simulations. As far as solid-state is concerned, the level of theory currently used reaches up to hybrid functional (including a share of exact Hartree-Fock exchange). In the specific case of point defects, because the supercells are quite large (usually several hundreds of atoms and most importantly up to a thousand electrons) and symmetry reduction is forbidden during geometry optimization, most modern studies resort to the Generalized-Gradient Approximation (GGA [128]) approximation.[82, 129–133] A step higher, at the hybrid level, screened hybrid functionals like HSE06 are on the rise for point defect studies.[81, 134–139] Let us shortly review the main differences between some of these advanced methodologies.⁵

As stated before, the GGA approximation is an improvement over the LDA Fermi free electron gas which corresponds to a first-order Taylor expansion of the electronic density. A natural step to improve the description further is to take into account the gradient of the density into the exchange correlation $E_{XC}(\rho, \nabla\rho, \nabla^2\rho)$. The derived class of functionals is called the “meta-GGA” functionals. As usual in DFT, there are several paradigm on which to build a functional. One can try to match experimental values such as ionisation energies on a set of compounds such as the AE6 set,⁶[141, 142] or try to match post-Hartree Fock calculation results on a given test set of molecules and properties such as the G3 test set.⁷[143] Yet another approach is to try to respect theoretical constraints such as conditions on the norm, asymptotic behaviours and boundary conditions. This gives rise to a jungle of functional for each class of approximation, and meta-GGA is no exception. For instance, several different meta-GGA density functionals are implemented in VASP. The most famous ones are TPSS,[144] M06L,[145] MBJ[146, 147] and SCAN.[148] In our work which uses meta-GGA func-

5. This paragraph is largely taken from our work published in reference.[140]

6. Atomisation Energies of SiH_4 , S_2 , SiO , C_3H_4 (propyne), $\text{C}_2\text{H}_2\text{O}_2$ (glyoxal), and C_4H_8 (cyclobutane)

7. Gaussian-3 is a calculation scheme and by extension a test set of thermochemical data for validation of quantum chemical methods proposed by Pople *et al.* which includes more than 200 enthalpies of formation for a wide range of molecules.[143]

tionals, we select the Strongly Constrained and Appropriately Normed (SCAN) density functional which satisfies all known constraints for meta-GGA functionals. There are also clues that it outperforms both GGA and older meta-GGA such as TPSS in the prediction of solid-state properties.[149]

Starting from the observation that the Hartree-Fock theory is the limit of electronic localisation, taking into account only exact analytic physical terms, and that LDA is the opposite limit of the free electron gas with electrons delocalized over the crystals, mixing GGA, an improvement over LDA, with Hartree-Fock expression is a seducing idea to try to correct the bandgap problem. This is the fundamental principle of construction of hybrid functionals.

The PBE0 functional adds $\frac{1}{4}$ of exact Hartree-Fock (HF) exchange to the GGA-PBE functional and tends to slightly overestimate the observed band gap (around 10-15%) according to a benchmark from Marsman *et al.* on a set of elemental solids and binary compounds.[150] We also obtain such a deviation for ternary compounds.[140] This can be condensed into equation 1.16.

$$E_{XC}^{PBE0} = \frac{1}{4}E_X^{HF} + \frac{3}{4}E_X^{PBE} + E_C^{PBE} \quad (1.16)$$

Deriving from it, the aforementioned HSE family has become a popular screened functional in solid-state.[151, 152] To reproduce the screening of the Coulomb interaction in semiconducting materials, the Coulomb kernel of the HF exchange was decomposed into a short-range (SR) and a long-range (LR) tuned by the ω inverse distance as expressed in equation 1.17. Only the short-range part of the functional includes a fraction α of HF exchange, so that the computational cost is reduced, and the general expression yields equation 1.18.[151]

$$\frac{1}{r} = \underbrace{\frac{1 - \text{erf}(\omega r)}{r}}_{SR} + \underbrace{\frac{\text{erf}(\omega r)}{r}}_{LR} \quad (1.17)$$

$$E_{XC}^{HSE(\alpha,\omega)} = \alpha E_X^{HF-SR} + (1 - \alpha) E_X^{PBE-SR} + E_X^{PBE-LR} + E_C^{PBE} \quad (1.18)$$

As far as the HSE06 flavour of the HSE functional family is concerned, the HF exchange part is the same as in PBE0, $\alpha = \frac{1}{4}$ and the screening parameter ω is equal to $0.2 \text{ \AA}^{-1}$.

All these approaches (meta-GGA, hybrid, screened-hybrid) start from DFT, traditionally the realm of quantum chemists. The condensed-matter physics community has proposed a different approach, dropping DFT in favour of a many-body scheme. Our intention here is not to give a deep understanding of the quasiparticle method as it is not the scope of this work, nevertheless, we provide a brief insight into the basic underlying mechanisms.[153–156] The calculated bandgap using DFT is strictly speaking the Kohn-Sham gap. It is the difference between the eigenvalue associated to the lowest empty state (CBM) and the one corresponding to the highest occupied state (VBM). Conversely, the many-body approach models the addition and removal of an electron from the system, comparable to photoemission spectroscopy experiments, to compute the bandgap.

The theoretical problem is the following. How do N electrons behave when submitted to the electrostatic potential generated by the ions, located at the equilibrium positions in the crystal? The central quantity one will be interested in is the Green's function G , also called the one-particle propagator. It is the probability amplitude

for the propagation of an added or removed electron in the many-body system from the position in space $\mathbf{r}_1$ at instant t_1 in spin σ_1 , which form a five-coordinates vector $(\mathbf{r}_1, t_1, \sigma_1)$, to $(\mathbf{r}_2, \sigma_2, t_2)$, as illustrated in Figure 1.9. To lighten the equations and as usually done in this field, we will use the notation originally proposed by Hedin in 1965, [157] which introduces $1 = (\mathbf{r}_1, \sigma_1, t_1)$. Determining the exact time-ordered one-particle interacting Green's function $G(1, 2)$ would give the exact solution to the behaviour of the N electron system.

The interacting Green's function G is developed as a sum of the independent-particle Green's function G_0 and the product of G_0 , the self-energy Σ and itself, in the so-called Dyson equation 1.19. The self-energy includes all interaction effects.

$$G(1, 2) = G_0(1, 2) + \int G_0(1, 3) \Sigma(3, 4) G(4, 2) d34 \quad (1.19)$$

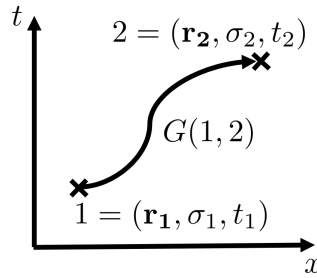


Figure 1.9: Illustration of the physical interpretation of $G(1, 2)$ as the propagator of an electron from 1 to 2.

Hedin derived a set of interdependent equations expressing the relationship between G , Σ and material-related quantities, as reported in equation 1.20.[157]

$$\begin{cases} \Sigma(1, 2) &= i \int G(1, 3) W(1, 4) \Gamma(4, 2, 3) d34 \\ \Gamma(1, 2, 3) &= \delta(1, 2) \delta(1, 3) + \int \frac{\delta \Sigma(1, 2)}{\delta G(4, 5)} G(4, 6) G(5, 7) \Gamma(3, 6, 7) d4567 \\ \chi_0(1, 2) &= -i \int G(1, 3) G(4, 1) \Gamma(2, 3, 4) d3 \\ W(1, 2) &= \int \epsilon^{-1}(1, 3) v(3, 2) d3 \end{cases} \quad (1.20)$$

Let us explain the remaining terms within equation 1.20. δ is the Dirac function. Γ , known as the vertex function, describes the interaction between the virtual hole and the electron. χ_0 is the irreducible polarisability of the material, describing the linear response of the material to an electric field. W is the dynamically screened Coulomb interaction. Due to the presence of the other electrons in the material, the electron can be seen as evolving in a dielectric medium. W captures the potential felt by the electron from the others through such screening as illustrated in Figure 1.10. This is a frequency-dependent quantity. The vertex function Γ also corrects the fact that W corresponds to the interaction between classical particles as opposed to the real ones which are fermions, and thus obey Pauli exclusion principle.[156] Its expression naturally introduces the dielectric tensor ϵ , linked to the polarisability by equation 1.21, where v is the bare coulombic potential occurring between two charges in the vacuum.

$$\epsilon(1, 2) = \delta(1, 2) - \int v(1, 3) \chi_0(3, 2) d3 \quad (1.21)$$

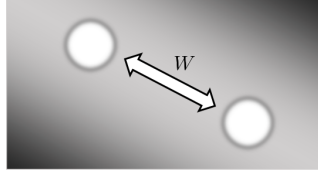


Figure 1.10: Schematic representation of the dynamically-screened coulombic potential felt by quasiparticles in a general dielectric medium.

This would theoretically allow to calculate iteratively G as summarised in the well-spread Figure 1.11a. However, there is an important difficulty emerging from the three-point vertex Γ and the derivative within its expression. The GW approximation consists in replacing Γ by a simple point function $\Gamma(1, 2, 3) \simeq \delta(1, 2)\delta(1, 3)$. This is known as the Random Phase Approximation (RPA). Then, χ_0 describes non-interacting excitons, which seem a fair approximation as the excitons are charge-neutral. Then the self-energy Σ is expressed as $\Sigma = iGW$, giving its name to the approximation. It corresponds to skipping the vertex Γ summit in the pentagon of Figure 1.11a as sketched in Figure 1.11b. Starting by injecting the independent Green's function G_0 and iterating the four-step loop of Figure 1.11b is an algorithm implemented in several quantum codes. This is sometimes referred to as “self-consistent” GW . However, it is still a cumbersome computational task and an additional simplification is often made, the so-called G_0W_0 scheme. It consists in starting from the independent Green's function G_0 as before and going only once through each step, stopping the calculation at the self-energy, as illustrated in Figure 1.11c.

As stated before, these advanced methods allow to correct the band-edges positions.

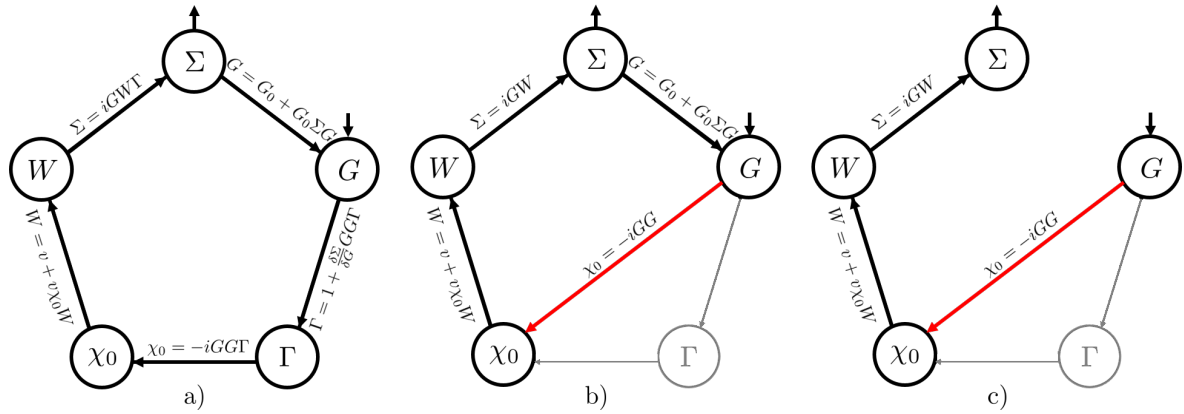


Figure 1.11: a) Hedin's pentagon: solving self-consistently the represented system of equations would yield the fully-dependent Green's function G . b) The GW approximation to the many-body problem is obtained by skipping the vertex summit of Hedin's pentagon. One starts by injecting the independent Green's function G_0 and iterates the four-step loop. c) The G_0W_0 ansatz consists in a single loop without further iteration.

Potential alignment (PA)

The introduction of a charged defect shifts the electrostatic potential by an unknown value.[121, 158] In practice, a homogeneous background charge (jellium) is added in the otherwise divergent charged DFT calculation.[48, 121] In order to be able to compare

the energies of the host and charged cells, one needs to recover the reference energy for the charged calculations.

The electrostatic potential induced by charges q_i can be expressed as stated in equation 1.22. This is the bare coulombic potential v discussed in the *GW* section. The inverse distance dependence of the potential, added to the screening due to the neighbouring ions, leads to the fact that further from the second coordination sphere of the defect, the electrostatic potential felt by the ions is the same with or without the defect. This is illustrated in Figure 1.12 in a model one dimensional case with an interstitial defect. One can see that the difference between the electrostatic potential before defect introduction (black line) and after (red line) becomes negligible further than the second neighbour of the defect. Generalising to the 3D case most of interest for material science, outside of an exclusion sphere centred on the defect, the atoms feel the same potential as in the host cell. Thus, the shift in potential introduced by the defect can be obtained by recalibrating the charged cells energies by the average of the difference weighted by the charge as written in equation 1.23. This is illustrated in Figure 1.13 where the excluded region is represented in white and the region over which the potential is averaged in blue. The difference between the two situations provides the correction mentioned before.

$$V(r) = \frac{1}{4\pi\epsilon_0} \sum_i \frac{qq_i}{|r - r_{q_i}|} \quad (1.22)$$

$$\Delta E_{PA} = q \times \overline{(V_{D,q}^r - V_{host}^r)} \quad (1.23)$$

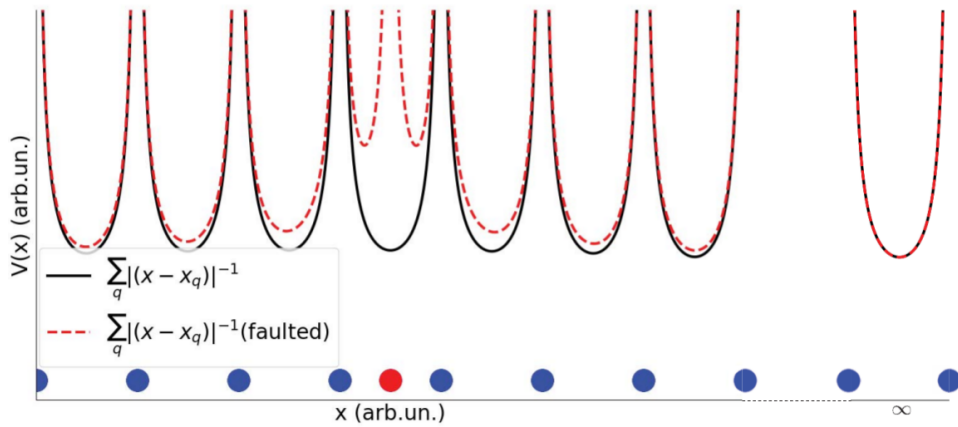


Figure 1.12: Electrostatic potential before (black line) and after (red line) introduction of a defect (red sphere) in a model 1D case. The blue spheres symbolise the ions.

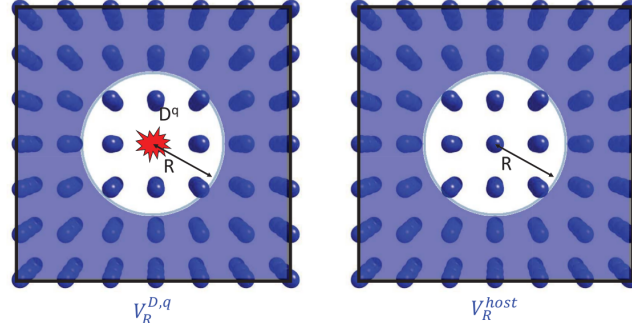


Figure 1.13: Potential alignment correction principle. The difference of electrostatic potential felt by the ions between the faulted supercell (left) and ideal host supercell (right) is averaged over the blue region excluding the white sphere centred on the defect.

1.3.2 Finite size corrections

Moss Burstein type band filling

Typical defect concentrations in semiconductors are of 10 ppm (10^{-5} , equivalent to 10^{17} cm^{-3} for a $100 \text{ \AA}^3$ cell).[93] When applying a supercell approach, one cannot choose a (super)cell so large that it naturally reflects such low level concentrations because of computational limitations. Indeed, the biggest systems which can be calculated using DFT are of a few hundreds of atoms, as pointed out previously. Thus, one has to work with a smaller cell. But how small can it be? The first limitation comes from the periodic boundary conditions. In the real material, defects approach the infinitely diluted limit and can be considered isolated. If the supercell is too small, the defect can feel the electrostatic interaction of its periodic images in the neighbouring cell. A simple calculation gives an idea of the minimum distance between a defect and its periodic image required to have them feel no electrostatic interactions from one another. One can use the classical expression of the norm of an electrostatic force exerted on one another by two point charges q_1 and q_2 separated by a distance r in a homogeneous dielectric medium of permittivity $\epsilon = \epsilon_0 \epsilon_r$ reported in equation 1.24, which can be inverted as equation 1.25 for non-zero forces.

$$F(r) = \frac{1}{4\pi\epsilon} \frac{q_1 q_2}{r^2} \quad (1.24)$$

$$r = \sqrt{\frac{q_1 q_2}{4\pi\epsilon_r \epsilon_0 F}} \quad (1.25)$$

For the test values $q_1 = q_2 = +e$ and $\epsilon_r = 10$ (as a reference, $\epsilon_r(\beta\text{-In}_2\text{S}_3) \simeq 13.82$),[159] if one wants to satisfy the criterion $F < 5 \cdot 10^{-2} \text{ eV/\AA}$, equation 1.25 yields $r \simeq 5 \text{ \AA}$. Note that the rule-of-thumb for the minimum distance between defects when building the supercell is usually $10 \text{ \AA}$, which nicely matches this result. It means that in the case of our $100 \text{ \AA}^3$ cell example, supposed to be cubic ($a \simeq 4.6 \text{ \AA}$), a $3 \times 3 \times 3$ supercell will be big enough to respect this constraint. Nevertheless, this $\frac{1}{9} \simeq 0.11$ concentration is very far from the realistic 10 ppm mentioned above. Of course, one could argue that a bigger supercell is required, and that convergence with respect to the size of the supercell should be checked.⁸ As discussed by Lany *et al.*,[103] the convergence

8. by comparing defect energies with respect to the supercell size, *i.e.* calculating the energy difference for the same defect using successively a $2 \times 2 \times 2$, $3 \times 3 \times 3$ -supercell and so on, to make

with supercell size is slow [75, 160] and the finite-size corrections allow accurate energy predictions while guaranteeing affordable computational costs.

Yet, Moss and Burstein have reported in the 1950s a band-filling effect in heavily doped semiconductors due to low effective mass charge carriers thermally filling the bottom(top) of the conduction(valence) band for a $n(p)$ -type semiconductor.[161, 162] As the computationally affordable supercells are quite small, these effects can be artificially induced in the model. One needs to correct this artefact by removing the contribution to the total energy of electrons spuriously located in the CB of the host and of holes in the VB. It can be done by applying the following correction[48, 79, 103]

$$\begin{cases} \Delta E_{MB}^{e^-} &= - \sum_{n,\mathbf{k}} \omega_{\mathbf{k}} \eta_{n,\mathbf{k}} \tilde{E}_{n,\mathbf{k}}^{CBM} \mathcal{H}(\tilde{E}_{n,\mathbf{k}}^{CBM}) \\ \Delta E_{MB}^{h^+} &= - \sum_{n,\mathbf{k}} \omega_{\mathbf{k}} (2 - \eta_{n,\mathbf{k}}) \tilde{E}_{n,\mathbf{k}}^{VBM} \mathcal{H}(\tilde{E}_{n,\mathbf{k}}^{VBM}) \end{cases} \quad (1.26)$$

where

$$\begin{cases} \tilde{E}_{n,\mathbf{k}}^{CBM} &= E_{n,\mathbf{k}} - (E_{CBM}^H + \overline{\Delta V}) \\ \tilde{E}_{n,\mathbf{k}}^{VBM} &= (E_{VBM}^H + \overline{\Delta V}) - E_{n,\mathbf{k}} \end{cases}$$

and the n index refers to a summation over the bands, $\mathbf{k}$ over the k-points, $\omega_{\mathbf{k}}$ the k^{th} k-point weight, $E_{n,\mathbf{k}}$ the n^{th} band energy at the k^{th} k-point in the faulted cell, $\eta_{n,\mathbf{k}}$ is the occupation of the n^{th} band at k-point $\mathbf{k}$, $\mathcal{H}$ is the Heaviside function and $\overline{\Delta V}$ the difference in electrostatic potential as defined by the PA correction. It expresses the removal of the spuriously filled energy levels within the host VB and CB as illustrated in Figure 1.14. Note that the Heaviside function $\mathcal{H}$ acts as a filter to ensure that the correction only removes spurious filling of the host bands and not defect levels located inside the gap, hence the use of the shifted band energies $\tilde{E}_{n,\mathbf{k}}$ taking into account the band-edge and PA correction and not directly the GGA eigenvalues for the faulted supercell.

Makov Payne type electrostatic correction

In the real material, point defects are well separated from one another, whereas in the supercell model with periodic boundary conditions, the defect and its images in the neighbouring cells may interact electrostatically, as illustrated in Figure 1.15. Indeed, unlike the simple picture of punctual charges used above to get a first idea of the necessary supercell dimensions, the charge distribution may in fact be (partially) delocalized. In order to eliminate the spurious interactions which may emerge from them, different corrections [163] have been proposed, first by Makov and Payne,[164] followed by a different scheme by Freysoldt, Neugebauer and Van de Walle [165] and a simplified version of the first by Lany and Zunger.[121] Implementations from Freysoldt *et. al.* and Lany and Zunger[121] were compared in the case of CsCu_5Se_3 cationic vacancies and found to give rise to a discrepancy of $\simeq 0.07$ eV for the sum of the PA and MP correction. This encouraged us to use the expression proposed by the latter two derived from the first, expressed as

$$\Delta E_{MP} = (1 + c_{sh}(1 - \epsilon^{-1})) \frac{q^2 \alpha_M}{2\epsilon V^{\frac{1}{3}}} \quad (1.27)$$

where c_{sh} is a geometry dependent correction term, of which the different values are listed in Table 1.4, ϵ is the dielectric constant of the material, α_M the Madelung constant

sure that the asymptotic limit is reached.

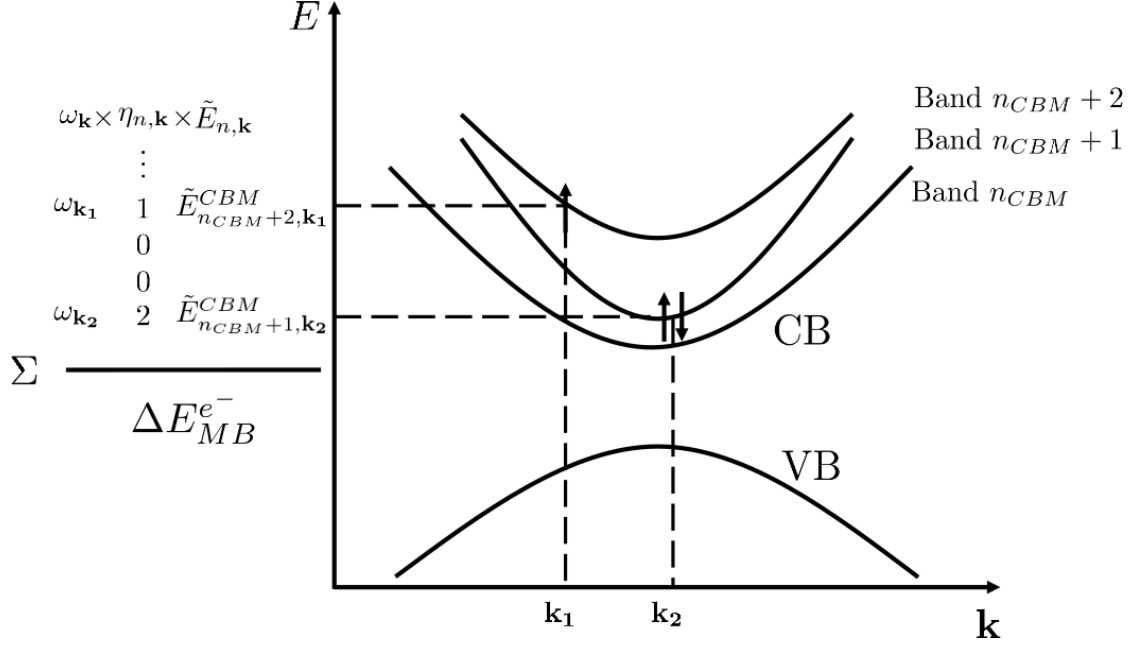


Figure 1.14: Illustration of the Moss-Burstein type correction for the spurious filling of the CB by three electrons from the faulted supercell (a single electron on band $n_{CBM} + 2$ at $\mathbf{k}$ -point $\mathbf{k}_1$ and one pair on band $n_{CBM} + 1$ at $\mathbf{k}$ -point $\mathbf{k}_2$). The correction is calculated by multiplying the different columns and summing the lines as displayed on the left-hand side of the Figure.

and q the charge of the defect. The different versions of this correction can be found in different programs[166]: Pylada[167] and PyDEF[117, 168] implement the Lany-Zunger flavour, CoFFEE[169] and sxdefectalign[165] propose the Freysoldt, Neugebauer and Van de Walle version and PyCDT[170] even includes a further refinement by Kumagai and Oba.[158]

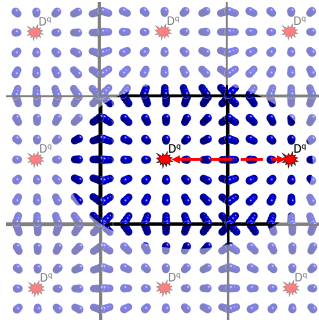


Figure 1.15: Electrostatic interactions between the defect and its periodic images.

Perturbed Host States (PHS)

Deep defects have transition levels located inside the bandgap, far from the band edges. They lead to localized electronic states which can be viewed as electron/holes traps. The electronic state associated to a deep defect is often called a Defect Localised State (DLS). For a shallow defect, the mechanism is different.[48, 79, 103, 112] It is described in Figure 1.16 for the case of a shallow donor. The creation of the point defect creates a DLS inside the CB which is populated by one or several electrons

Table 1.4: Values of the adimensional c_{sh} parameter in the Makov-Payne like correction with respect to the geometry.

Geometry	c_{sh}
Simple cubic	-0.369
Face-centred cubic	-0.343
Body-centred cubic	-0.342
Hexagonal compact	-0.478
Other	$-\frac{1}{3}$

(left-hand side of Figure 1.16). The electron is then released to the CB by ionising the defect. This creates a hole-electron pair and lowers the energy of the defect state to a value just below the CBM. The screened coulombic potential resulting from the addition/removal of an ion perturbs the host conduction band, so that the dispersion of the newly created defect state in the supercell model is that of the CBM. The final state is a Perturbed Host State (PHS). The mechanism is similar for a shallow acceptor with the liberation of a hole at the top of the VB, creating a PHS just above the VBM. Shallow defects are responsible for the electronic conductivity of the material, n -type for shallow donors and p -type for shallow acceptors.

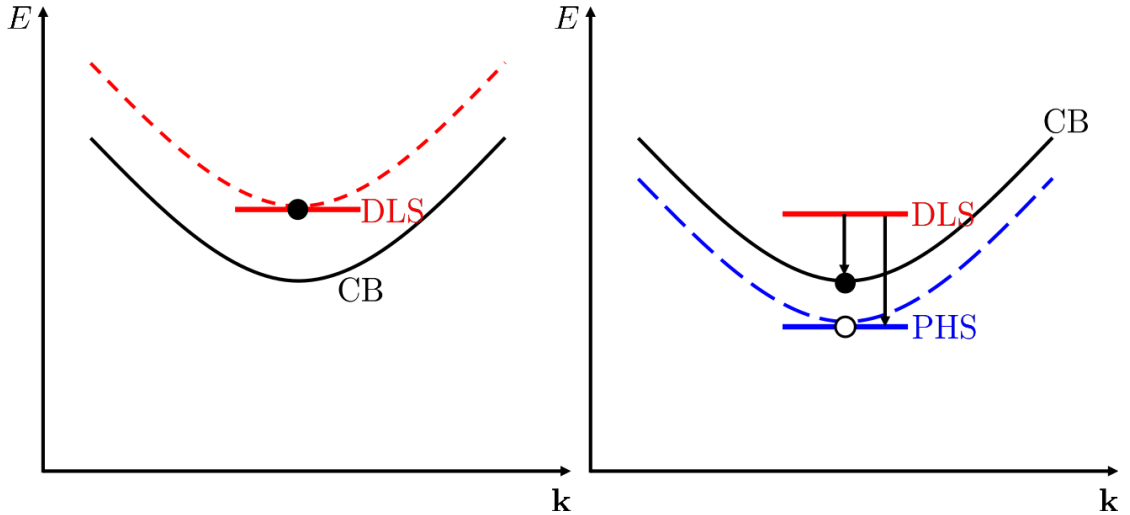


Figure 1.16: Perturbed Host State creation in the case of a shallow donor. First, an occupied DLS is created in the CB (left-hand side). The electron is released to the CB, which creates a PHS lying in the gap just below CBM (right-hand side). The red colour symbolises the initial state before defect ionisation and the blue one the final state. Dashed lines indicate the band dispersion induced by the finite-size supercell whereas solid lines refer to single isolated defect states.

The energetic position of the PHS in the gap is closely linked to the one of the relevant band-edge, so that the correction of the band-gap affects the energy of the level. More precisely, one should correct the DFE by the band-edge shift ($\Delta E_C/\Delta E_V$) weighted by the number of electrons z_{e-} /holes z_{h+} populating the DLS as reported in equation 1.28 as illustrated in the case of a shallow donor in Figure 1.17.[48, 103, 112]

$$\Delta E_{PHS} = z_{e-}\Delta E_C - z_{h+}\Delta E_V \quad (1.28)$$

Numerous reviews discuss these energetic corrections.[48, 79, 103, 121]

1.3.3 Quantitative impact of the corrections

Let us have a look at a numerical example on two vacancies in Sb_2Se_3 to grasp the relative importance of each correction. Note that there are several crystallographically distinct vacancies for anions and cations, however, for clarity we arbitrarily display only one site for each type of vacancy (anionic or cationic). The amplitude in electronvolt of the different terms composing $\Delta H_f(0)$ are presented in the form of a cumulated bar chart in Figure 1.18 and available in Table 1.5. First, the host cell here is composed of 60 atoms, so the total energy is several hundreds of electronvolts. However, the difference of energy between the faulted and the host cell, displayed in blue in Figure 1.18, is only a few electronvolts. It stems from the difference in the number of ions and the difference in energy due to the structural rearrangement. This order of magnitude of a few electronvolts highlights the need for precise (enough) DFT calculations. Secondly, note the weight of the chemical potentials presented in orange in Figure 1.18. Their values are in the same order of magnitude as the difference in energies. Note that the term $\sum_i n_i \mu_i$ is negative in the case of a vacancy ($n_i = 1$ to compensate for the atom removed and $\mu_i < 0$ eV) but can be positive in other cases, such as an interstitial ($n_i = -1$ to compensate the supplementary ion and $\mu_i < 0$ eV).

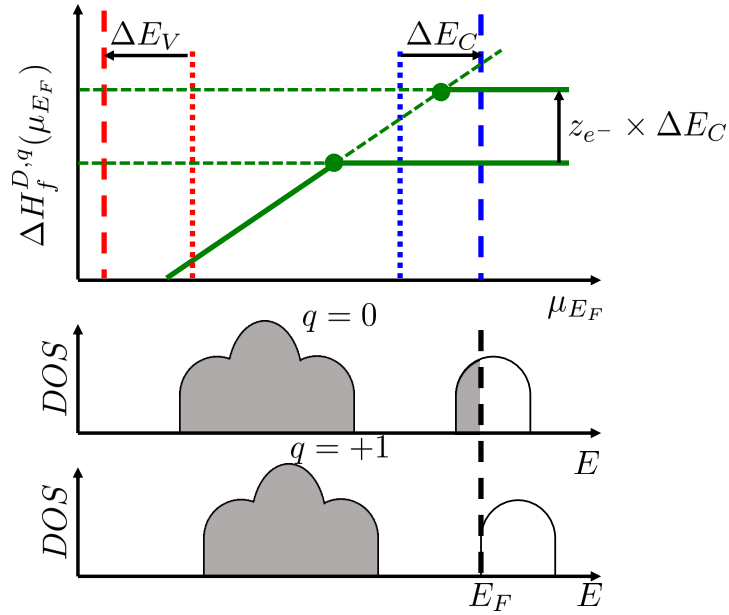
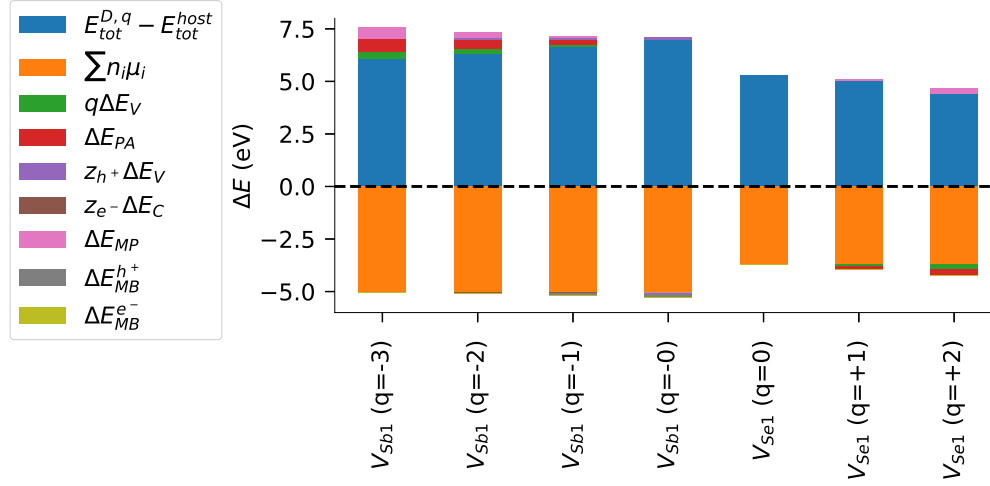


Figure 1.17: Schematic representation of the PHS enthalpy correction for a shallow donor defect. The red lines represent the VBM, calculated at the GGA level in dotted line and at the advanced theory level (GW or hybrid) in dashed line. The blue lines represent the CBM using the same convention with linestyles.

Let us now detail the corrections to see numerically their weights. The values are summarized in Table 1.5. The most important correction in this case is the PA correction with up to $\simeq 0.6$ eV. The following corrections in decreasing order of magnitude are the electrostatic Makov-Payne like correction and the VBM correction. Then the MB and PHS corrections punctually correct spurious effects on designated cells. Figures 1.19a to 1.19d show the share of the non-zero corrections in the sum of the absolute values of the energy corrections ($\frac{|\Delta E_{corr}|}{\sum |\Delta E_{corr}|}$). This quantity allows us to assess which corrections are the most important in terms of amplitude, regardless of the sign. Indeed, the signed correction are summated and can reduce the total correction due to

the presence of negative ΔE_{corr} values. Figures 1.19a to 1.19d highlight the importance of the PA as the most important correction in the case of V_{sb1} , representing $\simeq 40\%$ of $\sum |\Delta E_{corr}|$. It also stresses out the fact that VBM correction and electrostatic corrections are equally important. Whenever the LDA or GGA levels of theory are used for the faulted cell calculations, the VBM correction is deemed to be very important due to the unrealistic exchange-correlation behaviour of such energy functionals.



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Figure 1.18: Amplitude of the different contributions to the DFE of V_{Sb1} and V_{Se1} in Sb_2Se_3 in Sb-poor/Se-rich synthesis conditions at $\mu_{E_F} = 0$ eV.

Table 1.5: Energy corrections to the defect formation enthalpy of two vacancies in Sb_2Se_3 in Se-rich/Sb-poor atmosphere. All values are presented in electronvolt.

Name	$E_{tot}^{D,q} - E_{tot}^{host}$	$\sum n_i \mu_i$	$q\Delta E_V$	ΔE_{PA}	$z_{h+}\Delta E_V$	$z_{e-}\Delta E_C$	ΔE_{MP}	ΔE_{MB}^{h+}	ΔE_{MB}^{e-}	Total corr
$V_{Sb1} (q=-3)$	6.083	-5.064	0.330	0.621	0.000	0.000	0.552	0.000	0.000	1.503
$V_{Sb1} (q=-2)$	6.318	-5.064	0.220	0.446	0.110	0.000	0.245	-0.034	0.000	0.987
$V_{Sb1} (q=-1)$	6.631	-5.064	0.110	0.239	0.110	0.000	0.061	-0.116	0.000	0.405
$V_{Sb1} (q=0)$	7.005	-5.064	0.000	0.000	0.110	0.000	0.000	-0.220	0.000	-0.110
$V_{Se1} (q=0)$	5.286	-3.702	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
$V_{Se1} (q=+1)$	5.053	-3.702	-0.110	-0.132	0.000	0.000	0.061	0.000	0.000	-0.181
$V_{Se1} (q=+2)$	4.423	-3.702	-0.220	-0.298	0.000	0.000	0.245	0.000	0.000	-0.273

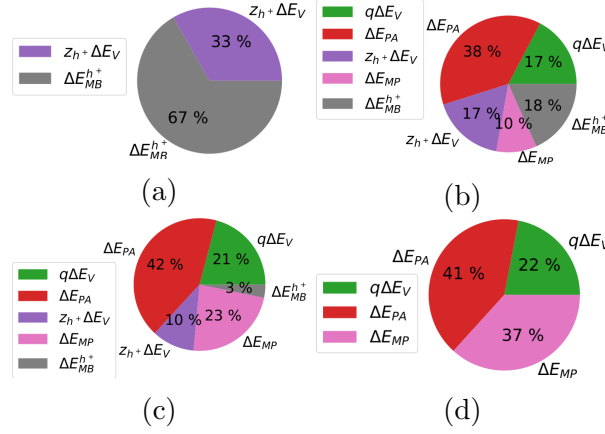


Figure 1.19: $\frac{|\Delta E_{corr}|}{\sum |\Delta E_{corr}|}$ ratio for each state of charge of V_{Sb1} in Sb_2Se_3 a) $q = 0$ b) $q = -1$ c) $q = -2$ d) $q = -3$.

1.3.4 DFE plots, transition levels and dopability domain

This type of calculations allows one to represent the DFE with respect to the Fermi level. As expressed in equation 1.7, $\Delta H_f^{D,q}(\mu_{E_F})$ is a linear function of μ_{E_F} . A graphical representation of $\Delta H_f^{V_{Sb1}}(\mu_{E_F})$ in Sb_2Se_3 is given in Figure 1.20 as an example. For each value of μ_{E_F} , the state of charge of the defect is determined by the lowest formation enthalpy. Thus, the minimum useful information is contained in the lowest formation enthalpy within the bandgap (coloured in brown in Figure 1.20).

The charge may change depending on the position of μ_{E_F} in the gap. The special Fermi level values at which these switches happen are called transition level. For a transition between state of charge q_1 and q_2 , it is noted ϵ_{q_1/q_2} . Because of the linear relation between $\Delta H_f^{D,q}(\mu_{E_F})$ and μ_{E_F} shown in equation 1.29, straightforward algebra yields the expression 1.30 for the transition level.

$$\Delta H_f^{D,q}(\mu_{E_F}) = \Delta H_f^{D,q}(0) + q\mu_{E_F} \quad (1.29)$$

$$\epsilon_{q_1/q_2} = -\frac{\Delta H_f^{D,q_1}(0) - \Delta H_f^{D,q_2}(0)}{q_1 - q_2} \quad (1.30)$$

For chemists, an analogy can be drawn between the transition level ϵ_{q_1/q_2} and the pKa of an acid/base species, where the Fermi level μ_{E_F} corresponds to the pH . When $pH = pKa$, $[acid] = [base]$. Identically, when $\mu_{E_F} = \epsilon_{q_1/q_2}$, $[D^{q_1}] = [D^{q_2}]$ as the formation energies $\Delta H_f^{D,q_1}(\epsilon_{q_1/q_2})$ and $\Delta H_f^{D,q_2}(\epsilon_{q_1/q_2})$ are equal. As discussed in the defect concentration section, as for $pH > pKa$, the ratio $\frac{[D^{q_1}]}{[D^{q_2}]}$ decreases sharply for μ_{E_F} values above ϵ_{q_1/q_2} so that one can consider that the whole population of defect D switches charge from q_1 to q_2 when the Fermi level jumps over ϵ_{q_1/q_2} particular value. Of course, the same is true for $\mu_{E_F} < \epsilon_{q_1/q_2}$. Note that the position of transition level within the gap is independent from the synthesis conditions, *i.e.* chemical potential in the model, it is a property of the defect itself. In the model, it is visible in equation 1.30 as the chemical potentials hidden in $\Delta H_f^{D,q}(0)$ simplify in the energy difference.

The $\Delta H_f(\mu_{E_F})$ plots as presented in Figure 1.20 gives us two types of information. The most obvious one is the energetic cost associated to the creation of the defect, and this associated state of charge (exhibiting the lowest formation enthalpy of all possible states of charge of the considered defect at the value μ_{E_F} of interest). The

more important ΔH_f is, the less concentrated the defect will be in the material. The concentration can be approximated as will be discussed in the dedicated section of the manuscript. This information is available on the y axis of the plot and allows to see which defects will be the most present. As we consider semiconducting hosts, defects can be charged and we have just introduced the related charge transition level ϵ_{q_1/q_2} . The second type of information which can be extracted from this type of plot lies in the analysis of the position of the transition levels with respect to the bandgap. They give clues of the electronic activity of the defect, more precisely its ability to create charge carriers. This analysis will allow us to characterise the defect as a donor or an acceptor, and as a shallow or deep defect.

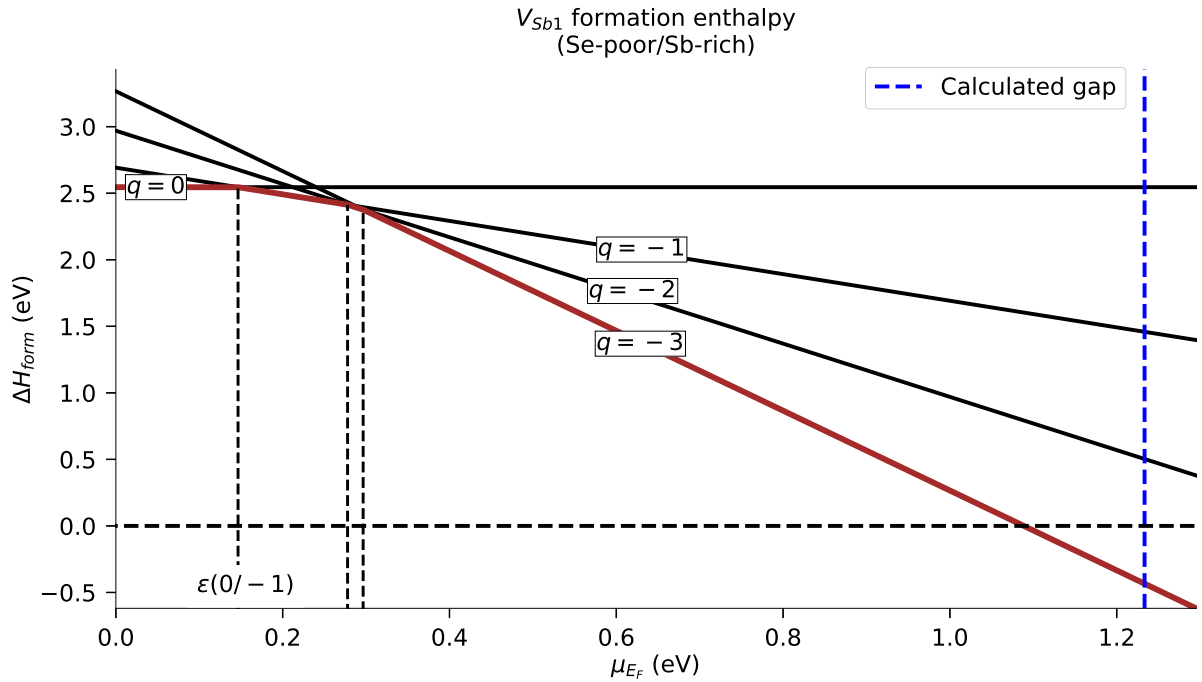


Figure 1.20: V_{Sb1} in Sb_2Se_3 formation enthalpy (Sb-rich/Se-poor synthesis conditions).

The defect is a donor defect favouring electron conductivity if it exhibits a transition level between a state of charge q and another $q' < q$ close to the CBM (which can be thermally activated). Conversely, it is an acceptor defect a transition level between charges q and $q' < q$ in the vicinity of the VBM, as sketched in Figure 1.21. In a n -type semiconductor at low temperature, the Fermi level is pinned between the donor level and the CBM and decreases with temperature increase. The ionization of the defect frees an electron in the system and can be written as $D^{q'} = D^q + (q - q')e^-$. In a p -type material, the Fermi level is located close to the VBM at low temperature and then increases with temperature. The acceptor defect ionization is written as $D^q + (q - q')e^- = D^{q'}$. Defects exhibiting transition levels close to the band edges are called shallow defect and participate in the electronic properties of the materials desired for its application. Conversely, defects which have transition levels buried in the bandgap far from the band edges are called deep defect. In the best case, they are electrically passive. In the worst, they act as recombination centres for the electron-hole pairs and are detrimental to the conductivity.

Our example presented in Figure 1.20, V_{Sb1} in Sb_2Se_3 , is an acceptor defect because of the 0/-1 charge transition level located 0.15 eV above the VBM. In Se-poor/Sb-rich conditions, it is quite high in enthalpy with more than 2.5 eV, so will not be very

concentrated in the material in absolute value. However, the analysis of only one potential candidate is a weak argument to try to rationalise the properties of the material and it seems relevant to try to take into account as many realistic defects as possible altogether.

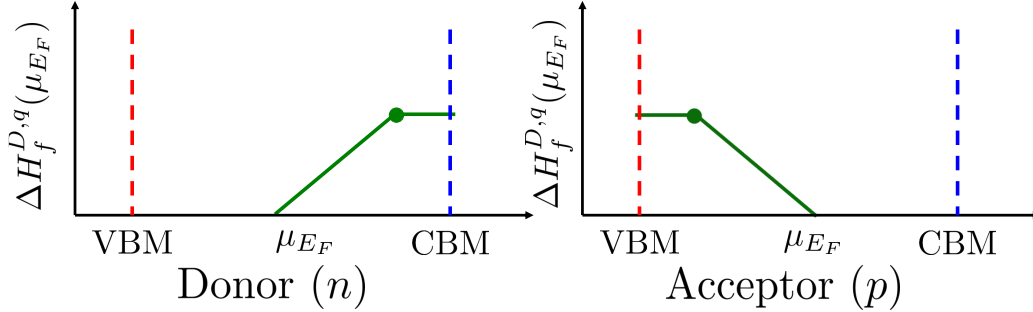


Figure 1.21: Example of donor and acceptor defects DFE.

Then, all defect formation enthalpies can be summarized in Figure 1.22. Note that these enthalpies correspond to a set of synthesis conditions reflected by the choice of chemical potentials as highlighted previously. In the case of a binary material, there are two atmospheres to consider as explained previously, which will result in two sets of DFE to analyse, here Se-poor/Sb-rich and conversely Se-rich/Sb-poor conditions.

As mentioned earlier, there are several distinct crystallographic sites to consider for the vacancies, more precisely two for V_{Sb} and three for V_{Se} , due to low crystal symmetry of the pristine material. Let us start with a few general comments. The behaviour of $V_{\text{Sb}1}$ and $V_{\text{Sb}2}$ is quite close, both in terms of enthalpy and position of the transition levels. $V_{\text{Se}1}$ and $V_{\text{Se}2}$ are very close to one another ($\Delta H \simeq 0.07$ eV) and the transition level $+2/0$ of $V_{\text{Se}3}$ is quite distinguished from the other two. Selenium vacancies display a negative U behaviour as the intermediate charge level $+1$ is not thermodynamically stable (not visible on the plot).⁹ This is the case for chalcogenide vacancies (sulphur and selenide) in most of the different materials studied ($\beta\text{-In}_2\text{S}_3$, TiS_2 , CsCu_5Se_3). Then, let us focus our attention on the electronic properties of the defects by looking at the position of the transition levels. As mentioned before, both cationic vacancies are acceptor defect, but they are quite high in formation enthalpy so will not be very concentrated. The anionic vacancies have a $+2/0$ transition level, so should be donor defects thanks to the mechanism $V_{\text{Se}}^0 = V_{\text{Se}}^{+2} + 2 e^-$. However, they are very deep, with $\epsilon_{+2/0}$ more than 0.6 eV below the CBM, so will not give electrons to the CB of the host material. Nevertheless, they may very well capture the holes liberated by the formation of V_{Sb} , even more so as they are higher in concentration due to a lower formation enthalpy.

Experimentally, Sb_2Se_3 is known to be a p -type semiconductor.[171] The vacancies do not quite explain the origin of the properties of the material. Other defects need to be considered in order to rationalise the origin of the p -type. Interstitials were studied and both found to be very high in enthalpy. Antisites were also considered. Thanks to the ability of antimony to act both as a cation Sb^{3+} ($5p^0$) as in the host lattice and an anion Sb^{3-} ($5p^6$), the substitution Sb_{Se} is very likely, especially in Se-poor conditions logically (more V_{Se}), as shown in Figure 1.23. Usually, the coulombic repulsion energetically hinders the presence of an cation on an anionic site and the

9. Although not thermodynamically stable, the metastable state of charge may intervene in some optical phenomena. Defect-induced luminescence can be related to electrons trapped in such state for a finite time.

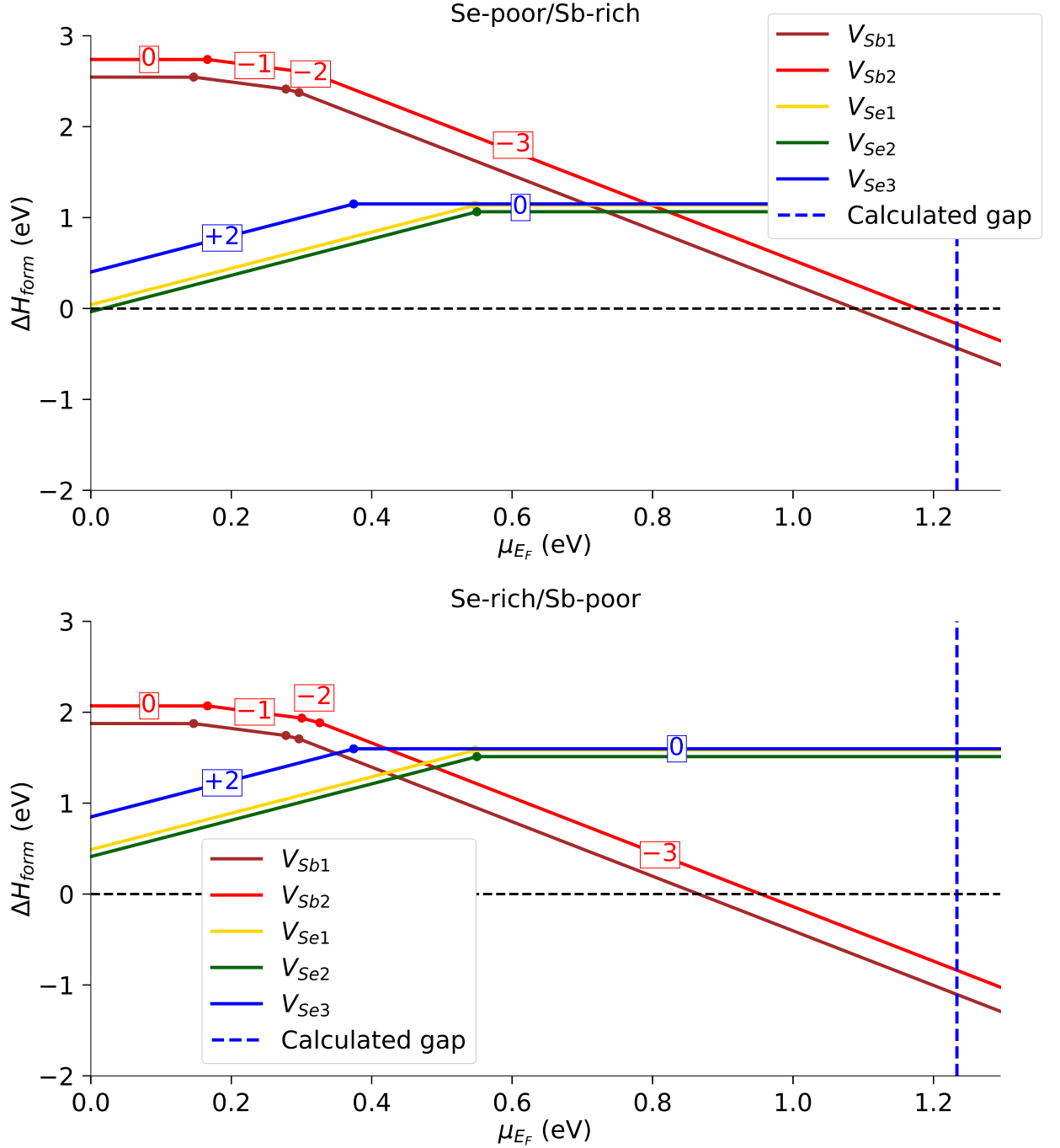


Figure 1.22: Sb_2Se_3 vacancies formation enthalpies.

other way around. $\text{Sb}_{\text{Se}3}$ is the best acceptor of all three Sb_{Se} antisites as its charge transition level is the closest to the VBM. However, it is not a very shallow defect as $\epsilon_{0/-1} \simeq 0.2$ eV and it explains the fair but insufficient for application p -type of the material. This highlights the amount of information which can be extracted from such plots and the power of rationalisation of such method.

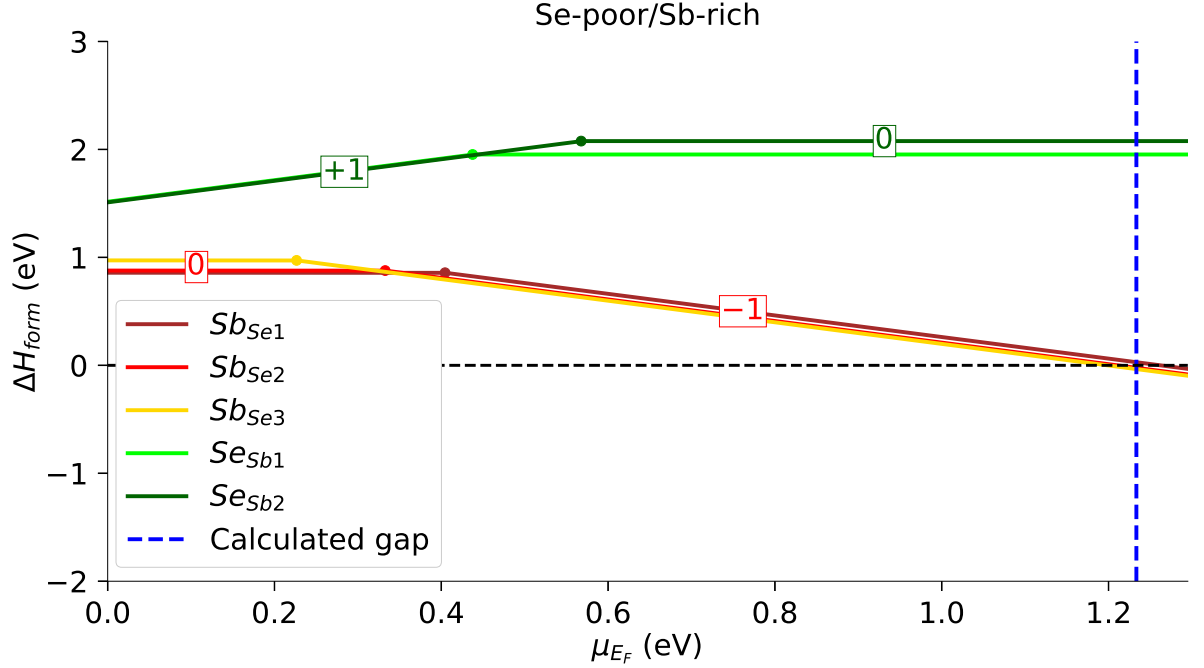


Figure 1.23: Antisites in Sb_2Se_3 formation enthalpy (Sb-rich/Se-poor synthesis conditions).

Finally, the dopability limit of the material can be deduced from the defect formation enthalpies. Indeed, a negative formation enthalpy means that the defect will always be created. For example, in the case of an interstitial atom, it means that any extra atoms added during the crystal growth process will favour the interstitial position over its “normal” crystallographic site. Thus, the host material in such conditions is not stable: as more and more defects add up during growth, the crystal’s stoichiometry drives away from the desired one and the material will ultimately undergo a phase transition towards another compound. As one is looking at the stabilisation of defects in the host, this forbids for μ_{E_F} all the domains where at least one defect has a negative defect formation enthalpy. Thus, the defect with the lowest DFE sets the limits of the range allowed for μ_{E_F} . This is the principle of the determination of the dopability domain of a material, as sketched in Figure 1.24.

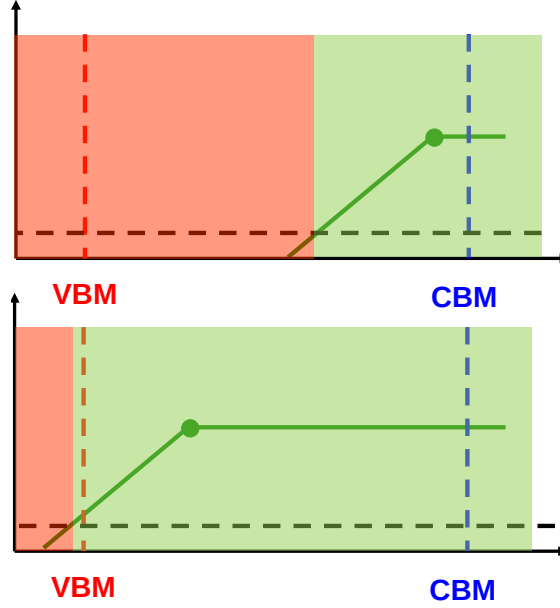


Figure 1.24: Dopability domain (green) and forbidden domain for μ_{E_F} (red). The black dotted line is the zero enthalpy limit. The first material (top) cannot be p -doped because the Fermi level cannot approach the VBM. Conversely, p -doping of the second (bottom) is allowed because the vicinity of the VBM is an allowed region for μ_{E_F} .

1.4 Fermi level and defect concentrations

Following the hypothesis that all defects are formed during synthesis and that the structure is then quenched to room temperature, the concentration n_D of defect D appearing during crystal growth is modelled by a Boltzmann statistic,[172] as expressed in equation 1.31 (N_D^{sites} is the number of sites available for the defect, T_{gr} the growth temperature and E_F^{gr} the Fermi level at growth temperature).

$$n_D = N_D^{sites} \cdot \left(e^{\frac{-\Delta H_{form}^{D,q(E_F^{gr})}(E_F^{gr})}{k_B T_{gr}}} \right) \quad (1.31)$$

The other underlying assumption is that the whole population of this defect is in one stage of charge $q(E_F^{gr})$ determined by the Fermi level during synthesis E_F^{gr} . A quick calculation confirms that this approximation is fairly reasonable. The difference in energy of two states of charge q and q' can be expressed as $(q - q')(\mu_{E_F} - \epsilon_{q/q'})$, hence $\ln \frac{[D^q]}{[D^{q'}]} = \frac{(q - q')(\mu_{E_F} - \epsilon_{q/q'})}{k_B T}$. Numerical application gives 2% for $\mu_{E_F} - \epsilon_{q/q'} = 0.1$ eV at 300 K.

To do so, one must first know the position of the Fermi level during crystal growth E_F^{gr} . The material must stay globally electrically neutral, so the balance of charge must be zero. This is formalised as equation 1.32 which can be solved iteratively with any standard root-finding algorithm.

$$-n_{e^-}(E_F^{gr}) + n_{h^+}(E_F^{gr}) + \sum_D q_D n_{D,q,T_{gr}}(E_F^{gr}) = 0 \quad (1.32)$$

where n_{e^-} and n_{h^+} are the concentrations of free electrons and holes expressed as Fermi-Dirac distribution as given in equation 1.33. The effective masses needed in the theoretical expression of the DOS given in equation 1.34 can be obtained through the

popular parabolic band hypothesis by fitting equation 1.35 to the band extrema.

$$\begin{cases} n_{e^-} &= \int_{E_{CBM}}^{+\infty} g_{e^-}(\mu) f_{FD}(\mu) d\mu \\ n_{h^+} &= \int_{-\infty}^{E_{VBM}} g_{h^+}(\mu) (1 - f_{FD}(\mu)) d\mu \end{cases} \quad (1.33)$$

$$g_p(\mu) = \frac{1}{4\pi^2} \left(\frac{2m_p^*}{\hbar^2} \right)^{\frac{3}{2}} \sqrt{(\mu)} \text{ with } p \in \{e^-, h^+\} \quad (1.34)$$

$$\begin{cases} E_{VB} &= E_{VBM} - \frac{\hbar^2}{2m_{h^+}^*} k^2 \\ E_{CB} &= E_{CBM} + \frac{\hbar^2}{2m_{e^-}^*} k^2 \end{cases} \quad (1.35)$$

Defect concentrations for the Sb_2Se_3 example are shown in Figure 1.25.

The material is then considered quenched: all the defects are formed during synthesis and the population is supposed not to evolve. Only the charges can change. This approach remains valid for quite a long period of time, as long as oxidation caused by O_2 and water in the environment and migration/clustering of defects are negligible. The same approach can be used to deduce the Fermi level at work temperature T_w E_F^w (with $T_w < T_{gr}$). In the previous expression 1.32, the defect concentration is kept constant to $n_{D,T_{gr}}$, which yields equation 1.36. The behaviour of the Fermi level in Sb_2Se_3 is plotted against room temperature in Figure 1.26. One can recognise the typical behaviour of a p -type semiconductor with the Fermi level located near the VBM at low temperature and increasing towards the middle of the bandgap at higher temperature as the defects are ionised.

$$-n_{e^-}(E_F^w) + n_{h^+}(E_F^w) + \sum_D q_D n_{D,T_{gr}} = 0 \quad (1.36)$$

Noteworthy, this methodology is not limited to the study of point defects in the bulk material (3D). It can be easily adapted to materials with lower dimensionality¹⁰ provided that the theoretical expressions of the DOS given for the 3D case in equation 1.34 are replaced by the appropriate ones. Such method has been applied for instance to single layer of MoS_2 . [173, 174]

1.5 Integration into PyDEF 2.0

As seen in the previous part, one must compute a set of calculations per defect and per charge, quickly leading to quite a handful of files to manipulate. An automated solution may come quite handy. Several open source tools exist, most notably Pymatgen, [175]. However, one must have programming skills to use it. In order to promote point defect modelling among a broader community and possibly enlarging the users to experimentalists, PyDEF, featuring a Graphical User Interface (GUI), was developed in the laboratory. Version 1.1 [176] offered useful post-treatments such as band diagrams, density of states...

We proposed PyDEF 2.0 [117] in 2018, featuring a brand new GUI to enable a better user experience with an advanced file management system and new functionalities (band diagram for hybrid functionals, optical indices, multiple defect formation energies...). The source code is available on the sharing platform GitHub¹¹.

10. For instance, 2D materials such as single layers of Transition Metal Dichalcogenides (TMD)

11. <https://github.com/PyDEF2/PyDEF-2.0>

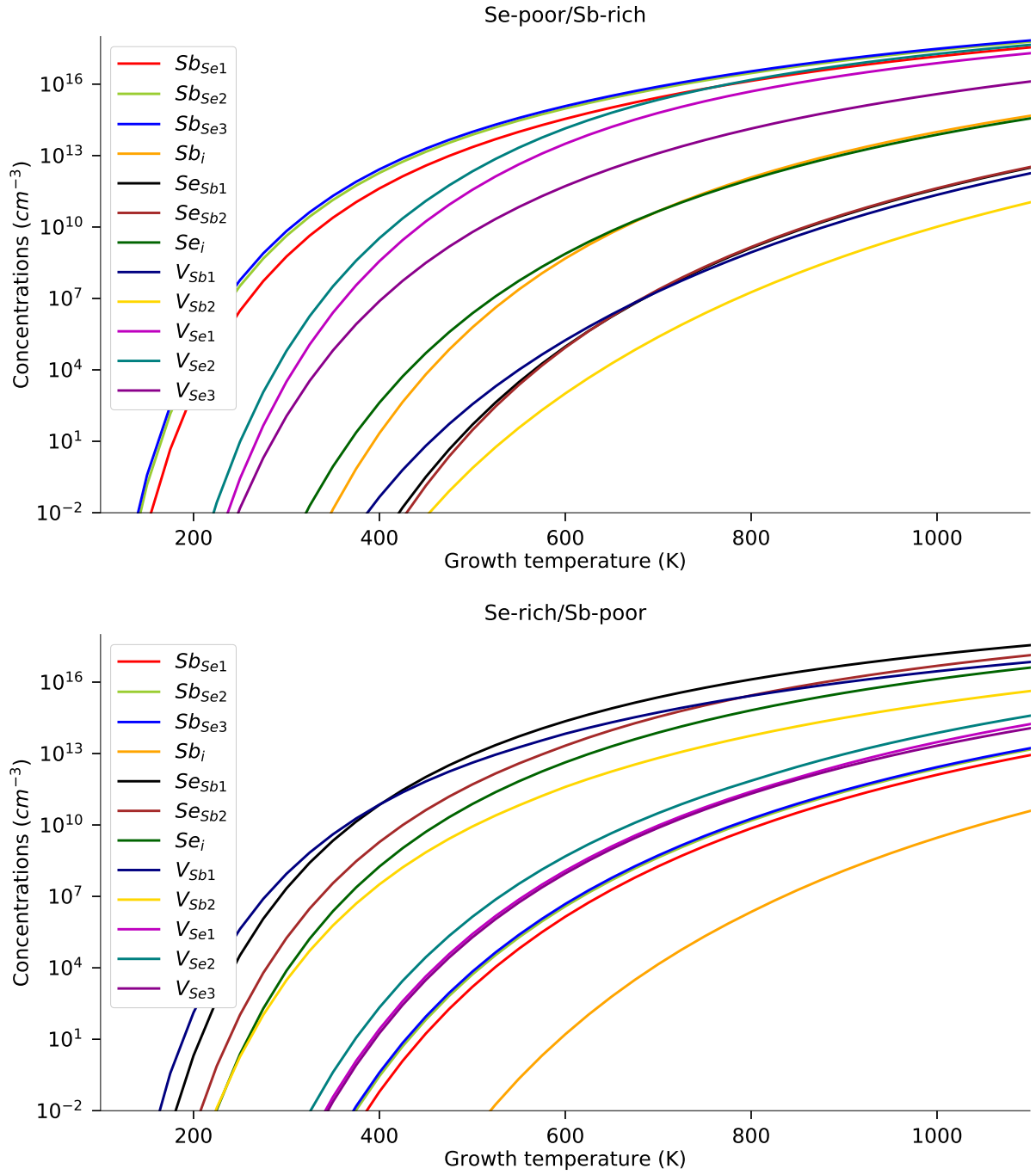


Figure 1.25: Sb_2Se_3 intrinsic defect concentrations.

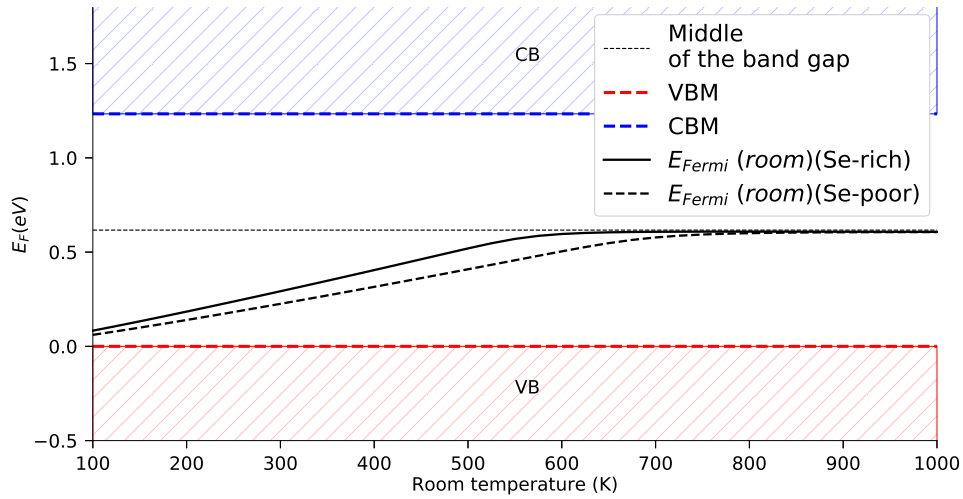


Figure 1.26: Sb_2Se_3 Fermi level plotted against room temperature as determined by solving equation 1.36.

The chosen programming language is Python to enhance readability and flexibility. The detailed list of functionalities offered by PyDEF 2 is the following:

- electronic properties (band diagram, DOS)
- optical indices
- stability domain plots
- defect formation enthalpies
- parabolic fit of band extrema
- defect concentrations
- Fermi level variations

Additionally, the following functionalities are under test for PyDEF 3:

- Birch-Murnaghan equation of states
- phonon-related properties *via* the incorporation of Phonopy[177] and Phonopy-Spectroscopy[178]
- calculation of the stability domain in any dimension
- post-treatment of TD-DFT[179] computations
- Bethe-Salpeter equation[180] compatibility

Chapter 2

Intrinsic and extrinsic point defects in β -In₂S₃

2.1 Introduction

As mentioned in the introduction, the electronic properties of applicative materials are often driven by point defects. Now that relevant tools for their modelling has been introduced in Chapter 1, let us apply this methodology to materials exhibiting interesting properties for potential applications.

One current motivation behind the search for new materials is to tackle the issue of sustainable energy generation faced by our societies. Photovoltaic (PV) electricity generation has emerged as one key technology in the portfolio of potential tools to address this problem. The first generation of industrial PV solar cell is built on the knowledge acquired by the electronic industry on silicon. However, the indirect character of its bandgap results in thermal losses under light absorption. The thickness of the active layer, and subsequently the amount of material used, is more important than for other types of absorbers. For these reasons, competing technologies have been developed. Among the 2nd generation materials, CdTe and chalcopyrite CuIn_{1-x}Ga_x(S_ySe_{1-y})₂ (CIGS) thin films are the most mature technologies with efficiencies routinely outperforming the 20% threshold.[181]

Our research team has an expertise in the second, CIGS-based, thin film technology with the French record of 20.0% for the CIGS technology.[182] The typical architecture SLG¹/Mo/CIGS/CdS/ZnO/Ni:Al of such device is visible in Figure 2.1a.² The role of each layer is detailed in Figure 2.1b. The active layer of the solar cell is the chalcopyrite *p*-type absorber, in which the absorbed light generates electron-hole pairs due to the photovoltaic effect. To generate the *p* – *n* junction which will allow the charge separation, a *n*-type buffer layer is deposited on top of it. In industrial architectures, the usual buffer material is cadmium sulphide.[183] However, this choice has two main drawbacks. Cd is a rare and toxic element. Environmental concerns, potential future legislation and additional worker protection costs constitute a risk for industrial production. Secondly, the Chemical Bath Deposition (CBD)³ required to synthesise the buffer breaks the otherwise all-vacuum deposition process, raising production costs.[184]

1. Soda-Lime Glass

2. courtesy of Dr. S. Harel

3. CBD consists in dipping the substrate in a solution containing the dissolved precursors, which react to form the desired material onto the substrate.

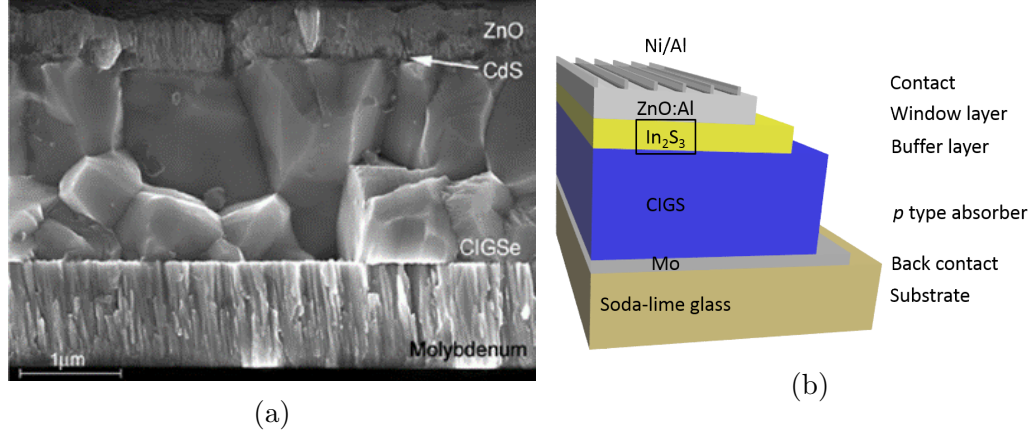


Figure 2.1: a) Scanning electron microscope cross-section of a typical CIGS photovoltaic solar cell b) CIGS photovoltaic solar cell.

For these two reasons, alternative buffer materials have been considered, such as ZnS, $\text{Zn}_{1-x}\text{Mg}_x\text{O}$, $(\text{Zn},\text{Sn})\text{O}_y$ and In_2S_3 . [183, 185] The latter is of longstanding interest within our team. [186–191]

In_2S_3 was suggested for use as a buffer after the presence of CdIn_2S_4 compounds was noticed at the interface between the CIGS absorber and the traditional CdS buffer. [192, 193] The role of intrinsic defects in the parent compound CdIn_2S_4 was investigated within our team prior to this work. [168] Removing cadmium from this structure, it is possible to obtain the solid-solution $\text{Cd}_{1-x}\text{In}_{2+\frac{2x}{3}}\text{S}_4$ for $x \in [0, 1]$, which undergoes a phase transition from the CdIn_2S_4 spinel structure to the tetragonal one of $\beta\text{-In}_2\text{S}_3$ at $x \simeq 0.7$. [194] Although a wet chemistry process is possible to synthesise In_2S_3 , [195] Physical Vapour Deposition (PVD) is of practical interest to prepare devices. The principle of this technique is reminded in Figure 2.2.

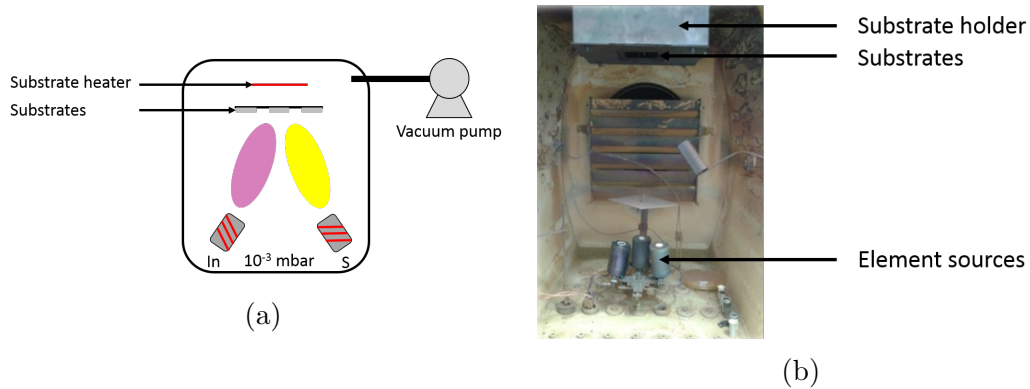


Figure 2.2: a) Principle of PVD. Under vacuum, the elemental sources are heated to evaporate the elements which react together to form a thin film of material on the substrate. b) Picture of the experimental setup.

In spite of the applicative potential of In_2S_3 , a study of intrinsic point defects of indium trisulphide was still missing at the time. This study aims at filling this gap to provide the missing elements to rationalise the electronic properties of buffer material $\beta\text{-In}_2\text{S}_3$.

2.2 Computational details

DFT calculations were performed within the GGA approximation using the PBE functional[196] in a planewave scheme as implemented in the Vienna Ab Initio Simulation Package (VASP).[197–200] The planewave energy cutoff was set to 550 eV. The energy difference between steps in the cycle was converged down to 10^{-5} Å together with a stopping criteria on forces inferior of 10^{-2} eV/Å. $4 \times 4 \times 2$ and $9 \times 9 \times 3$ Monkhorst-Pack grids[201] were used to sample the first Brillouin zone for structural relaxation and DOS calculations, respectively. The fairly big conventional cell of ideal β -In₂S₃ (roughly $7.6 \times 7.6 \times 32$ Å) containing 80 atoms was used throughout the point defect study. A calculation was performed on a $2 \times 2 \times 1$ supercell of 320 atoms and confirmed the supercell convergence size. $5s^25p^1$, $3s^23p^4$, $(n-1)p^6ns^1$, $(n-1)s^2(n-1)p^6ns^2$ valence electrons were explicitly treated for In, S, Na ($n=3$), K ($n=4$), Rb ($n=5$), Cs ($n=6$), and Mg ($n=3$), Ca ($n=4$) and Sr ($n=5$) atoms, respectively. Careful checks were carried out to ensure that In-4d¹⁰ electrons can be safely neglected. Test calculations demonstrated that spin-polarisation is negligible.

In order to correct the band edge positions, a PBE0 DOS calculation was performed on top of the PBE geometry, a scheme often referred to as PBE0@PBE. It yields a bandgap 8% higher than the experimental one, much more appropriate than the 60% underestimation of PBE. To validate our methodology, we checked the obtained DFE against full hybrid PBE0@PBE0 calculation for V_S . These results are also fully consistent with an independent and simultaneous study reported by Ghorbani *et al.*[202] performed at the hybrid level of theory with a tuned HSE functional ($\alpha = \frac{1}{4}$, $\omega = 0.13$ Å⁻¹). As described in details in Chapter 1, a potential alignment energetic correction was employed, along with electrostatic Makov-Payne like correction, Moss-Burstein-type spurious band filling and Perturbed Host States (PHS) correction.

All post-treatments were performed using our in-house code PyDEF.[117, 176]

2.3 Results and discussion

2.3.1 Properties of the pristine material

Before studying point defects, one must first pay attention to the properties of the pristine material and make sure that the model captures enough physics to reliably reproduce experimental data. The starting point is of course a good description of the system, *i.e.* of the crystallographic structure. Three different phases are reported for the In₂S₃ stoichiometry, depending on synthesis temperature.[203] At the relatively low temperatures used during the solar cell elaboration, the compound adopts the tetragonal form β , following the $I4_1$ /amd-141 space group symmetry as presented in Figure 2.3b. Indium atoms occupy three distinct crystallographic positions, namely 8c, 16h and 8e Wyckoff sites, split between octahedral environment (green) for two-thirds (8c and 16h) and the remaining third in tetrahedral environment (orange) (8e Wyckoff position). The S²⁻ anions occupy the same crystallographic position (16h). Three different environments can be distinguished. S₁ refers to 4 folded S atom, coordinated to three In in octahedral environment (O_h) and one In in tetrahedral environment (T_d). S₂ is tricoordinated (3O_h), as well as S₃, (2O_h + 1 T_d). The structure derives from the spinel structure with an organisation of the vacancies leading to an empty T_d 4a site. Noteworthy, a high-temperature α -phase with random occupations of this site

exhibits a spinel structure,[203] which is also the structural type adopted by the parent compound CdIn_2S_4 as discussed at the beginning of the present chapter.[168] The computed $\beta\text{-In}_2\text{S}_3$ cell parameters of $a = b = 7.776 \text{ \AA}$ and $c = 33.097 \text{ \AA}$ overestimate the experimental ones by no more than 2.5%. As discussed previously, this good reproduction of the structure is consistent with general trends in GGA.

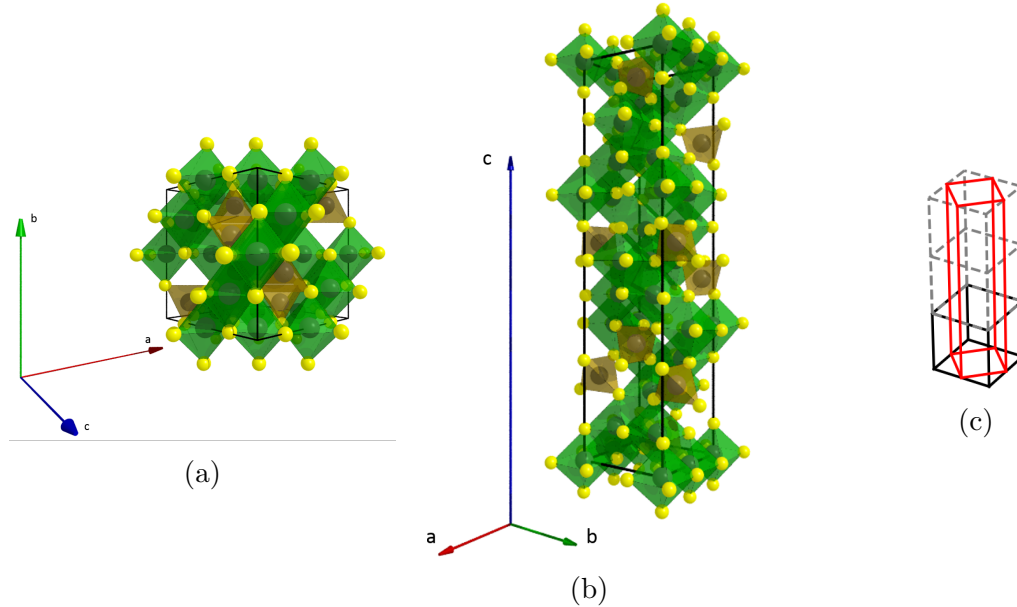


Figure 2.3: a) Crystallographic structure of spinel $\alpha\text{-In}_2\text{S}_3$ high temperature phase. Vacancies are randomly distributed on the tetrahedral sites, resulting in a $Fm\bar{3}m$ (no 225) space group symmetry. $a = 10.8315(2) \text{ \AA}$. [203] b) Crystallographic structure of $\beta\text{-In}_2\text{S}_3$ ($I4_1/\text{amd}$, no 141). It is obtained from the α spinel structure by an ordering of the vacancies along the c axis, and can thus be viewed as a faulted spinel structure $(\square_{\frac{1}{3}}\text{In}_{\frac{2}{3}})_{\text{Td}}\text{In}_{2(\text{Oh})}\text{S}_4$. Yellow spheres represent sulphur atoms while dark spheres represent indium atoms. Two-thirds of the In sit in octahedral environment (green) and the remaining third in tetrahedral environment (orange). $a = b = 7.6205(2) \text{ \AA}$, $c = 32.3603(7) \text{ \AA}$. [204] c) Relationship between α spinel cell (black and grey) and β cell (red).

Next, we investigate the electronic properties of the ideal material. The GGA-PBE electronic band structure and associated DOS of the pristine material are presented in Figure 2.4. It exhibits a direct bandgap of 0.79 eV reached at the Γ point. As expected, this value is largely underestimated by roughly 60% compared to the experimental gap of 2.05 eV [205]. The top of the VB is very flat while the bottom of the CB is highly dispersed. This will induce high hole effective mass and low mobility, and conversely high electron mobility. The effective masses of the charge carriers are obtained by fitting a parabola onto the band edges as stated in equation 1.35 of Chapter 1, yielding $m_h^* = 23.14m_e$ and $m_e^* = 0.082m_e$. The top of the VB is mainly build on sulphur p orbitals while In s orbitals fairly contribute to the CB in the vicinity of the CBM.

As the positioning of the Defect Transition Levels (DTL) with respect to the band edges is key to evaluate the propensity of the defects to create free charge carriers, it is necessary to correct the energetic level of the VBM and CBM. Herein, we use PBE0@PBE band structure to do so. PBE0@PBE DOS calculation yields a more appropriate bandgap value of 2.22 eV, overestimating the experimental by only 8%. This leads us to shift the bands by $\Delta E_V = -0.99 \text{ eV}$ and $\Delta E_C = 0.48 \text{ eV}$.

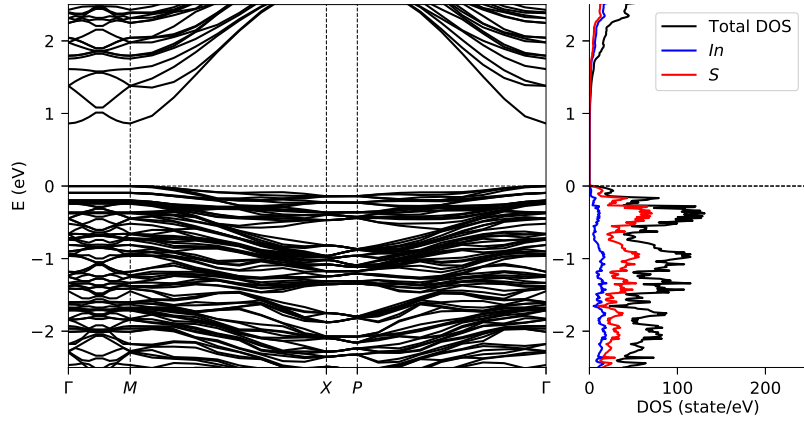


Figure 2.4: Electronic band diagram and DOS of ideal β - In_2S_3 calculated using GGA-PBE functional. The VBM has been taken as reference for the energies, corresponding to the horizontal dashed line. The vertical dashed lines correspond to high symmetry k -points in reciprocal space.

2.3.2 Intrinsic defects

As mentioned in Chapter 1, one needs to evaluate the possible range of chemical potentials of the two chemical species involved, In and S, by calculating the stability domain. Consistently with the rest of the study, it is computed at the GGA level. The calculated stability domain is presented in Table 2.1 and Figure 2.5. The sulphur rich limit is determined by the formation of the first grain of crystalline sulphur S_8 . In this case, the chemical potential of sulphur μ_{S} remains equal to the reference thermodynamic potential of this element μ_{S}^0 and the deviation is zero $\Delta\mu_{\text{S}} = 0$. Conversely, the existence of another possible binary compound within the In-S system, InS, pushes the S-poor/In-rich limit above the $\Delta\mu_{\text{In}} = 0$ limit case set by the formation of In grains during synthesis. In summary, the stability domain of β - In_2S_3 is bounded by the ones of sulphur on the S-rich/In-poor side and of InS on the S-poor/In-rich side.

Table 2.1: Chemical potential limits of β - In_2S_3 stability domain. ($\mu_{\text{S}}^0 = -4.00$ eV, $\mu_{\text{In}}^0 = -2.31$ eV).

(eV)	$\mu_{\text{S}} (\Delta\mu_{\text{S}})$	$\mu_{\text{In}} (\Delta\mu_{\text{In}})$
S-poor/In-rich	-4.90 (-0.90)	-2.78 (-0.47)
S-rich/In-poor	-4.00 (0.00)	-4.12 (-1.81)

Both anionic and cationic vacancies are studied. Rigorously, crystallographic positions must be distinguished, leading to three different sulphur vacancies and three indium ones. Additionally, as we are looking for electron donor defects, we also study cation self-interstitials within the two different environments, octahedral and tetrahedral, labelled accordingly. The DFE curves plotted against Fermi level are presented in Figure 2.6.

Let one start the analysis with the S-rich/In-poor limit synthesis conditions. β - In_2S_3 is known experimentally to be a n -type material, thus we look at potential donor defects, namely the three sulphur vacancies and the indium interstitials. $\text{In}_i(\text{T}_d)$ has a transition level $+2/+1$ 0.2 eV under the CBM. $\epsilon_{+2/+1}$ and $\epsilon_{+3/+2}$ are also very close, so that the simplification to $+3/+1$ states of charge appears as a reasonable shortcut.

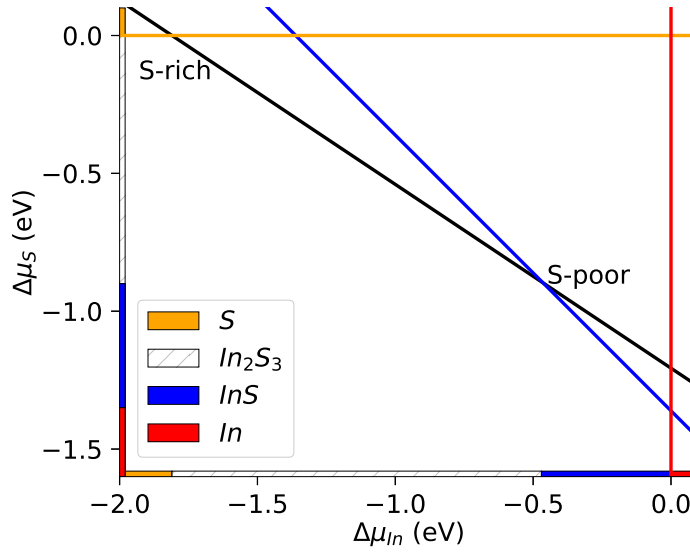


Figure 2.5: Stability domain of β - In_2S_3 presented in $(\Delta\mu_{\text{In}}, \Delta\mu_{\text{S}})$ chemical potential plane.

V_{S} transition levels are a bit further from the CBM, roughly 0.3 eV under the CBM. The best donor defect thus appears to be $\text{In}_i(\text{T}_d)$, and then to a lower extent V_{S_1} . However, in S-rich/In-poor synthesis conditions, the DFE of both donors is fairly high, above 2 eV. Most importantly, a (very deep) acceptor, $V_{\text{In}}(16\text{h})$, has a lower DFE. It means that $V_{\text{In}}(16\text{h})$ will be more concentrated in the material than the donors, and will act as an electron killer, annihilating the electrons formed during the creation of $\text{In}_i(\text{T}_d)$ and V_{S_1} . The electronic conductivity of a β - In_2S_3 sample synthesised in such conditions is thus expected to be quite low.

All intermediate synthesis conditions between the S-rich/In-poor and S-poor/In-rich limits are reachable given the appropriate setup, but looking at the two limit cases is enough to get the trends. Indeed, any intermediate atmosphere is a linear combination of the two. This is why we then focus our attention onto the S-poor/In-rich limit condition set by the formation of InS . First, let us note that the DFE of V_{S} and V_{In} is lower, respectively higher, than in the previous conditions. The model is coherent with the intuition that V_{S} are easier to form in S-poor atmosphere. Interestingly, the formation of $\text{In}_i(\text{T}_d)$ and V_{S_1} donors is now energetically favoured over that of electron killer $V_{\text{In}}(16\text{h})$. From these results, one can conclude that one should synthesise β - In_2S_3 in S-poor/In-rich conditions in order to get more free electrons in the CB and a material of better n -type character.

Noteworthy, one can notice that, although the crystallographic site of the defect induces some differences in DFE between defects of the same type, the coordination of the ion is the driving force for the different defect behaviour. This can be seen especially on V_{In} here, with six-folded vacancies $V_{\text{In}}(16\text{h})$ and $V_{\text{In}}(8\text{c})$ having roughly the same transition levels, quite distinct from those of $V_{\text{In}}(\text{T}_d)$. This can help reduce the number of computations when necessary.

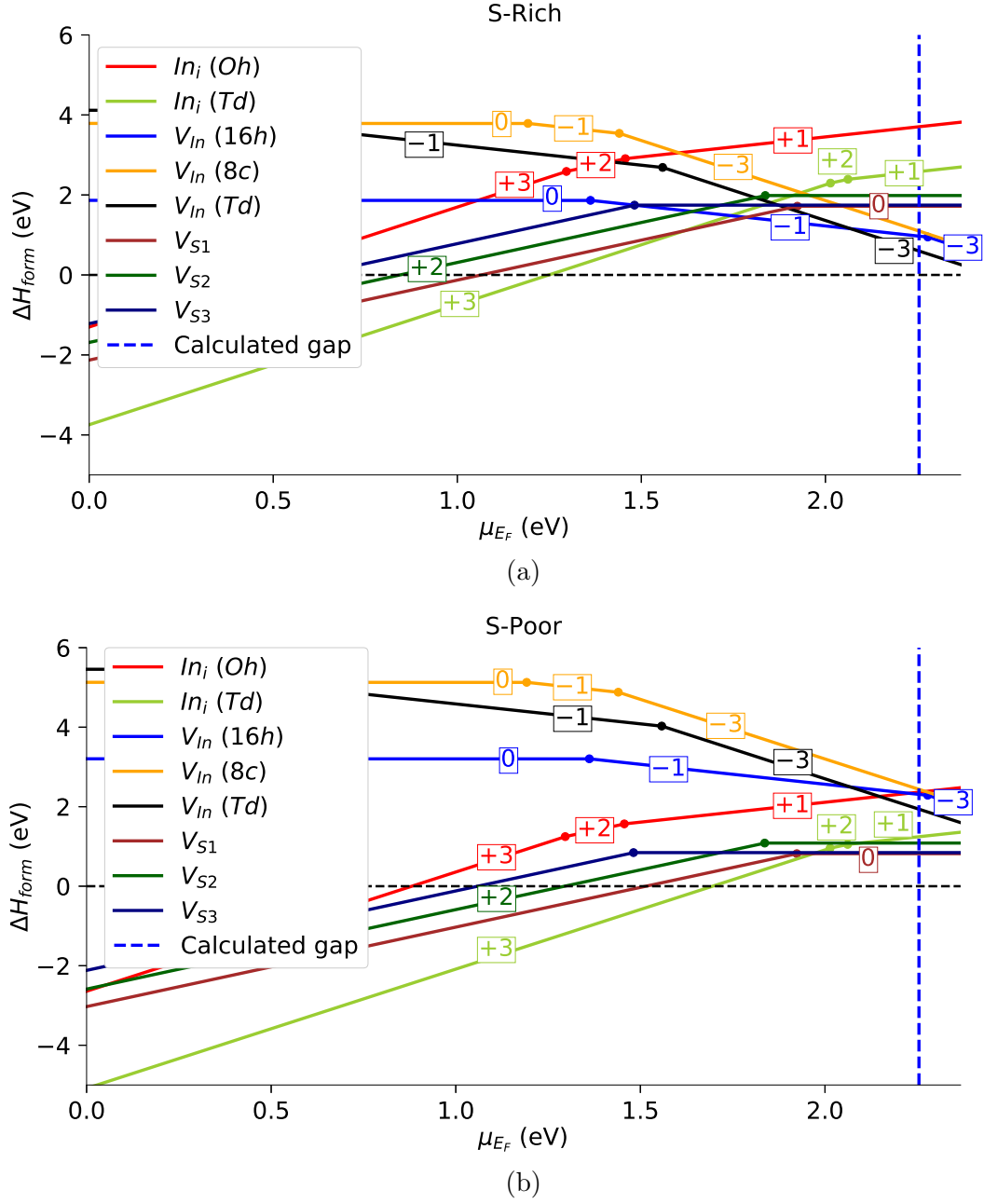


Figure 2.6: $\beta\text{-In}_2\text{S}_3$ intrinsic defects formation enthalpy *vs.* Fermi level a) in S-rich/In-poor synthesis conditions ($\Delta\mu_{\text{In}} = -1.81$ eV, $\Delta\mu_{\text{S}} = 0.00$ eV) b) in S-poor/In-rich synthesis conditions ($\Delta\mu_{\text{In}} = -0.47$ eV, $\Delta\mu_{\text{S}} = -0.90$ eV).

Then, defect concentrations can be calculated, as presented in Chapter 1. The evolution of simulated defect concentrations with respect to crystal growth temperature is presented in Figures 2.7b and 2.7a. The temperature range is chosen very wide to highlight the trends, although some temperatures are unrealistic for real-life synthesis. More specifically, temperatures below 300 K and above the sublimation temperature of the material at synthesis pressure are shown only to check the consistency of the model. Defect concentrations increase with temperature, consistently with the Boltzmann distribution of equation 1.31 presented in Chapter 1. It translates the intuition that disorder increases with temperature, or conceptually the entropic contribution increases with temperature. In S-poor atmosphere, V_S become more concentrated than $In_i(T_d)$ over $\simeq 750$ K. At a realistic temperature for PVD of 550 K, the concentration of the majority defect $In_i(T_d)$ is $\simeq 10^{15} \text{ cm}^{-3}$ in S-poor synthesis conditions with the Fermi level lying $\simeq 0.10$ eV below the CBM. This concentration is coherent with orders of magnitude given in the introduction of the manuscript. The free electron carrier concentration of the same order of magnitude indicates a fair but not exceptional electronic conductivity which matches experimental knowledge on this material.[192]

2.3.3 Partial conclusion on intrinsic defects

Based on our calculation, we have identified a plausible origin of the n -type conductivity of buffer material $\beta\text{-In}_2\text{S}_3$. $In_i(T_d)$ and to a lesser extent V_{S_1} are the major donor defects in the material. In S-rich/In-poor conditions, $V_{In}(16 \text{ h})$ plays the role of an electron killer and is detrimental for the targeted properties. Thus, it appears more favourable to synthesise the material in S-poor/In-rich conditions for the solar cell application. Due to the low vapour pressure of sulphur, these conditions are realistically achievable experimentally when using PVD.

2.3.4 Study of the impact of alkali on the buffer layer

So far, our study has focused on intrinsic defects, inherent to the structure. However, in real materials, impurities can exist. In the CIGS community, a current interest is the impact of alkali on the cell efficiencies. Historically, Stolt *et al.* first noticed a significant positive effect of sodium and potassium diffusion from the SLG substrate to the solar cell's upper layers on its conversion yield.[206, 207]. A chemical bath post-deposition step with concentrated sodium/potassium fluoride (NaF/KF) was added to the process, driving performance upwards.[208–213] *Ab initio* investigations on the effects of alkali have recently been carried out [91, 139, 202, 214–217]. Meanwhile, the experimental community has been pushing further on this track. Heavier alkali elements namely rubidium [218–222] and caesium have even been tried out with success [223, 224]. Thus, we decided to study the impact of alkali defects on In_2S_3 , for Na, K, Rb and Cs. This is a subject of interest for experimentalists in our team[225–229] and still a relevant topic for the community as the mechanisms are still not fully understood [230, 231] It also raised interesting technical questions on the modelling details. The point defect model should give clues to distinguish between two scenarii: the formation of an alkali-rich phase at the grain boundaries or the stabilisation of alkali atoms as impurities in the bulk $\beta\text{-In}_2\text{S}_3$ as point defects, as depicted in Figure 2.8.

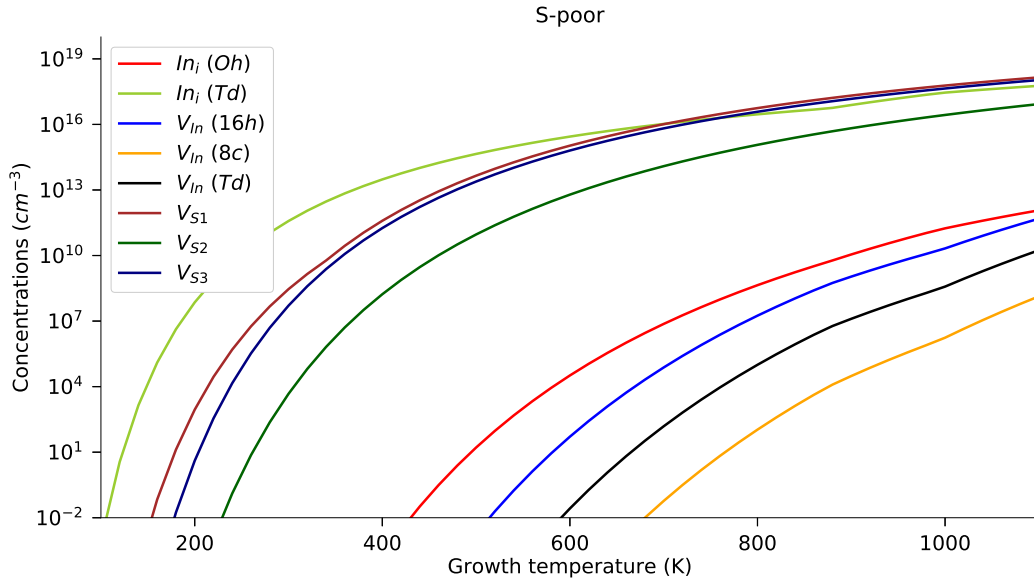
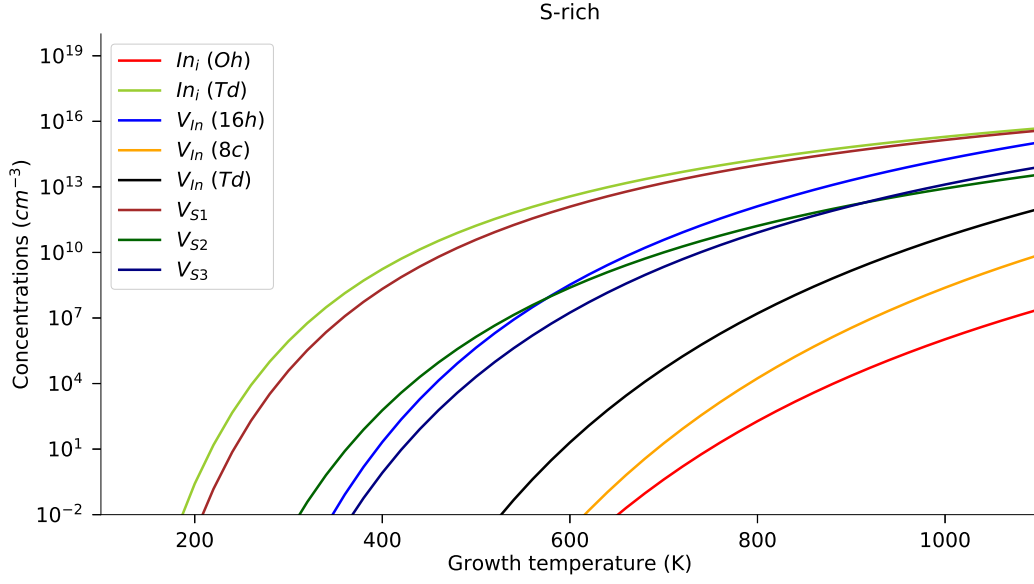


Figure 2.7: β - In_2S_3 intrinsic defect concentrations *vs.* synthesis temperature a) in S-rich/In-poor synthesis conditions ($\Delta\mu_{\text{In}} = -1.81$ eV, $\Delta\mu_{\text{S}} = 0.00$ eV) b) in S-poor/In-rich synthesis conditions ($\Delta\mu_{\text{In}} = -0.47$ eV, $\Delta\mu_{\text{S}} = -0.90$ eV).

The same methodology as for intrinsic defects is employed. Note that the methodology presented in Chapter 1 only relies on the diluted hypothesis. The intrinsic or extrinsic character of the defect does not matter, as long as the defect concentration remains low. Of course, when the extrinsic species is intentionally introduced in the material, the amounts may be more important than in the case of impurities. As long as the dilute approximation stands, the methodology can provide relevant information. The case of solid-solutions ought to be distinguished. However, even in the dilute case for an extrinsic defect, a conceptual problem emerges for the model. Whereas it was clear that host element chemical potentials are obtained from the computation of the stability domain of the host phase, In_2S_3 , how to chose the chemical potential of the impurity is a bit less clear. In several DFT point defect studies involving extrinsic defects, the chemical potential of the impurity is taken as the reference thermodynamic value.[232, 233] Some other authors recommend to calculate a wider stability domain including potential compounds formed by the host chemical species reacting with the impurity.[234, 235] Based on the method presented in Chapter 1, the latter seems more theoretically justified. This study gives us an opportunity to clarify this technical point on a matter of applicative interest.

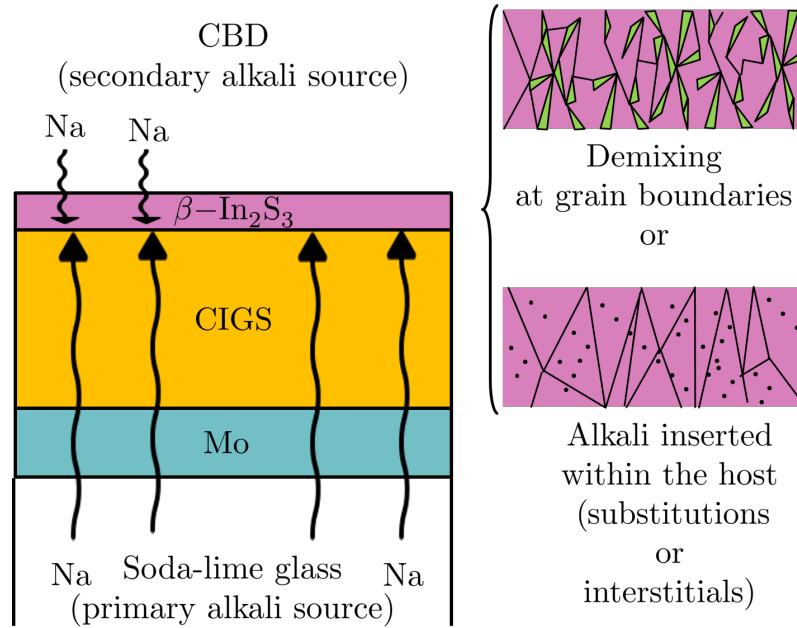


Figure 2.8: Considered scenarii for the effect of alkali diffusion in CIGS solar cells. The diffusion was first coming from the soda-lime glass substrate (primary source) and following its positive impact on the cell efficiency, an additional CBD treatment was added to the fabrication process (secondary source), as depicted in the left-hand side. Two different physical mechanisms can be triggered by the presence of extrinsic sodium in the buffer layer, as represented in the right-hand side. Green regions represent new phases and black dots the insertion of the alkali atoms in the $\beta\text{-In}_2\text{S}_3$ host lattice. The calculations aim at understanding which one most probably happens during the deposition process.

For the sake of clarity, the chemical potentials issue is presented first for the cases of Na and K impurities in $\beta\text{-In}_2\text{S}_3$. The analysis on Rb and Cs will be included within the discussion once the chemical potential choice problem is settled. The first method consists in keeping the In-S chemical space to compute the stability domain of In_2S_3 as obtained in Figure 2.5 and using the reference value for Na $\mu_{\text{Na}}^0 = -1.06 \text{ eV}$ ($\Delta\mu_{\text{Na}} = 0$)

and K $\mu_K^0 = -0.80$ eV ($\Delta\mu_K = 0$), as calculated by Stevanovic *et al.* within the FERE scheme.[236] Alternatively, one can work within the Na/K-In-S system. This bigger system additionally includes binary and ternary compounds containing the impurity element such as NaS₂ and NaInS₂. The stability domain of In₂S₃ in this system is defined by the limit of formation of all possible phases, as expressed for the Na-case in equation 2.1, and plotted in Figure 2.9. NaInS₂ exhibits the lowest formation enthalpy. Thus, it sets the upper limit for μ_{Na} in In₂S₃ stability domain. This way, we obtain the maximum possible value for $\Delta\mu_{Na}^{max} = -1.79$ eV, corresponding to $\mu_{Na}^{max} = -2.85$ eV. This is significantly lower than the FERE value $\mu_{Na}^0 = -1.06$ eV taken as the reference for metallic sodium. A similar scheme yields $\Delta\mu_K^{max} = -1.99$ eV set by KInS₂.

$$\left\{ \begin{array}{l} \Delta\mu_{Na} + \Delta\mu_S \leq \Delta H_f(\text{NaS}) \\ \Delta\mu_{Na} + 2\Delta\mu_S \leq \Delta H_f(\text{NaS}_2) \\ \Delta\mu_{Na} + \Delta\mu_{In} \leq \Delta H_f(\text{InNa}) \\ 2\Delta\mu_{Na} + \Delta\mu_{In} \leq \Delta H_f(\text{InNa}_2) \\ \Delta\mu_{Na} + 3\Delta\mu_{In} \leq \Delta H_f(\text{NaIn}_3) \\ 2\Delta\mu_{Na} + 5\Delta\mu_S \leq \Delta H_f(\text{Na}_2\text{S}_5) \\ 2\Delta\mu_{Na} + \Delta\mu_S \leq \Delta H_f(\text{Na}_2\text{S}) \\ 3\Delta\mu_{Na} + \Delta\mu_{In} + 3\Delta\mu_S \leq \Delta H_f(\text{InNa}_3\text{S}_3) \\ 5\Delta\mu_{Na} + \Delta\mu_{In} + 4\Delta\mu_S \leq \Delta H_f(\text{InNa}_5\text{S}_4) \end{array} \right. \quad (2.1)$$

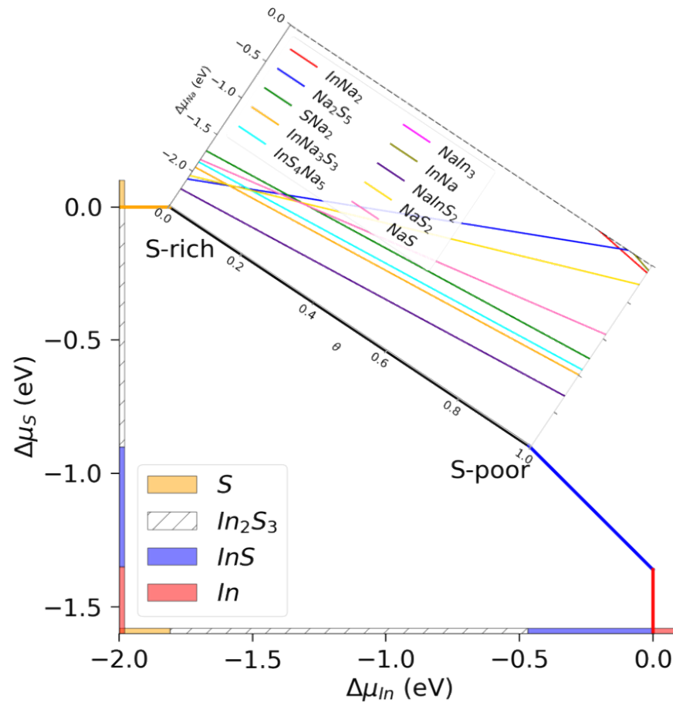


Figure 2.9: Na - In - S phase diagram intersection with β -In₂S₃ stability domain (encapsulated) shown in the $(\theta, \Delta\mu_X)$ plane, with θ the progression from S-rich to S-poor in the stability domain of β -In₂S₃ ($\theta \in [0, 1]$).

The DFE of Na_i and K_i with each choice of chemical potentials are compared in Figure 2.10. The analysis of the DFE of Na_i is not so straightforward, so let one start with K_i. When taking $\Delta\mu_K = 0$, the DFE is negative for the whole bandgap. It means that the formation of K_i would be energetically favoured over that of the host. Any additional potassium atom added to the In₂S₃ matrix would necessarily take the

interstitial position and the stoichiometry of the crystal under formation would not grow to be In_2S_3 but another compound. However, let one keep in mind that the situation $\Delta\mu_K = 0$ represents growth conditions so K-rich that they are on the edge of forming solid potassium. This is hardly representing the situation of an impurity element in a matrix, and intuitively consists in taking a chemical potential value far too high (too small in absolute value). Then, let one take the chemical potential calculated within the K-In-S system. This time, $\Delta\mu_K < 0$. The value set by the lowest formation enthalpy compound KInS_2 is $\Delta\mu_K = -1.99$ eV. Since $\mu = \mu^0 + \Delta\mu$ and the chemical potential of an interstitial atom is subtracted to the total supercell ($n_K = -1$ in equation 1.7), going from $\Delta\mu = 0$ to $\Delta\mu < 0$ lifts the DFE up. As can be seen in Figure 2.10, for $\Delta\mu_K = -1.99$ eV corresponding to the upper μ_K limit of the stability domain of $\beta\text{-In}_2\text{S}_3$, the DFE of K_i is positive. Thus, it should be possible to stabilise K_i interstitial defects within the $\beta\text{-In}_2\text{S}_3$ matrix. However, the limit of solubility of K in $\beta\text{-In}_2\text{S}_3$ is not set by solid potassium but by KInS_2 . This has a strong impact on the behaviour of the point defect model. Taking $\Delta\mu_K = 0$ ($\mu_K = \mu_K^0$) as a value leads to an inappropriate conclusion of destabilisation of the host, because it represents growth conditions at the limit of forming $\text{K}_{(s)}$. It is much more justified to calculate the stability domain of the host within the K-In-S system and use the (much lower) value obtained this way.

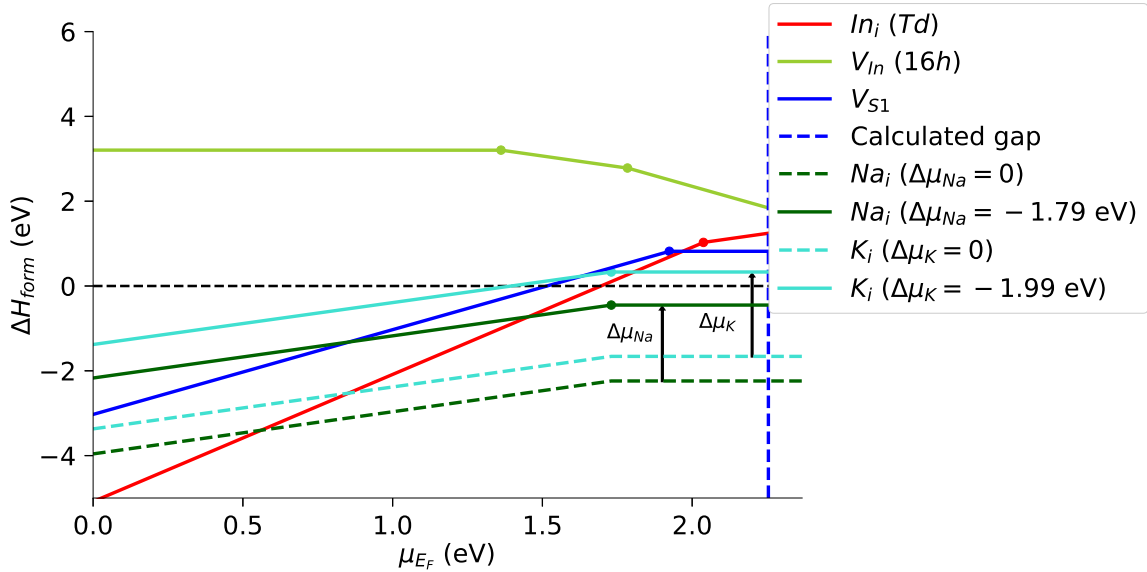


Figure 2.10: DFE plotted against Fermi level for the main intrinsic defects of $\beta\text{-In}_2\text{S}_3$, Na_i and K_i in S-poor atmosphere. The chemical potential of the impurity is taken as the reference thermodynamic potential (FERE) value (dashed line) and at the limit of formation of AInS_2 ($\text{A} = \text{Na}, \text{K}$) (solid line).

Now that this technical point has been clarified and before moving on to Rb and Cs, let one examine the Na case. As for K, using $\Delta\mu_{\text{Na}} = 0$ in the point defect model leads to a negative DFE. As exposed for K, it is more realistic to take into account the possible formation of competing compounds. The same stoichiometry 1:1:2 sets the boundaries of the domain as for the K case. The resulting DFE is improved, however is still negative ($\Delta H^{\text{Na}_i, 0} = -0.44$ eV). One can provide an explanation for this behaviour. The host structure grown in S-poor conditions is the one containing the most defects, as highlighted by the previously calculated defect concentration. The

stability domain however is calculated using only ideal structures. The true boundary of In_2S_3 stability domain on the μ_{Na} axis should ideally be calculated while taking defects into account. However, as practically it is needed for the DFE, it would be an iterative process, and would multiply the already high number of calculations by the number of phases in the ternary system.

The limit chemical potential value can be calculated for Rb and Cs as well. All values are summarised in Table 2.2. They decrease (increase in absolute value) with the atomic number and the cation size. From these values, one can calculate the DFE of other extrinsic defects. A_{In} substitutions DFE were calculated, as presented in Figure 2.11. They are found to be much higher in enthalpy than intrinsic defects and thus will not play a major role. Noteworthy, the transition levels do not depend much on the atomic number within the alkali column, and the DFE increases with the atomic number.

Table 2.2: Maximum chemical potentials for extrinsic alkali dopants in $\beta\text{-In}_2\text{S}_3$ in S-poor atmosphere.

Alkali	$\Delta\mu^{\text{max}}$ (eV)	Phase
Na	-1.79	NaInS_2
K	-1.99	KInS_2
Rb	-2.03	RbInS_2
Cs	-2.11	CsInS_2

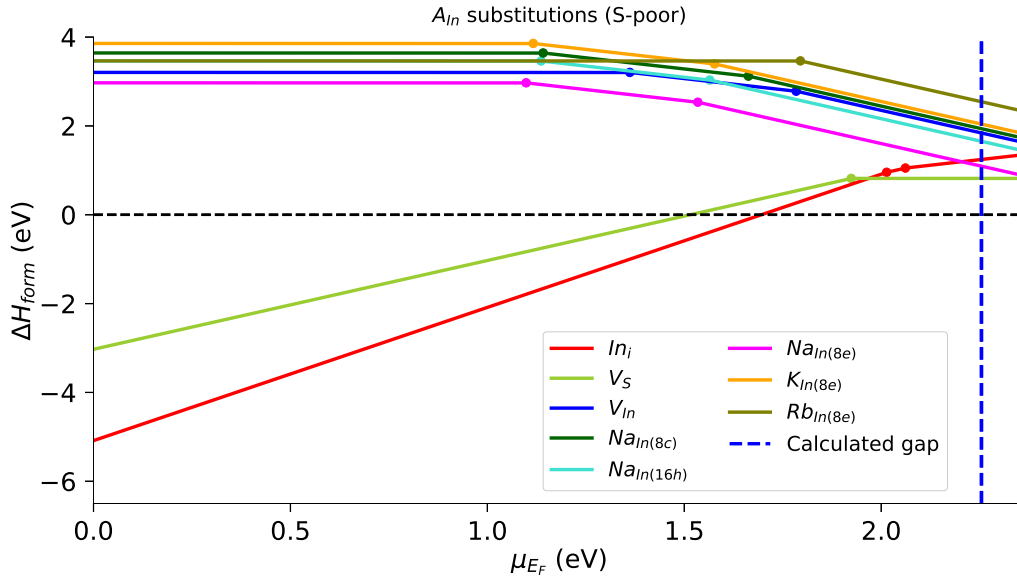
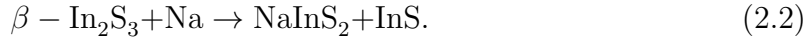


Figure 2.11: DFE plotted against Fermi level for the main intrinsic defects of $\beta\text{-In}_2\text{S}_3$, and A_{In} ($\text{A}=\text{Na}, \text{K}, \text{Rb}, \text{Cs}$) substitutions in S-poor atmosphere. Once the lowest DFE substitutional site has been identified for Na, it is the only site shown for the remaining alkali elements.

A study of Ghorbani and Albe was published shortly before the end of the present work on this matter.[202] The DFE of interstitials and substitutional defects obtained in this work match those from ref[202]. However, since ref[202] discussed an unlikely cation impurity on anionic site substitutional defect, we investigated this Na_{S} defect as well. We found that the structural relaxation leads to a $\text{V}_{\text{S}} + \text{Na}_{\text{i}}$ complex.

2.3.5 Partial conclusion on alkali defects

On the simulation side, the investigation of alkali impurities in buffer material β - In_2S_3 clearly shows that it is necessary to take into account all possible competing compounds containing the impurity element and not only its thermodynamic state of reference to provide realistic chemical potential values. It should be highlighted that this task is now made easier by open access simulation databases which offer pre-converged starting geometries for numerous structures.[237] The values were obtained for all alkali from Na to Cs and the AInS_2 (A= Na,K,Rb,Cs) phase always incriminated for limiting the host stability domain. All four alkali exhibit interstitial defects as the major extrinsic defect in the material. From the electronic point of view, their transition level does not depend on the atomic number. However, the DFE increases with Z , probably due to size effects. The negative DFE of Na_i in S-poor atmosphere singles out but can be correlated to a different crystallographic structure, as NaInS_2 crystallises within the R-3mH (166)[238] space group whereas all AInS_2 (A=K, Rb, Cs) structures are isostructural and within the $C2/c$ (15) space group.[239, 240] This negative DFE suggests the decomposition of the host matrix following the reaction 2.2.



In fact, the maximum chemical potential value allowed for the host is so small (very negative), even for the other alkali elements, that one can wonder whether the concentrations used experimentally do not overcome it, and lead to a similar decomposition for the other alkali as well. This interpretation is corroborated by experimental data on the presence of related compounds such as RbInSe_2 at the interface with the absorber[241] and the subsequent use of similar compound as alternative buffer.[242, 243] The study of the extrinsic point defects involved allow to identify the mechanism of degradation as an attack of the alkali element on the vacant interstitial site of the structure.

2.3.6 Further investigations on chemical potentials: experimental clues with the case of alkali-earth

Following this principle to calculate more relevant chemical potential values for extrinsic elements, one can wonder if it is possible to forecast difficult doping (in the thermodynamic limit) from very negative limit values of chemical potentials before starting the point defect calculations. We embarked on a joint experimental and theoretical study on alkali-earth doping of β - In_2S_3 to try to give food for thought regarding this question. The stability domain of β - In_2S_3 was calculated for alkali-earth doping from Mg to Sr using the same methodology as described in section 2.2. Ba was not studied to alleviate the computational cost, as spin-polarisation effects ought to be taken into account for such element. Mg-doping of β - In_2S_3 was also investigated experimentally.

2.3.7 Experimental setup

Synthesis

First trials were conducted by PVD on a SLG substrate successively depositing MgF_2 then In_xS_y , in the hope that Mg would migrate from the middle layer to the upper layer. These trials proved unsuccessful. Joint evaporation of MgS , In and S on three different

substrates, namely SLG/SiN, SLG/Mo and directly upon SLG allowed to synthesise thin-film samples, but the film morphology proved to be inappropriate for several characterisation techniques on questions related to doping. In particular, X-Ray Diffraction (XRD) patterns were unexploitable, and Transmission Electronic Microscopy (TEM) as well.

In the end, it was found most appropriate to synthesise powder in sealed silica tubes, from MgS and β -In₂S₃. Several synthesis protocols were tested on a combination of different heating programs, carbonated silica tubes or pure silica tubes, use of MgS+In+S or MgS+ β -In₂S₃ as precursors and with and without an annealing step.

β -In₂S₃ was prepared in sealed silica tubes from In (pellets, Sigma-Aldrich, 99.99% purity) and S (powder, Fluka, 99.999% purity) heated at 20°C.h⁻¹ up to 450°C.h⁻¹. They were kept at this temperature for 1h, then underwent a temperature ramp of 100°C.h⁻¹ up to 1000°C. The obtained bulk material was manually grinded to powder and mixed with MgS (200 mesh powder, Cerac, 99.9% purity) and placed in a carbonated silica tube. Heating steps were the same as for obtaining the β -In₂S₃ precursor.

Target compositions including different amounts of Mg were tested during the successive trials (%_{mol} = 1, 5, 10, 15, 40). Typical sample masses were roughly 1 g.

Analysis

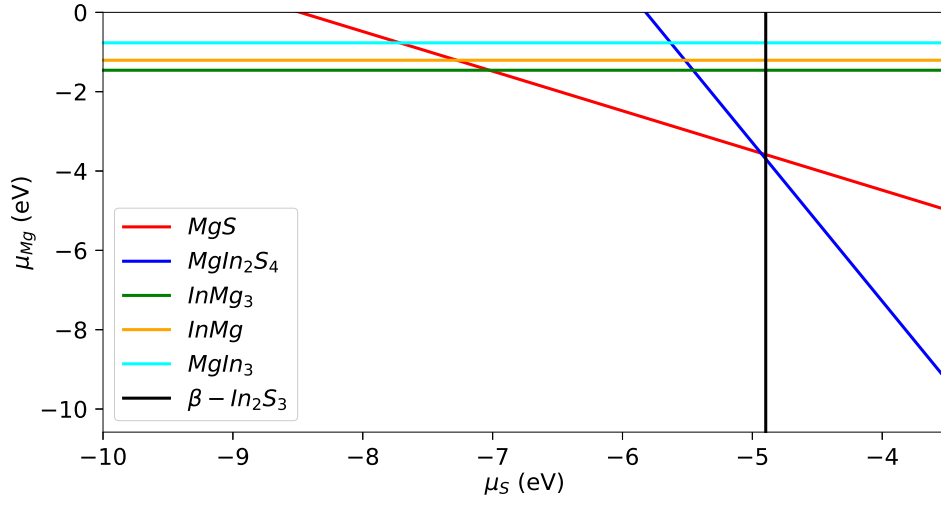
Diffraction patterns were first recorded at ambient temperature using a Bruker D8 Advance diffractometer (Bragg-Brentano geometry, Cu-K α ₁ X-ray source emission wavelength) with a Ge (111) monochromator. However, Rietveld refinements, performed with the Jana2006 program[244], could not converged due to very important β -In₂S₃ grain anisotropy. Subsequently, diffractograms were obtained on an Inel CPS120 diffractometer (Debye-Scherrer geometry, Cu-K α ₁ X-ray source emission wavelength) using a 0.1 mm capillary.

Energy-dispersive X-ray spectroscopy (EDX) was performed on polished sections of samples embedded in epoxy using a Scanning Electron Microscope (SEM)(5800LV from Jeol) operating at 7 kV. In L α , S K α , Mg K α and O K α spectral lines were used for elemental mapping.

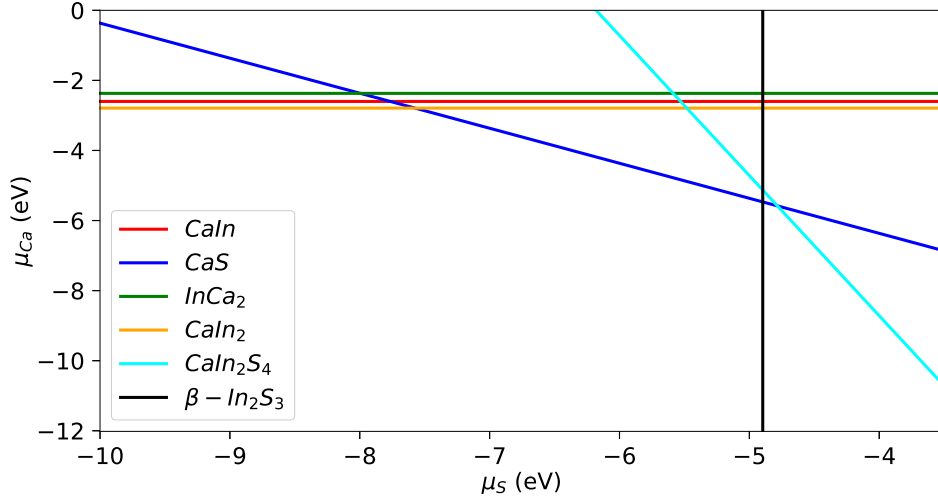
2.3.8 Results and discussion

The stability domain of the β -In₂S₃ host within the A_E-In-S (A_E=Mg, Ca, Sr) chemical space as for the alkali case. The upper chemical potential limit for the impurity is shown at the S-poor end of β -In₂S₃ stability domain in Figure 2.12. It corresponds to the $\theta = 1$ end of the encapsulated domain in Figure 2.9. The chemical potential limits for Mg to Sr are summarised in Table 2.3. They are once more found to be of a few electronvolts, a significant value as commented before. The behaviour of the alkali-earth family is not as consistent as for the alkali-case. In both cases of Mg and Sr, the compound limiting the stability domain of the host is the spinel A_EIn₂S₄ (A_E=Mg, Sr). However, in spite of the existence of isostructural CaIn₂S₄, the CaS material exhibits a lower formation enthalpy, setting the maximum chemical potential limit of Ca within the host stability domain.

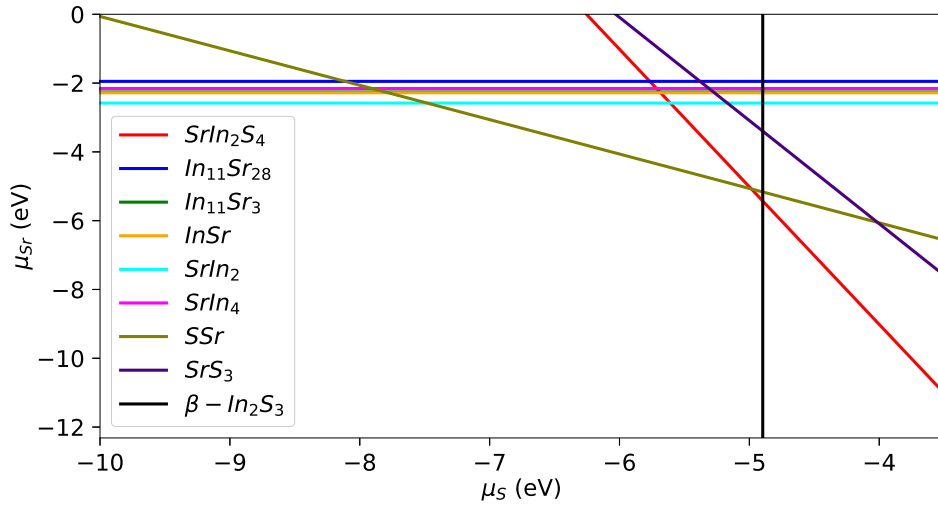
Now that the most probable competing compounds for alkali-earth doping of β -In₂S₃ have been determined, this can be investigated experimentally. One can expect to observe one single (doped) β -In₂S₃ phase for very low alkali-earth contents, growth conditions modelled by a chemical potential of dopant inferior to the calculated limit, and a material containing two phases, namely the host β -In₂S₃ and the competing



(a)



(b)



(c)

Figure 2.12: Limit of β - In_2S_3 stability domain in S-poor atmosphere ($\mu_{\text{In}} = -2.70$ eV, $\mu_{\text{S}} = -4.90$ eV) for a) μ_{Mg} b) μ_{Ca} c) μ_{Sr} .

compounds, MgIn_2S_4 , CaS and SrIn_2S_4 , respectively. In this work, we focus on the Mg-doping case.

Table 2.3: Maximum chemical potentials for extrinsic alkali-earth dopants in $\beta\text{-In}_2\text{S}_3$ in S-poor atmosphere.

Elt.	$\mu_{\max}$ (eV)	μ_{FERE} (eV)	$\Delta\mu_{\max}$ (eV)	Phase
Mg	-3.69	-0.99	-2.70	MgIn_2S_4
Ca	-5.47	-1.64	-3.83	CaS
Sr	-5.43	-1.17	-4.26	SrIn_2S_4

Five different target compositions were tested ($\%_{\text{mol}} = 1, 5, 10, 15, 40$). As EDX analysis showed the presence of Si and O from the tube inside the samples synthesised with simple silica tubes, carbonated tubes were selected for the final synthesis. The annealing step did not seem to bring much change in behaviour (XRD and EDX) and was removed from the final synthesis process. The behaviour discussed hereafter was found to be independent from the composition tried out, so we use the most concentrated one ($\%_{\text{mol}}^{\text{Mg}} = 0.4$) for the discussion, as they provide clearer pictures and more accurate analysis. The trends are the same for the lower contents tested.

A typical XRD pattern along with the residual from Rietveld refinement are presented in Figure 2.13. The behaviour is similar for all samples. All diffraction peaks can be explained by the $\beta\text{-In}_2\text{S}_3$ structure ($I4_1\bar{a}md$, no. 141) drawn in Figure 2.3, as proven by the Rietveld refinement. Either the sample is composed of one crystallised phase Mg-doped $\beta\text{-In}_2\text{S}_3$ or the crystals contain a tiny amount of Mg to none at all and co-exist with a second non-diffracting phase (amorphous or with too small crystallites). Given the compositions targeted, with quite large amounts of Mg, the first scenario seems unprobable or could only happen with a loss of Mg. The MEB and EDX analysis help to discriminate between those two possibilities.

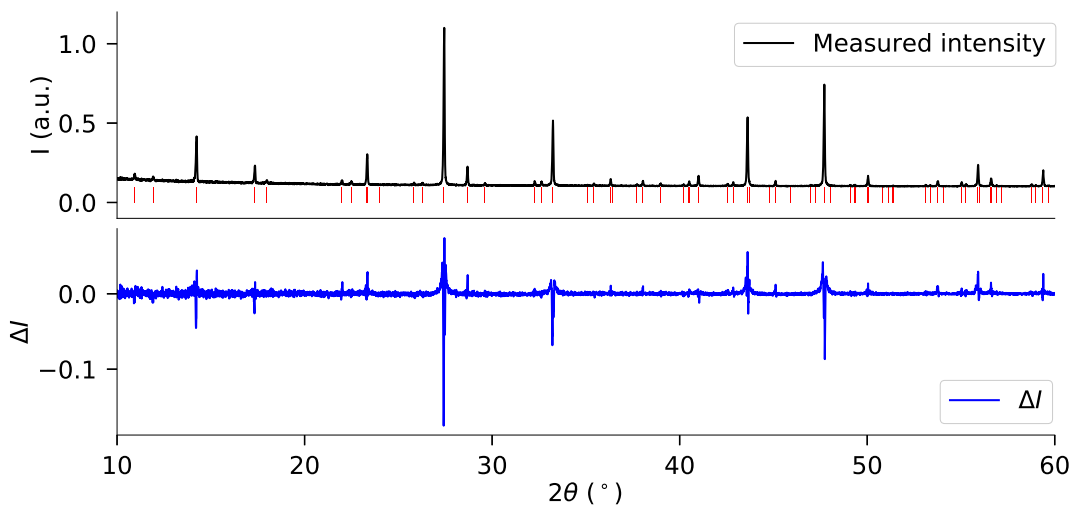


Figure 2.13: X-ray diffraction pattern (top, black solid line) of one sample. All present similar features. The pattern is explained by the $\beta\text{-In}_2\text{S}_3$ structure ($I4_1\bar{a}md$, no. 141) presented in Figure 2.3. Rietveld refinement was performed using Jana2006. The difference between the measured and simulated signal (bottom, blue solid line) as well as the position of the diffraction peaks (top, red ticks) are plotted against 2θ (°).

Figure 2.14 (top) shows MEB images of the sample, mostly using secondary electrons. It displays grains several tens of micrometres wide, seemingly of an approximate parallelepiped shape. They are very similar to what was observed for the $\beta\text{-In}_2\text{S}_3$ precursor used as a reference, both in terms of size and shining. Light colour is a clue of the presence of heavy elements, here most probably In, due to the higher number of electrons re-emitted after irradiation of the sample. The smaller scales allow to notice a second type of grains, which appear much darker in term of chemical contrast and are smaller, typically no more than a few tens of micrometers. These grains are much less concentrated in the sample than the previous ones, by at least one order of magnitude.

In order to clarify what distinguishes the two and locate the Mg element in the sample, EDX elemental mapping was performed on areas of roughly $225\text{ }\mu\text{m}^2$ containing a few grains of which at least one was of the second smaller and darker type. One of such maps is presented in Figure 2.14 (bottom). Two completely different compositions emerge from this picture. The large light-grey grains contain no Mg or O above the detection thresholds, only In and S. As could be suspected from the similarity with the indium sulphide precursor reference, quantification reported in Table 2.4 confirm the In_2S_3 composition. Mg is located in detectable amounts only in the second smaller grains, where O is also present. Quantification summarised in Table 2.4 clearly points toward MgO.

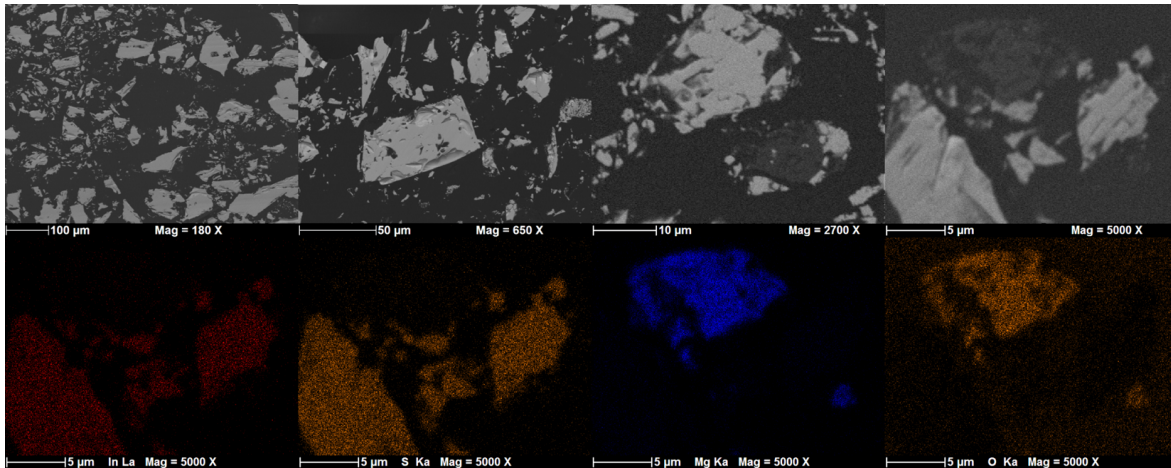


Figure 2.14: MEB images of the $\text{MgS}+\beta\text{-In}_2\text{S}_3$ ($\text{Mg}_{0.4}$) samples at different scales (top) and EDX elemental mapping (bottom). All images are taken using secondary electrons except at the $50\text{ }\mu\text{m}$ scale (backscattered ones). The elemental mapping corresponds to the MEB picture at the top right.

Table 2.4: EDX quantification, given in atomic percentage. (7 kV)

Grain type	In (% _{at})	S (% _{at})	Mg (% _{at})	O (% _{at})
1	39.96	55.73	0.00	4.32
1	37.57	55.79	0.14	6.50
2	0.72	1.84	51.03	46.41

The source of oxygen was identified. The magnesium sulphide reactant appeared to have been hydrated. It is already interesting to note that the formation of MgO is favoured over the stabilisation of Mg in β -In₂S₃.

As we did not manage to avoid O presence in the sample experimentally, we enlarged the chemical space initially considered for the calculation of the stability domain to Mg-In-S-O. The computed domain corresponds to the hatched area presented in Figure 2.15. The Mg-rich (O-poor) boundary is set by MgIn₂S₄ as calculated previously, and the O-rich (Mg-poor) boundary quite intuitively by the oxide In₂O₃. The top right corner of this domain, *i.e.* the most O-rich and simultaneously Mg-rich conditions, is delimited by MgO.

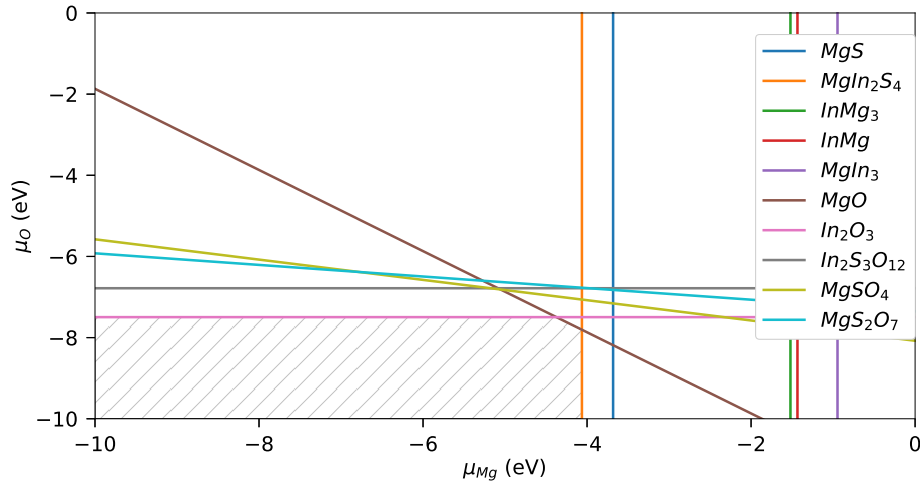


Figure 2.15: β -In₂S₃ stability domain (hatched area) in S-poor atmosphere within the Mg-O-In-S system.

It matches the observation of β -In₂S₃ and MgO grains in our samples. It seems that for all the compositions tried out, the experimental synthesis conditions correspond to the Mg-rich/O-rich limit within the model. It is consistent with the intuition formulated beforehand of a very negative impurity chemical potential limit making the appearance of competing phases easy, making in turn solubilisation of the impurity as a defect within the host (doping) difficult.

The same extrinsic defects DFE were calculated as in the alkali case, namely interstitials, cationic and (pseudo) anionic substitutions. As for the alkali case, the interstitials largely dominate the defect landscape. The DFE in S-poor atmosphere are presented in Figure 2.16. The same behaviour as before appears, with a slightly negative DFE in spite of the refined scheme to evaluate the impurity chemical potential. As discussed previously, this is probably linked to the fact that ideal structures are used to compute the different stability domains. Note that the DTL of alkali-earth interstitials are deeper than those of alkali interstitials.

The β -In₂S₃ structure seems to have a large propensity to tolerate interstitial defects in the T_d 4a vacant site without inducing destabilisation. The idea of exploiting voids in the structure to place interstitials has been explored in Sb₂Se₃ through charge density plots, and will be further discussed for the Transition Metal Dichalcogenide (TMD) investigated in the next Chapter, TiS₂.

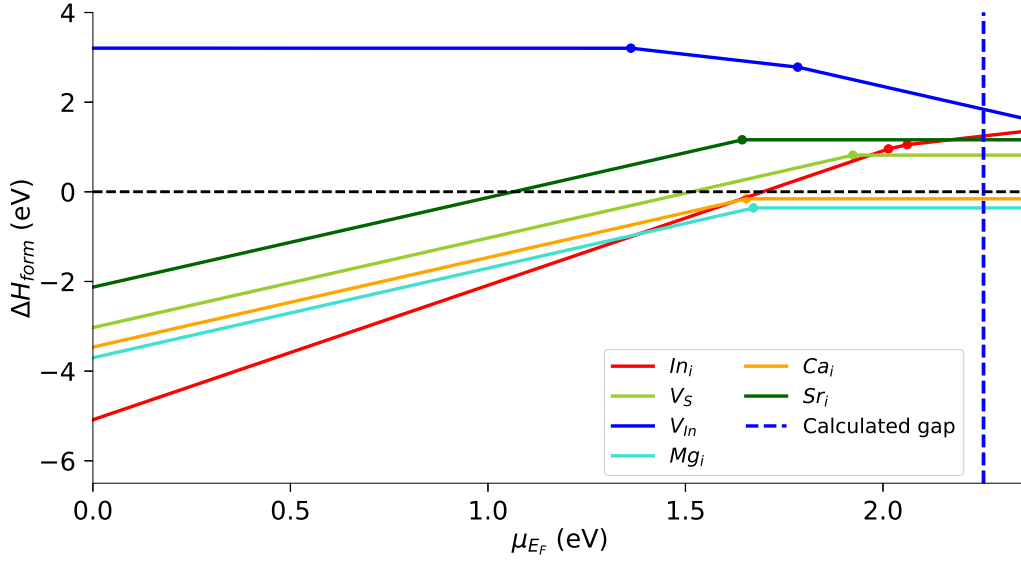


Figure 2.16: DFE plotted against Fermi level for alkali-earth interstitials in β - In_2S_3 synthesised in S-poor atmosphere.

2.4 Conclusion on defects in β - In_2S_3

The point defect methodology introduced in Chapter 1 was successfully applied to the determination of intrinsic point defects in buffer material β - In_2S_3 . The n -type conductivity was linked to indium interstitial defects in tetrahedral environment and to a lesser extent to a sulphur vacancy. The most favourable synthesis conditions for electronic applications such as PV solar cells was found to be the S-poor/In-rich limit of the stability domain. The PV application often involves the presence of alkali elements in the absorber and buffer layer. This second subject was naturally treated subsequently. After showing that all phases in the extended A-In-S stability domain must be taken into account in the computation of the chemical potential of the dopant, the alkali extrinsic defects were investigated. The vacant T_d 4a site in the structure was found to be very suited for the insertion of alkali interstitials in the structure. This defect creation was found to be so energetically cheap that the formation of AlInS_2 is very likely in realistic conditions. It was suspected that the very negative chemical potential values could have indicated this prior to the defect study. This question was investigated by joint computational and experimental means. It was verified on Mg doping that very negative values of impurity chemical potential are matched in experiments by the easy formation of competing compound, here MgO as the oxygen presence could not be avoided.

Chapter 3

Elucidating the versatile electronic behaviour of TiS_2 with the help of the point defect model

3.1 Interest of TiS_2

The next system we investigated is a transition-metal dichalcogenide (TMD), TiS_2 . Since the discovery of graphene in 2004,[245, 246] 2D materials have attracted the attention of researchers due to the new physics they open.[247–250] In particular, non-metallic 2D materials are of interest to develop new optoelectronic devices.[251–253] Some TMD, such as the archetypal MoS_2 , [254] fall into this category. Titanium disulphide TiS_2 is another TMD of long-standing scientific interest, in particular, at the Jean Rouxel Material Institute. It was first studied as an intercalation material for lithium battery electrodes.[255–258] This field of research has seen its pioneers awarded the Nobel prize in Chemistry in 2019.¹ Its layered structure allows the intercalation of various chemical species other than lithium, among which can be cited other alkali such as caesium [259, 260] and sodium [261–264] and also metals like mercury,[256, 265] and silver.[266, 267] Then, other types of applications were considered for TiS_2 , such as hydrogen production [268] and storage [269] or more recently thermoelectricity.[270–273] However, despite several decades of scientific studies on the subject, the question of the metallic or semiconducting character of TiS_2 remains controversial.[274–283] This is of capital importance for the latter application, as the properties of interest of the material captured through the Seebeck coefficient depend deeply on its electronic behaviour.

TiS_2 has been characterised as a semi-metal (SM) by some groups,[278, 284] while others report it as a semiconductor (SC).[281, 285] The discrepancies continue on the theoretical side, some simulations leading to a SM behaviour[284, 286, 287] while others yield a SC.[288–290] Specifically, two simulation difficulties emerge for this compound, namely the importance of long-range van der Waals type interactions and the very small (if existing at all) band gap. This has prompted computationally-oriented scientists to adopt a wide range of modelling strategies with various degrees of theoretical reliability to tackle these issues. Structures following the ideal stoichiometry are sometimes built using the experimental parameters without any relaxation to keep the observed $\frac{c}{a}$ ratio.[291] The use of such non optimal² structure with respect to the functional

1. Laureates were John Goodenough, Stanley Wittingham and Akira Yoshino.

2. in terms of Potential Energy Surface (PES)

used does not guarantee the quality of the obtained electronic structure. Additionally, as discussed hereafter, the stoichiometry of the experimental reference is sometimes difficult to ensure. Other studies rely on semi-empirical total energy corrections such as DFT-D2 proposed by Grimme[292] to account for long-range interactions.[293] However, it is unclear whether the simulated semimetallic behaviour spuriously comes from the underestimation of the electronic band gap within the GGA approximation or is an intrinsic property of the material.

Besides, TiS_2 is known to have a large propensity for off-stoichiometry and its control during synthesis was early on identified as a challenge.[281, 285, 294, 295] It is a layered material with a van der Waals gap which can tolerate self-interstitials titanium atoms at low enthalpy cost.[285] Due to the heavy impact of point defects on electronic properties of materials, this has prompted us to investigate its intrinsic defects. First, we evaluate the different available and affordable methodologies before conducting the defect study itself.

3.2 Structure and position of the problem

TiS_2 crystallises within the CdI_2 structure type within the space group $\text{P}\bar{3}\text{m1}$ space group (164), as shown in Figure 3.1. The primitive (and conventional) cell contains only one formula unit, *i.e.* three atoms. The Ti and S atoms sit in 1a (0,0,0) and 2d ($\frac{1}{3}, \frac{2}{3}, z$) with $z \simeq \frac{1}{4}$ Wyckoff positions, building TiS_2 slabs upon $[\text{TiS}_6]$ edge-sharing polyhedra.

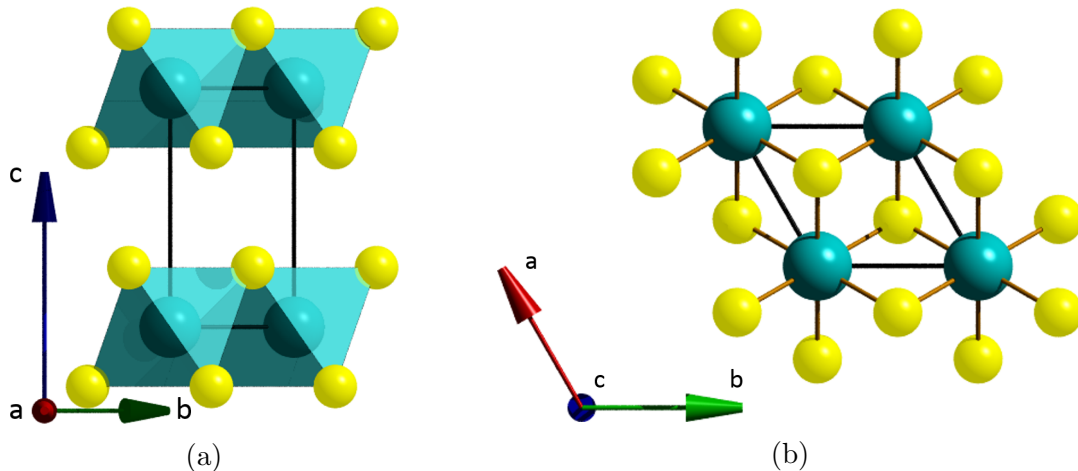


Figure 3.1: Conventional cell of TiS_2 ($\text{P}\bar{3}\text{m1}$ space group, no 164). Blue spheres represent cations Ti^{4+} while yellow spheres stand for the chalcogen anions S^{2-} . Solid black lines represent cell boundaries. TiS_2 : $a = b = 3.4097(5)$ Å and $c = 5.7052(5)$ Å, $V = 57.44$ Å³[296]. a) Side view of the CdI_2 structure type highlighting its layered character with a van der Waals gap along the c axis separating the layers. Ti^{4+} cations sit in an octahedral environment b) Top view showing the hexagonal lattice type.

Two different S-S distances appear: the intra- and the interslab S-S distances. To correctly model the system one must reproduce accurately enough the interlayer S-S distance. This can be assessed by ensuring the value of the $\frac{c}{a}$ ratio is close to the experimental one.

The first issue to model this system is to account for the van der Waals interactions which are responsible for the cohesion between layers. To address it, we include in our

calculations Grimme’s semi-empirical dispersion scheme of pair-wise corrections with Becke-Johnson damping (GD3-BJ). [297–299] Note that other dispersion schemes were also tested, namely dDsC proposed by Corminboeuf,[300–303] Tkatchenko-Scheffler and Tkatchenko-Scheffler with iterative Hirshfeld partitioning,[304] giving similar results.

The second issue is classically the bandgap problem, all the more here because of the uncertainty on the actual existence of a bandgap. To evaluate it, we climb the Jacob’s ladder of *ab initio* simulations, trying GGA functional PBE,[128] hybrid functional PBE0[152] and the dispersion corrected versions using GD3-BJ scheme, noted hereafter PBE-D and PBE0-D. To conclude on the electronic properties of ideal TiS_2 , many-body computation, namely GW, was conducted using PBE0-D wavefunctions as a starting point. To obtain reliable results on the optoelectronic properties, optical indices were simulated by solving the Bethe-Salpeter equation (BSE).[180]

3.3 Assessment of the different methodologies

Before starting the point-defect study, we must make sure we choose a relevant methodology to describe TiS_2 with *ab initio* techniques. Thus, we start with the identification of the most suitable method on the ideal 3 atom cell.

3.3.1 Computational details

We performed the *ab initio* simulations using the Vienna Ab Initio Simulation Package[197–200] using functionals PBE,[128] PBE0[152] in a Plane Augmented Waves (PAW) scheme. Dispersion effects were taken into account using the GD3-BJ dispersion scheme as mentioned previously.[297–299] The cutoff energy for the plane waves was set to 400 eV. GGA (hybrid) optimisations were conducted using a $7 \times 7 \times 7$ ($5 \times 5 \times 5$) k -points mesh generated following a Monkhorst-Pack scheme.[201] For Density of States calculations (DOS), we used a $17 \times 17 \times 11$, $7 \times 7 \times 7$, grid for GGA and hybrid functional, respectively. The Self-Consistent Field (SCF) stopping criterion was set to 10^{-6} eV and the forces stopping criterion for relaxation to 10^{-2} eV.Å⁻¹. Spin Orbit Coupling (SOC) effects were checked to be negligible (less than 10^{-2} eV) and were thus not taken into account.

3.3.2 Geometry

Structural parameters of the optimised geometries are summarised in Table 3.1. As expected, the GGA reproduces well the a parameter with a deviation towards experiment inferior to 1%. Indeed, the absence of van der Waals interactions does not influence this length and cell parameters are usually well described in GGA. However, the c parameters is severely overestimated (by 15%). There are no long-range cohesive forces to maintain the layers close to one another. The resulting $\frac{c}{a}$ ratio is overestimated by 16%. Climbing Jacob’s ladder using PBE0 functional improves this picture by a few per cent but still without giving satisfactory parameters. On the contrary, the inclusion of the dispersion correction GD3-BJ underestimates the parameters but gives values much closer to experiment (within 3%). Both PBE-D and PBE0-D yield convincing relaxed geometries. The contraction when going from PBE to PBE0 can be anticipated as hybrid functional provide a more localised electronic description than GGA functionals.

It shows that van der Waals forces must be accounted for in a TiS_2 model in order to reproduce the (structural) properties of the material.

Table 3.1: Simulated and experimental geometric parameters of TiS_2 , relative deviation of simulation with respect to experiment in brackets.[305]

	PBE		PBE0		PBE-D		PBE0-D		Expt.[306]
$a(\text{\AA})$	3.390	(-0.5%)	3.402	(-0.1%)	3.340	(-2.0%)	3.356	(-1.5%)	3.407
$c(\text{\AA})$	6.527	(-15%)	6.317	(-11%)	5.536	(-3%)	5.492	(-3.5%)	5.693
$\frac{c}{a}$	1.93	(16%)	1.86	(11%)	1.66	(-0.6%)	1.64	(-1.8%)	1.67
$\text{Ti-S}(\text{\AA})$	2.427	(-0.1%)	2.410	(-0.8%)	2.407	(-0.9%)	2.389	(-1.6%)	2.429
$\text{S-S}_{inter}(\text{\AA})$	4.150	(20%)	4.042	(17%)	3.282	(-5%)	3.319	(-4%)	3.460
$\text{S-S}_{intra}(\text{\AA})$	3.472	(0.3%)	3.407	(-1.6%)	3.466	(0.1%)	3.402	(-1.7%)	3.462
$V(\text{\AA}^3)$	64.97	(-14%)	63.30	(-11%)	53.48	(-6.6%)	53.57	(-6.4%)	57.26

3.3.3 Electronic structure

Then, we look into the electronic band structure of ideal TiS_2 described using the four methodologies as shown in Figures 3.2a-3.2d. The Fermi level is used as reference energy. The chosen path in the first Brillouin zone is $\Gamma(0, 0, 0)$, $A(0, 0, \frac{1}{2})$, $H(\frac{1}{3}, \frac{1}{3}, \frac{1}{2})$, $K(\frac{1}{3}, \frac{1}{3}, 0)$, $L(\frac{1}{2}, 0, \frac{1}{2})$, $M(\frac{1}{2}, 0, 0)$. Note that the $\Gamma - A$ segment is oriented along the c^* axis, perpendicular to the sheets.

The PBE band structure (Figure 3.2a) shows a SM behaviour. The CBM is reached at L and is 0.2 eV below the VBM. The Fermi level enters the CBM, forming a hole pocket. The VBM is reached at Γ and A. Interestingly, both the VBM and the CBM bands are constant on the Γ -A segment, as expected as no dispersion was included. The PBE-D band structure (Figure 3.2b) exhibits similar features. The behaviour is still SM. The VBM band is this time dispersed along the vertical direction, the maximum being reached at Γ . The energy has increased at Γ with respect to pure PBE and has been lowered at A. Indeed, an electron in a quantum state similar to a plane-wave of vertical wavevector (Γ -A segment along c^*) has a lower energy in the picture including dispersion corrections as the layers are closer to one another, reducing the distance between core electronic clouds. A tiny hole pocket appears at the summit of the Valence Band (at Γ).

However, GGA functionals are known to severely underestimate bandgaps,[122] whereas hybrid functionals give better predictions of this parameter. PBE0 gives a band structure (Figure 3.2c) closely related to the PBE one in shape but opening an indirect bandgap of 1.07 eV. Once more, without dispersion the VBM and CBM bands are flat between Γ and A. The inclusion of dispersion (Figure 3.2d) reduces the bandgap to 0.71 eV but the material is still SC. The impact on band dispersion is the same as in GGA.

To summarise, the GGA description of ideal TiS_2 is SM whereas PBE0 indicates a low (indirect $\Gamma - L$) bandgap SC. As GGA is known to severely underestimate bandgaps and hybrid functionals to yield more accurate bandgaps, one is enticed to see the ideal TiS_2 as a SC.

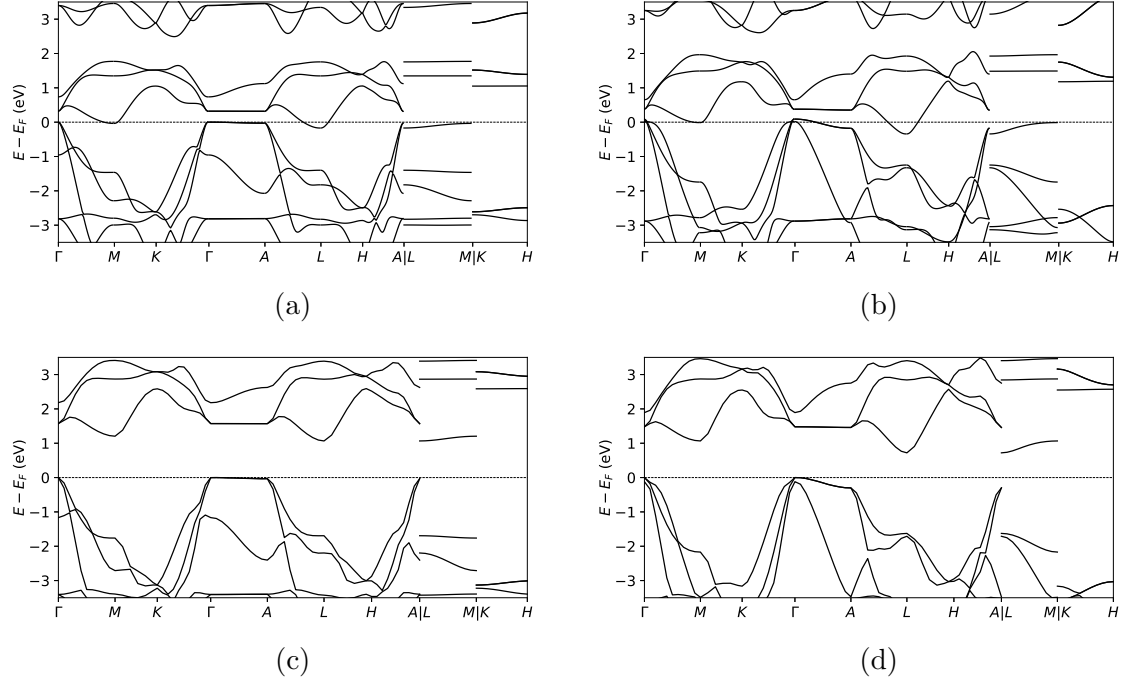


Figure 3.2: TiS_2 electronic band structure described with the a) PBE functional b) PBE-D approach c) PBE0 functional d) PBE0-D approach.

3.3.4 Comparison with experiment

To determine with confidence whether TiS_2 is indeed a SC, we proceed with the comparison of optoelectronic properties with available experimental data and more refined theories.

First, we compare the DOS obtained with PBE-D, PBE0-D and a many-body Green function calculation (GW) to XPS data,[307] as shown on Figure 3.3. To ease the comparison, simulated data has been smoothed through a moving average³. In the vicinity of the VBM ($E - E_F$ close to 0), the latter two methodologies reproduce the foot of the summit obtained experimentally, whereas PBE-D yields an incorrect rising trend, due to the SM behaviour obtained with such a level of theory. All three simulations exhibit two local maxima and a shoulder like the measurements.

Secondly, we compare the imaginary part of the dielectric function ϵ_2 obtained with PBE0-D hybrid density functional and solving BSE[180] with EELS spectrum, as shown in Figure 3.4.[308] One lacks experimental data between 0 and 2 eV. To improve the comparison, simulated curves were shifted to fit the position of the first local maximum around 4.5 eV. Both computations nicely reproduce the shape of the spectrum. The position of the PBE0-D curve with respect to the experimental data is a bit uncertain. Our simulations predict a first maximum reached around 2 eV, however this corresponds to the unsampled region of the experimental spectrum. By extending the foot of the first peak, one can notice that the BSE computation yields a gap. This confirms the SC behaviour calculated using PBE0 and PBE0-D.

3. A moving average of the data y of order n is given for each index p by the expression $\overline{y}_p = \frac{1}{n} \sum_{i=p-n+1}^p y_i$

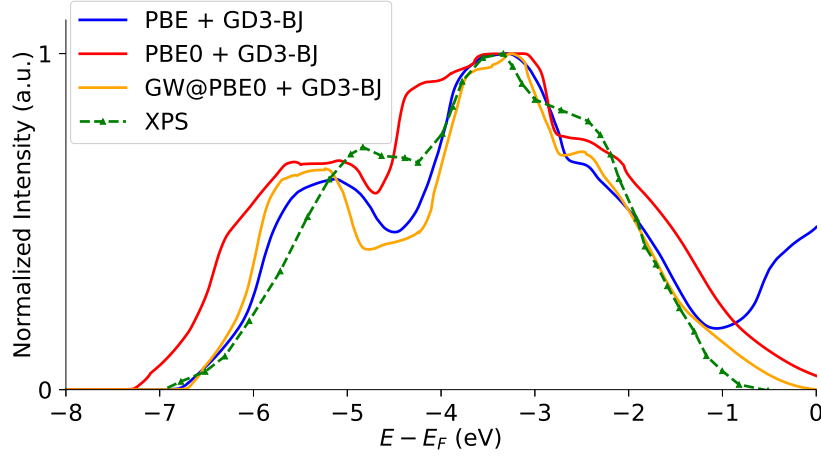


Figure 3.3: Comparison of smoothed DOS calculated using PBE-D (blue), PBE0-D (red) and GW (orange) with experimental XPS spectrum.[307] 300th, 400th and 250th orders were employed for the moving average smoothing of PBE-D, PBE0-D and GW curves, respectively.

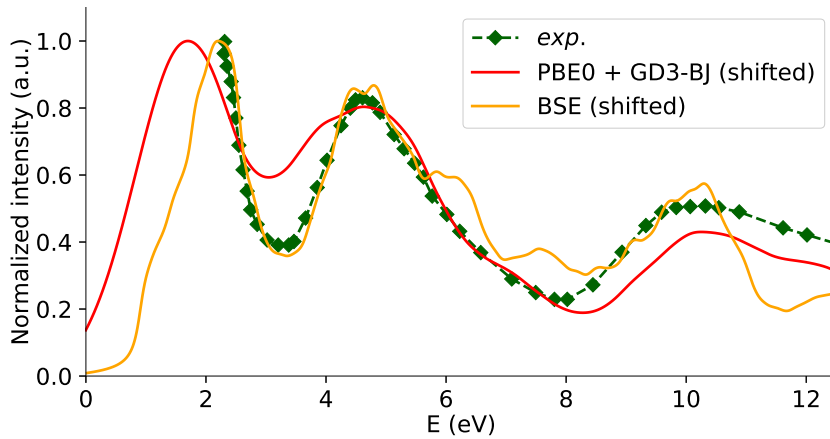


Figure 3.4: Comparison of the imaginary part of the dielectric function ϵ_2 obtained using PBE0-D hybrid density functional (red) and solving Bethe-Salpeter equation[180] (orange) with EELS spectrum.[308]

3.4 Point defects

3.4.1 Computational details

We have shown in the previous part that an *ab initio* model of TiS_2 must account for van der Waals forces and in order to reproduce electronic properties has to climb the Jacob's ladder at least up to hybrid functionals. Now that a relevant methodology has been identified, we can study the intrinsic point defects of the material using the PBE0-D approach. The computations are performed in a $4 \times 2 \times 2$ supercell containing 48 atoms using the same parameters as mentioned previously. We sampled the first Brillouin zone with a $3 \times 3 \times 3$ mesh following a Monkhorst-Pack scheme.[201] The $4 \times 2 \times 2$ supercell corresponds to a raw fraction of defect in the model of $\frac{1}{48} \simeq 2\%$ which is fair, especially given the high computational cost of a full study using a global hybrid.

3.4.2 Stability domain and chemical potentials

First, we need to assess the chemical potentials of the elements involved, namely titanium and sulphur. We screen stable phases around the ideal stoichiometry 1:2 on the experimental database ICSD[309], yielding TiS_3 ($P2_1/m$), Ti_2S_3 ($C2/m$) and TiS ($P\bar{6}m2$). In order to be as comprehensive as possible, we complete this set of compounds with a hypothetical compound Ti_7S_{12} (P1) obtained *via* high-throughput calculations.[237, 310] The latter structure results from the stabilisation of two interstitial titanium atoms in the van der Waals gap. The stability domain is shown in Figure 3.5, the different total energies are summarised in Table 3.2 and the obtained chemical potentials in Table 3.3.

The stability domain of TiS_2 is limited by the formation of TiS_3 on the Ti-poor/S-rich side and of Ti_7S_{12} on the Ti-rich/S-poor limit.⁴ These are binary phases so the deviation of chemical potential from the standard phases ($\alpha\text{-S}_8$ and Ti metal) is non zero.

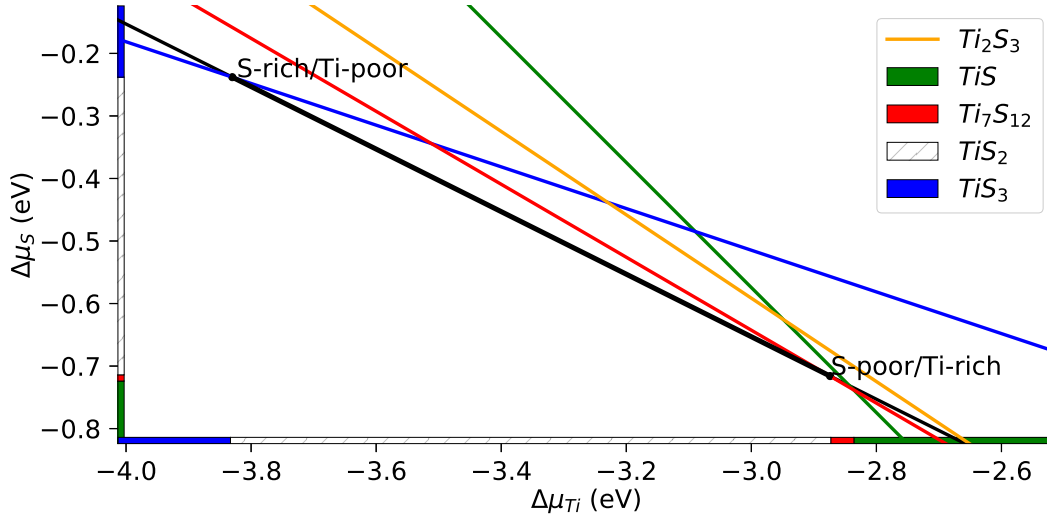


Figure 3.5: TiS_2 stability domain with respect to competitive phases and the chemical potentials in Ti and S in the $(\Delta\mu_{\text{Ti}}, \Delta\mu_{\text{S}})$ plane. It is highlighted by the black segment in the $(\Delta\mu_{\text{Ti}}, \Delta\mu_{\text{S}})$ plane and its projections onto the axis by the hashed domains.

Table 3.2: Total energies of the phases of TiS_2 stability domain calculated with PBE0-D.

	Total energy per formula unit (eV)
TiS	-20.537
TiS_2	-27.245
TiS_3	-33.459
Ti_7S_{12}	-177.332
Ti_2S_3	-47.676

4. Ignoring Ti_7S_{12} sets the Ti-rich/S-poor limit at the frontier of formation of TiS , which corresponds to a $\simeq 0.01$ eV change in μ_{S} and $\simeq 0.03$ eV in μ_{In} . This will not impact the results.

Table 3.3: Computed extrema chemical potentials to form TiS_2 ($\mu_S^0 = -5.976$ eV and $\mu_{\text{Ti}}^0 = -10.987$ eV).

(eV)	μ_S ($\Delta\mu_S$)	μ_{Ti} ($\Delta\mu_{\text{Ti}}$)
S-poor/Ti-rich	-6.692 (-0.716)	-13.862 (-2.875)
S-rich/Ti-poor	-6.214 (-0.238)	-14.817 (-3.830)

3.4.3 Defect formation enthalpies and origin of the versatility of the electronic properties of TiS_2

The obtained defect formation enthalpies are presented in Figure 3.6. In S-rich/Ti-poor synthesis atmosphere (frontier with TiS_3), the defect exhibiting the lowest formation enthalpy is the titanium interstitial inserted in the van der Waals gap, Ti_i (O_h). Its transition level $\epsilon_{+4/+2}$ is very close to the CBM, around 0.04 eV below the CBM, with a quite low formation enthalpy (< 1 eV). The position of the transition level associated with a low formation enthalpy translate a good donor defect which induces a very good n -type material. The two vacancies V_S and V_{Ti} are quite high in enthalpy, thus the most concentrated defect will overwhelmingly be the titanium interstitial.

In S-poor/Ti-rich atmosphere, at the frontier with Ti_7S_{12} , the sulphur vacancy V_S is logically lower in enthalpy than in the previous atmosphere and V_{Ti} even higher. The majority defect is still Ti_i . However, in S-poor/Ti-rich conditions the situation has changed: whatever the position of the Fermi level in the bandgap, the formation enthalpy of Ti_i is negative. As explained in Chapter 1, if the Fermi level during crystal growth were to fall into a region of the gap where a defect has a negative formation enthalpy, the creation of such a defect is no more a rare event but fatally happens and the resulting composition is driven away from the expected stoichiometry, leading to a phase transition towards a new structure. It means that in the present case μ_{E_F} cannot be located inside the gap and must enter the CBM. This is permitted by the fact that $\Delta H_{\text{form}}^{\text{Ti}_i}$ reaches the zero enthalpy not far above the CBM ($\simeq 0.1$ eV). The resulting TiS_2 has by definition a SM behaviour. The same logic applies for V_{Ti} to determine the other limit of the dopability domain. As this vacancy is the only potentially accepting defect, it would set the n -type limit of the dopability domain to the Fermi level value where it reaches the zero enthalpy. Because V_{Ti} is very high in enthalpy in both synthesis conditions, this value falls very high into the conduction band, so that there is effectively no limitation to the n -type dopability of the material.

The low formation enthalpies reflect well the experimentally reported propensity of the material to be off-stoichiometric.[285] The evaluated defect concentrations are summarised in Table 3.4. For a TiS_2 synthesised in S-rich/Ti-poor conditions, the concentration of titanium self-interstitials is $\simeq 10^{19} \text{ cm}^{-3}$ and is two orders of magnitude higher in S-poor/Ti-rich atmosphere.

Table 3.4: Defect concentrations of the investigated defects: Ti_i , V_S and V_{Ti} .

(cm^{-3})	Ti_i	V_S	V_{Ti}
S-rich/Ti-poor ($T_{gr} = 900$ K)	1.3×10^{19}	1.4×10^8	3.2×10^9
S-rich/Ti-poor ($T_{gr} = 1200$ K)	4.4×10^{19}	5.3×10^{11}	1.5×10^{12}
S-poor/Ti-rich ($T_{gr} = 900$ K)	5.1×10^{21}	9.2×10^{10}	2.9×10^9
S-poor/Ti-rich ($T_{gr} = 1200$ K)	9.1×10^{21}	8.5×10^{13}	1.0×10^{13}

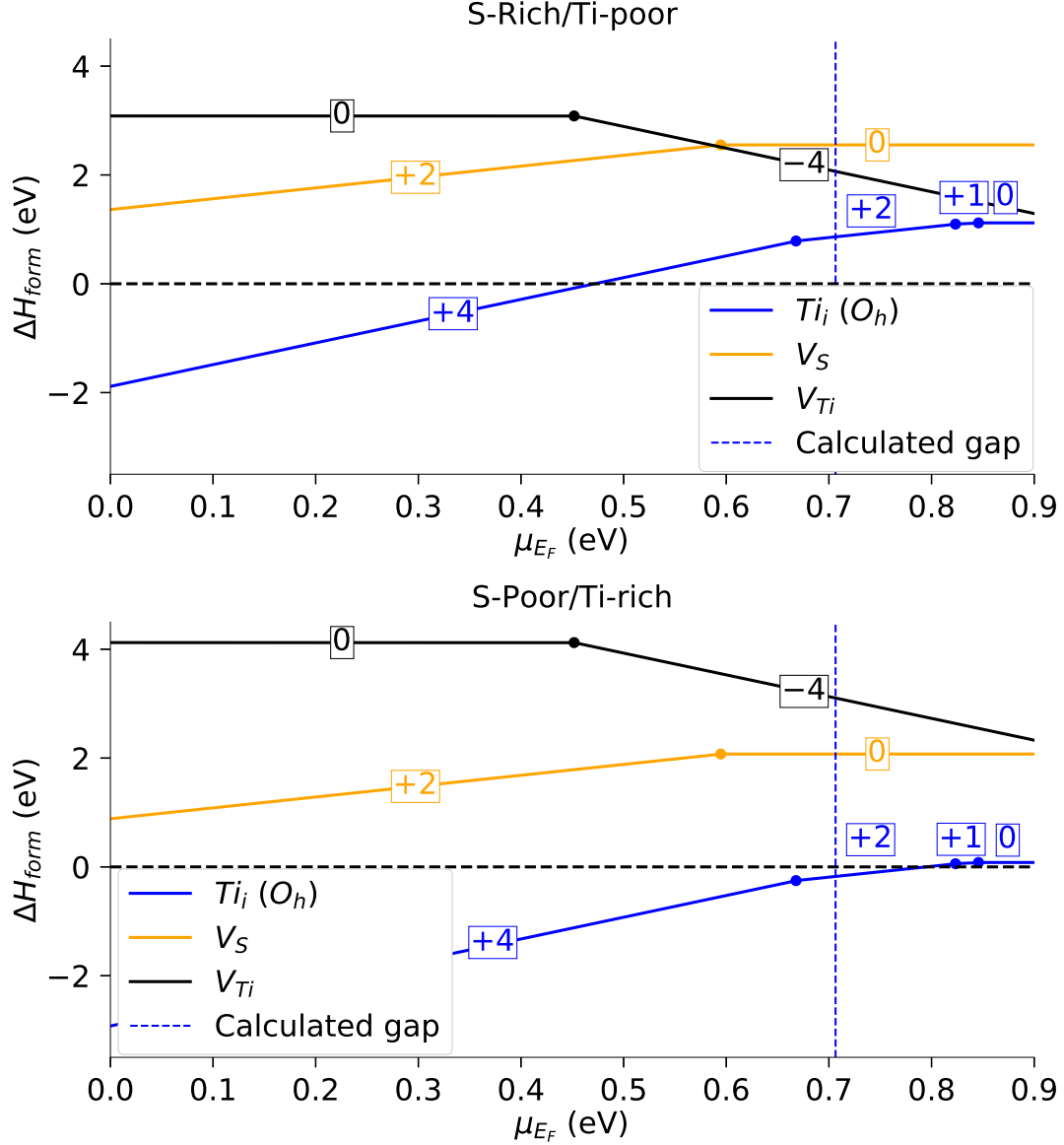


Figure 3.6: TiS_2 defect formation enthalpies *vs.* Fermi level, S-rich/Ti-poor (top) and S-poor/Ti-rich (bottom).

So far we have shown that by taking into account the intrinsic point defects of TiS_2 and the synthesis conditions, the S-rich/Ti-poor end of the stability domain leads to a (faulted) TiS_2 exhibiting (good intrinsic) *n*-type conductivity whereas the other limit synthesis conditions, namely S-poor/Ti-rich, lead to a SM.

The two limit cases giving opposite behaviour, one would like to know at which point of the stability domain the synthesis switches from yielding a SM to a SC. The limit situation between SM/SC is the point at which the Fermi level during synthesis equals the CBM. This can be implemented numerically as solving $\mu_{E_F}^{gr} = E_{CBM}$ where the *gr* subscript denotes crystal growth. As pointed out in Chapter 1, this also depends on the synthesis temperature.

The position of the SM/SC frontier with respect to growth temperature and position in the stability domain of TiS_2 is shown in Figure 3.7. Low temperatures lead to low energy, highly ordered, structures with low defect concentrations and the ranges of the SM and SC domain are approximately the same. Disorder, or conceptually, the weight

of the entropic part of the Gibb's energy of the system increases with the temperature, leading to more crystal defects, in particular, more titanium self-interstitials. The SM stability domain grows with temperature. The experimental synthesis temperature typically lies around 1000 K. Our simulation shows that at such temperature, if the growth conditions (Ti/S ratio) are not fully controlled, the probability of forming a SM compound is higher than a SC one. However, with appropriate carefully controlled conditions, obtaining a SC is still achievable. This explains the discrepancies observed in the literature regarding the electronic properties of TiS_2 . [274–284, 286–290]

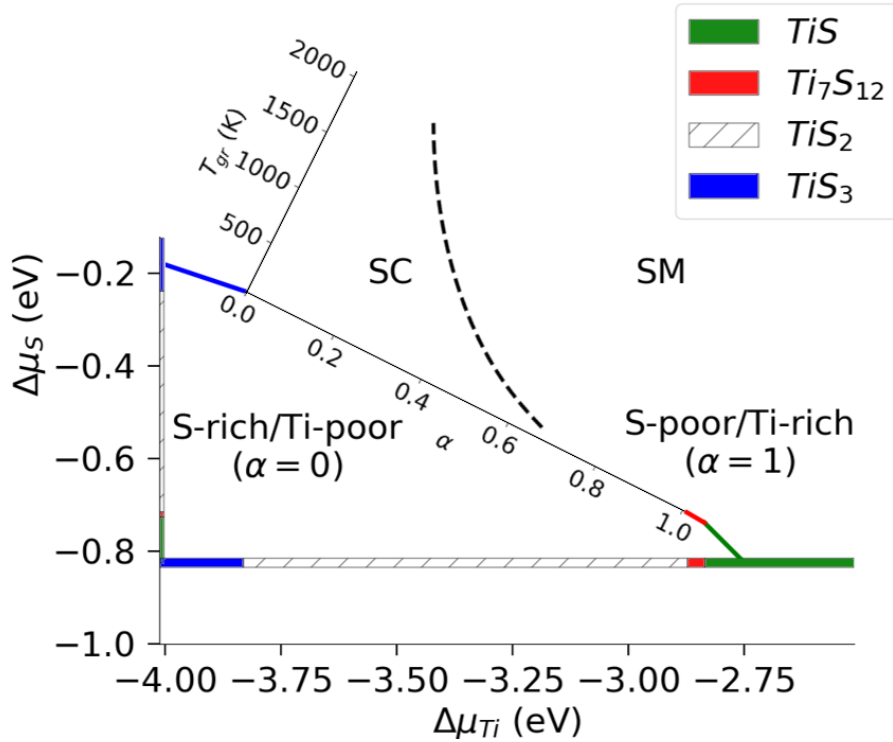


Figure 3.7: TiS_2 temperature of semiconductor/(semi)metal transition *vs.* atmosphere. The α parameter corresponds to the progression within the stability domain from the S-rich/Ti-poor limit ($\alpha = 0$) to the S-poor/Ti-rich one ($\alpha = 1$).

3.5 Simulation of thermoelectric properties

TiS_2 has recently (re)gained attention from the scientific community thanks to its thermoelectric properties. [273, 311, 312] The thermoelectric performance of a material is often assessed through its figure of merit $ZT = \frac{\sigma S^2}{\kappa} T$ where σ is the electrical conductivity of the material, S its Seebeck coefficient, κ its thermal conductivity and T the temperature.

Boltzmann semi-classical transport theory [313–315] allows one to evaluate the transport properties of a material from its electronic band structure. In the present study, the BoltzTraP implementation was used. [316] The band structure is calculated on the ideal cell. The impact of defect is modelled through the position of the Fermi level μ (rigid band model). Positive values correspond to the Fermi level entering the conduction band and negative values the valence band.

With this tool, we compute the Seebeck coefficient of the ideal TiS_2 structure, that is the amplitude of the response of the material to a gradient of temperature. The resulting simulation is shown in Figure 3.8. The symmetric shape of the Seebeck coefficient curve compares well with other compounds reported in the literature, such as Bi_2Te_3 . [316] Experimentally, the order of magnitude of the Seebeck coefficient of TiS_2 is $200\text{--}280 \mu\text{V}\cdot\text{K}^{-1}$ in absolute value. [273] Our simulation yields maximum values three times more important. As highlighted in the previous part, the ideality of the model may be responsible for this discrepancy. Furthermore, the Fermi level is pinned by defects. There is no particular reason for it to allow to get the maximum Seebeck value. Figure 3.9 highlights the detrimental effect of defects on the value of the Seebeck coefficient. Note that both Bourgès *et al.* [273] and our *ab initio* defect study point towards an order of magnitude of defect concentration of 10^{20} cm^{-3} , which according to Figure 3.8, leads to a Fermi level value of 0.05 eV. This is compatible with the picture given by Figure 3.9 and most importantly the defect formation enthalpies in S-poor/Ti-rich conditions given previously.

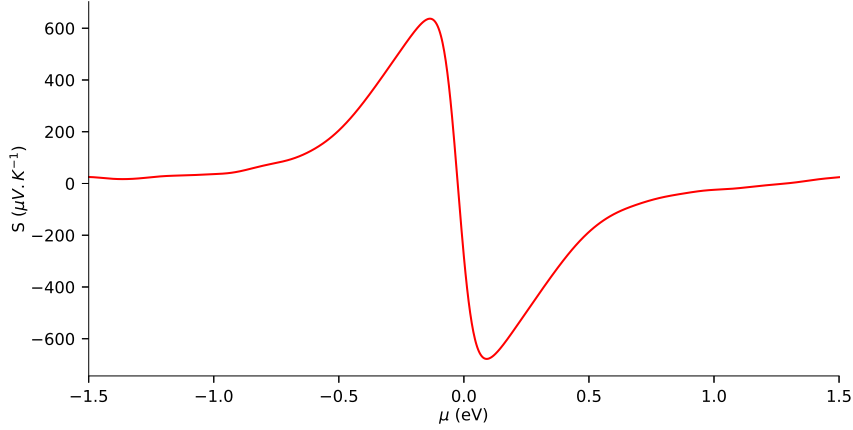


Figure 3.8: Simulated Seebeck coefficient of TiS_2 with PBE0-D functional at $T = 700\text{K}$.

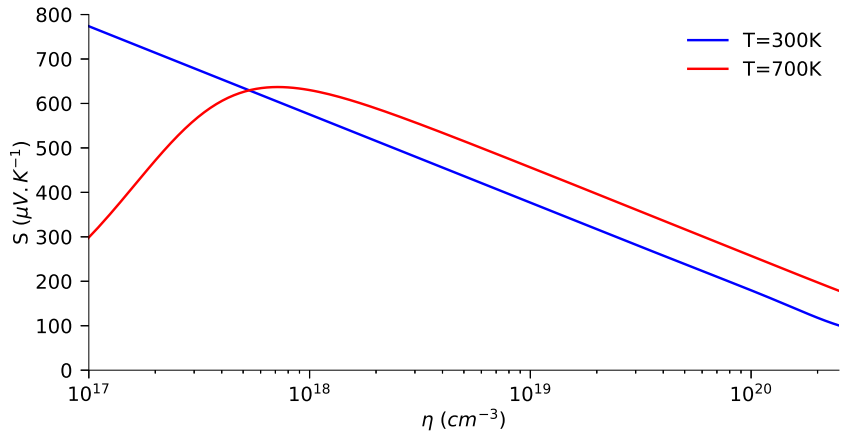


Figure 3.9: Simulated Seebeck coefficient of TiS_2 with PBE0-D functional *vs.* defect concentration.

To go one step further, one can simulate the figure of merit of TiS_2 . To do so, one must assess the electrical σ and thermal κ conductivities from Boltzmann equations. Physically, the thermal conductivity comes from the sum of two contributions, one from the electronic cloud of the ionic lattice κ_{elec} and the other from the vibration of the atomic cores $\kappa_{lattice}$ (phonons). Naturally, a method based on the electronic band structure keeping fixed ionic positions like the method described previously only yields a value of the electronic thermal conductivity. Here, as a first approximation, the ratio between the lattice part of the thermal conductivity and the electronic part was estimated to $\kappa_{latt} \simeq 11\kappa_{elec}$ from experimental literature.[272] The resulting ZT *vs.* Fermi level curve is shown in Figure 3.10. Note that the previously highlighted value of $\mu = 0.05$ eV yields poor ZT value ($\simeq 0.2$), comparable with experimental data of 0.3.[273]

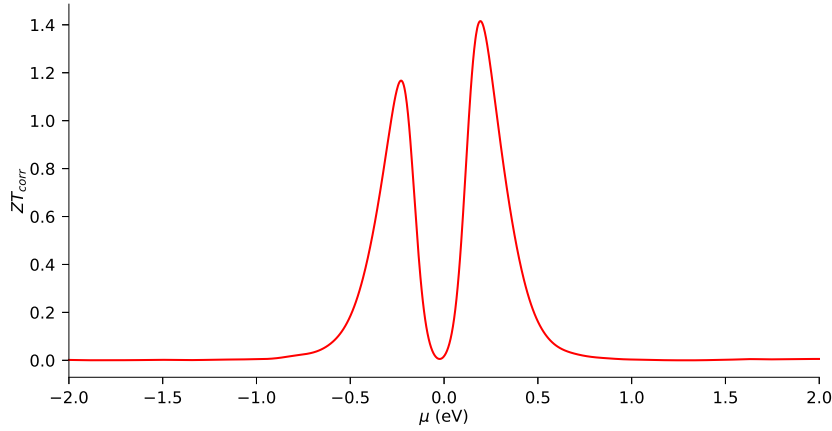


Figure 3.10: Simulated figure of merit of ideal TiS_2 with PBE0-D functional *vs.* Fermi level at $T = 700$ K.

3.6 Conclusion on TiS_2

A careful investigation of the different simulation means available leads to the conclusion that dispersion effects must be taken into account when studying TiS_2 . The total energy semi-empirical correction scheme GD3-BJ is adapted to this case. Electronic structure calculations performed with hybrid functional PBE0-GD3-BJ unambiguously show that the ideal 1:2 stoichiometry has a semiconducting behaviour with an indirect bandgap of $\simeq 0.7$ eV. The semimetallic character obtained on the ideal structure at the GGA level is due to the band gap underestimation. The ideal compound if it existed would be a semiconductor. The study of the intrinsic defects of the material using PBE0-GD3-BJ shows that irrespective of the synthesis conditions, Ti_i is the major defect and is present in huge amounts in the material. The very low calculated DFE confirms the experimental intuition of an overstoichiometry in titanium in this material. Depending on the synthesis conditions, the material is a semiconductor with a very pronounced *n*-type character (S-rich/Ti-poor limit) or the Fermi level falls within the CB, sign of a semimetallic behaviour (S-poor/Ti-rich limit). This totally explains the controversy around the electronic properties of the material. Note also that due to the high vapour pressure of sulphur, experimental conditions are expected to correspond in most cases to a situation closer to the S-poor/Ti-rich limit. In this case,

the material synthesised is semimetallic. Only very well controlled synthesis conditions may allow the formation of a semiconducting compound. This is coherent with the experimental literature. The peculiar properties of TiS_2 cannot be understood without taking into account point defects. Finally, thermoelectric properties of the material are simulated.

Chapter 4

Towards free energy - the work case of selenium

4.1 Context

The next material investigated is elemental selenium. This material has recently regained attention for its opto-electronic properties.[317] In the world of PV in particular, selenium is of historical interest as photoconductivity was first noticed in this material in 1873,[318] leading to the first PV solar cells[319] and in the first half of the next century to the Nobel-winning work of Einstein. The cell efficiency was improved from a few per cent to culminate in 1985 at the record efficiency of 5.0%.[320] Its high bandgap and the parallel development and success of the silicon industry resulted in it being set aside for PV application. However, it was very recently pointed out that the material could provide a convenient absorber for the top-cell of a tandem solar cell. Indeed, synthesising a unary material is much easier than ternary or quaternary materials now used in thin-film technologies such as CIGS and CZTS. In this vein, Todorov *et al.* optimised a selenium-based single-junction device and broke the previous record, reaching 6.5% efficiency.[317] The record architecture is Glass/FTO¹/Zn_xMg_{1-x}O/ γ -Se/MoO_x/Au as illustrated in Figure 4.1. This so-called “superstrate” configuration with the back contact deposited last is chosen due to synthesis constraints and benefits from the experience acquired by the perovskite community routinely using it.[321] The FTO acts as an electron collector, *n*-type Zn_xMg_{1-x}O as a buffer layer, crystallised grey selenium as an absorber, MoO_x as a hole selective layer and gold as the back contact. Todorov *et al.* note that the Open-Circuit Voltage (V_{OC}) is almost 1 V under the theoretical Shockley–Queisser limit, leaving much room for improvement, especially through the limitation of charge carriers recombinations. This issue is typically linked to point defects, both in the bulk and/or at the heterojunction. This brand new record translates the recent research activity around the application of selenium for solar devices, be it as an absorber for photoelectrochemical solar cells[322] and PV cells, in thin-films[323], as nanoparticles,[324] or as a hole conducting layer.[325, 326] More generally, the nanoscale forms have also attracted a fair deal of interest, partly due to its potential application in the fields of medicine and optical devices.[327, 328]

Looking at the material itself in more details, the phase diagram is quite complex even at low pressure and temperatures, with the coexistence of several allotropic forms due to the competition between short range covalent bonds and long range van

1. Fluorine-doped Tin Dioxide SnO₂:F

der Waals interactions.[329, 330] The same mechanism allows the existence of various structures at high pressures. Parthasarathy and Holzapfel reported a structural study up to 50 GPa, [331] later completed by Akahama *et al.* up to 140 GPa.[332] The results of the two differ on several points, however it can be reliably concluded that the first pressure-induced transition occurs at 14 GPa. The intermediate structure is unclear, but the material adopts a monoclinic lattice between 23 and 28 GPa. Both studies agree on the existence of a transition at 28 GPa but differ on the structural form directly above this limit. At higher pressures, a rhombohedral phase isostructural to β -polonium appears and a structural transition towards a Body-Centred Cubic (BCC) phase occurs at 140 GPa. The highest pressure phases have been more thoroughly studied, most notably for supraconducting properties, so that the existence of the two latter structures is corroborated by different teams.[332–335] The nomenclature of the different phases seems to have evolved within the literature and it is often a bit confusing which structure is being referred to. In ambient conditions, more of interest for the optoelectronic applications this work focuses on, the material can adopt three different forms, namely an amorphous form, and two crystalline ones. The first crystal phase, hereafter referred to as γ -Se, crystallises in a trigonal lattice, exhibiting a bandgap reported between 1.83 eV [336] and 2 eV.[337] This is without doubt the most stable phase of selenium at ambient pressure,[330, 338] and is often incorrectly referred to as “hexagonal” selenium in the literature. The crystallographic structure is described more in details hereafter. The second crystal form can be stabilised in ambient conditions, adopting a monoclinic lattice and labelled herein β -Se.[339, 340] The bandgap is reported as direct and is equal to 2.53 eV.[341]

The purpose of the work is to determine the intrinsic defects present in the two main crystal forms of selenium in order to identify the origin of the observed *p*-type conductivity. Extrinsic doping strategies are also investigated.

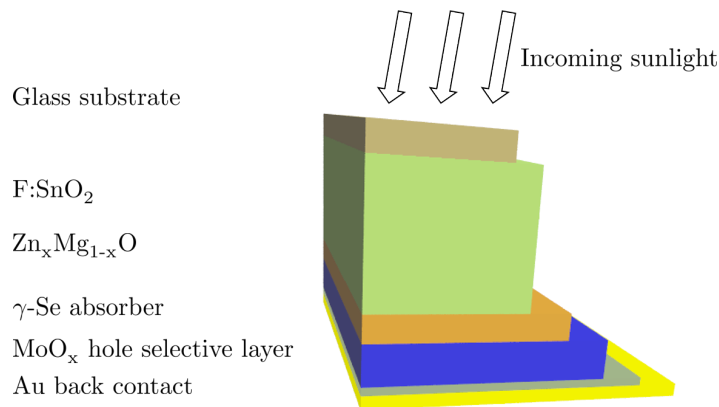


Figure 4.1: “Superstrate” architecture of efficiency record-breaking PV solar cell with selenium absorber.[317]

4.2 Defect formation energies

4.2.1 Computational details

Computations were performed using the plane-augmented waves scheme implemented in VASP.[197–200] Several approximations were tested, namely “pure” GGA functional PBE,[196] and including dispersion corrections GD3[297, 298] and GD3-BJ[297–299], meta-GGA functional SCAN[148] both without and with GD3 correction[297, 298] and screened hybrid functional HSE06,[151, 152] The calculation settings for the geometrical optimisation (optim.) and DOS for the two phases are summarised in Table 4.1.

Table 4.1: Computational details of the study of ideal cells. Number of irreducible K -points specified between brackets.

	β -Se (rings)	γ -Se (chains)
General		
E_{cut} (eV)	265	
Force conv. (eV.Å ⁻¹)	10 ⁻²	
SCF conv. (optim.) (eV)	10 ⁻⁵	
SCF conv. (DOS) (eV)	10 ⁻⁶	
PBE/PBE-GD3(BJ)/SCAN(-GD3)		
K-points grid (optim.)	MP 5 × 5 × 4 (30)	MP 10 × 10 × 8 (220)
K-points grid (DOS)	Γ-centred 5 × 5 × 4 (33)	Γ-centred 15 × 15 × 12 (284)
HSE06(-GD3)		
K-points grid (optim.)	Γ-centred 2 × 2 × 2 (8)	MP 5 × 5 × 4 (14)
K-points grid (DOS)	Γ-centred 3 × 3 × 3 (10)	Γ-centred 5 × 5 × 4 (17)

Based on the results presented hereafter, faulted supercells were built on the SCAN geometry. The cutoff energy was increased to 500 eV due to the study of extrinsic defects. The computational details are summarised in Table 4.2. All corrections described in Chapter 1 were taken into account. The band-edge references were taken from HSE06-GD3 calculations. The post-treatments were performed using our in-house software PyDEF.[117, 168]

Table 4.2: Computational details for the defect study. Number of irreducible K -points specified between brackets.

	β -Se (rings)	γ -Se (chains)
General		
E_{cut} (eV)	500	
Force conv. (eV.Å ⁻¹)	10 ⁻²	
SCF conv. (optim.) (eV)	10 ⁻⁵	
SCF conv. (DOS) (eV)	10 ⁻⁶	
Electronic density functional	SCAN	
Supercell	2 × 2 × 1 (128 atoms)	3 × 3 × 3 (81 atoms)
K-points grid (optim.)	MP 2 × 2 × 2 (4)	MP 3 × 3 × 3 (14)
K-points grid (DOS)	Γ-centred 2 × 2 × 2 (8)	Γ-centred 5 × 5 × 4 (51)

4.2.2 Ground state properties of the two allotropic crystal phases

As mentioned beforehand, selenium in solid-state can adopt several allotropic forms. The crystallographic structures of the two main crystal phases β -Se and γ -Se are drawn in Figures 4.2 and 4.3. The first crystallises in a monoclinic lattice following space group symmetry $P2_1/c$ (no 14), forming Se_8 crown-like rings. It is isostructural to α - S_8 . The rings consist in two (almost) parallel squares of four Se atoms shifted by 45° with a small deformation from this ideal description.[338] The conventional cell contains $Z = 4$ Se_8 rings for a total of 32 atoms. The 3 atom conventional cell of γ -Se is highly anisotropic with infinite helical chains of bicoordinated Se along the c axis of a trigonal lattice. The helical chain is so that every third Se atom is $\simeq 5 \text{ \AA}$ above the starting one. The structure exhibits a $P3_121$ (no 152) space group symmetry. The amorphous form, noted a-Se, might be apprehended as a mixture of the two moieties, chains and Se_8 rings, or a glass of either one. However, no structural model could be determined with certainty for a-Se and the amorphous structure may well vary with the synthesis process,[342–344] although a recent Nuclear Magnetic Resonance (NMR) spectroscopy study by Marple *et al.* suggest that their samples of a-Se contained only $1/\infty$ [Se] chains.[345] Hereafter, only the two β - and γ -Se forms are discussed.

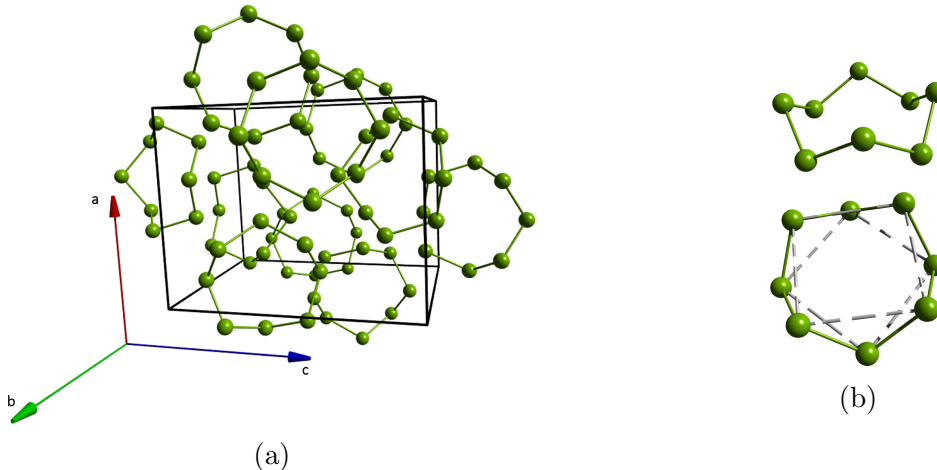


Figure 4.2: Crystallographic structure of β -Se, exhibiting a monoclinic lattice within $P2_1/c$ (no 14) space group symmetry. It is isostructural to α - S_8 . Green spheres represent selenium atoms. a) Conventional cell. Cell boundaries are represented in black. b) One isolated crown-shaped Se_8 ring moiety. $a = 8.894(2) \text{ \AA}$, $b = 9.000(2) \text{ \AA}$, $c = 11.383(2) \text{ \AA}$, $\alpha = \gamma = 90^\circ$, $\beta = 90.68(2)^\circ$, $V = 911.1 \text{ \AA}^3$. [340]

The two structures present voids (van der Waals gaps) between the chemical entities (Se_8 rings or infinite chains), a clue of the importance of weak interactions to maintain the cohesion of the microscopic organisation of matter. Computed geometric parameters are reported in Tables 4.3 and 4.4. Let one start the analysis of the ability of the different functionals to reproduce a correct geometry with β -Se. The large overestimation of the b and c lattice parameters using “pure”² PBE and HSE06, corrected by the use of dispersion schemes GD3 and GD3-BJ, demonstrates the importance of weak interactions in the structure. At the GGA level, PBE-GD3-BJ outperforms PBE and PBE-GD3 in terms of structural description. Note that going from GD3 to GD3-BJ

2. without any dispersion correction

shrinks the cell parameters and van der Waals distances. This trend was also observed on TiS_2 as mentioned in Chapter 3. Regarding nearest-neighbour Se-Se distance, the shortest Se-Se distance of the Se_8 is more overestimated than the longest one, all of them being close by less than 3% to the experimental one. The overall good prediction of nearest-neighbour distance with poor cell parameters and van der Waals distance predictions for the uncorrected functionals means that each moiety (chain or ring) is correctly reproduced, however the different entities are too far apart one another, *i.e.* the size of the van der Waals gap is overestimated. This can be explained by the fact that DFT functionals account well for short-range interactions but not long-range ones. Thus, separate non-interacting moieties in the uncorrected models tend to drift apart. It confirms the importance of weak interactions in the structures.

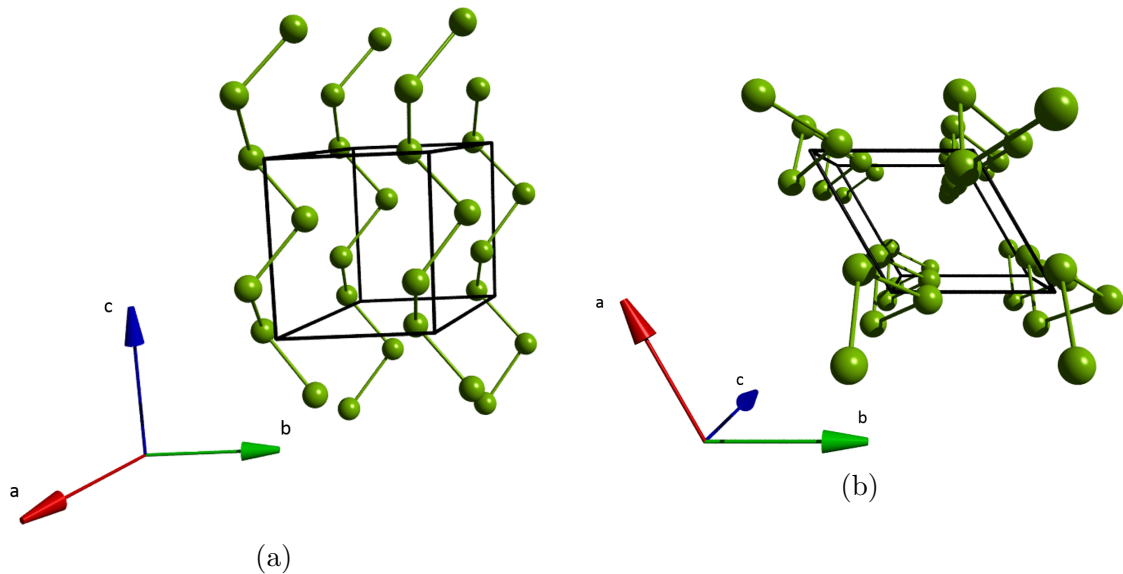


Figure 4.3: Crystallographic structure of γ -Se. The structure crystallises in a trigonal lattice, within the $P3_121$ (no 152) space group symmetry. It consists of $1/\infty$ [Se] helical chains along the c axis. a) Conventional cell. Cell boundaries are represented in black and green spheres represent selenium atoms. b) Top-view of the cell. The projection of the chains in the (a, b) plane draws isosceles triangles whose barycentres correspond to the cell corners. $a = b = 4.368(3)$ Å, $c = 4.958(4)$ Å, $V = 81.9$ Å³. [346]

The computational effort required for a hybrid functional calculation being very heavy, it is important to consider reliable and efficient methodologies. Going beyond the first order of the Taylor expansion of the electronic density as does the GGA approximation, meta-GGA takes into account the laplacian of the density, while offering an affordable computational cost. The SCAN functional, which gains in popularity among computationally-oriented material scientists, [149] was tested here. Interestingly, uncorrected SCAN leads to a relatively satisfying optimised geometry for β -Se, with a maximum relative deviation towards experimental cell parameters of 3.50%. The agreement with experiment is even improved with the addition of the GD3 scheme.³

To summarise, when considering the minimisation of cell parameters deviation between simulation and experiment for β -Se, PBE-GD3-BJ, SCAN and HS06-GD3 provide similarly satisfying results with a $\simeq 3\%$ maximum deviation in absolute value, and SCAN-GD3 an even closer description.

3. GD3 semi-empirical parameters are not yet available for the SCAN functional, so the values were kept identical to the PBE ones as the most closely related to SCAN.

Table 4.3: β -Se structure parameters calculated using different methodologies compared with experimental data. The van der Waals distance d_{vdW} corresponds to the inter-ring distance, while $d_{\text{Se-Se}}$ corresponds to closest neighbour distances (bonds within the same ring).

Source	a (Å)	b (Å)	c (Å)	β (°)	$d_{\text{Se-Se}}$ (Å)	d_{vdW} (Å)
ICSD 280666[340]	8.894(2)	9.000(2)	11.383(2)	90.68(2)	2.292-2.358 (2.345)	3.396
PBE	9.363	10.136	12.339	91.38	2.357-2.373 (2.364)	3.779
PBE-GD3	9.094	9.278	11.812	90.60	2.353-2.382 (2.367)	3.485
PBE-GD3-BJ	8.925	8.744	11.503	90.91	2.354-2.394 (2.372)	3.287
SCAN	9.187	9.255	11.784	91.14	2.335-2.358 (2.345)	3.519
SCAN-GD3	9.050	8.923	11.553	90.66	2.325-2.363 (2.344)	3.404
HSE06	9.365	10.213	12.531	91.76	2.322-2.331 (2.325)	3.882
HSE06-GD3	9.131	9.173	11.729	89.99	2.315-2.340 (2.326)	3.540
	Δa	Δb	Δc	$\Delta \beta$	$\Delta d_{\text{Se-Se}}$ (%)	Δd_{vdW} (%)
PBE	5.30%	12.60%	8.40%	0.77%	2.8-1.5 (2.3)	11.3
PBE-GD3	2.30%	3.10%	3.80%	-0.09%	2.6-1.9 (2.4)	2.6
PBE-GD3-BJ	0.30%	-2.80%	1.10%	0.25%	2.7-2.4 (2.6)	-3.2
SCAN	3.30%	2.80%	3.50%	0.51%	1.9-0.8 (1.5)	3.6
SCAN-GD3	1.80%	-0.90%	1.50%	-0.02%	1.4-1.0 (1.4)	0.2
HSE06	5.30%	13.50%	10.10%	1.19%	1.3- -0.3 (0.6)	14.3
HSE06-GD3	2.70%	1.90%	3.00%	-0.76%	1.0-0.0 (0.6)	4.2

Before discussing the bandgap values, let us investigate the γ -Se 1D structure. Once more, pure HSE06 severely overestimates the $a = b$ parameter due to weak interactions. Surprisingly, pure PBE does not have such a problem. The cell parameters decrease when adding dispersion schemes GD3 and GD3-BJ as expected. The GD3-BJ correction to PBE is inappropriate in the case of γ -Se, shrinking $a = b$ too much leading to a 7% underestimation with respect to experiment. The long range interactions seem less strong than in the β -Se case. The trend is the same at the meta-GGA level with SCAN-GD3 underestimating $a = b$ by 3.4% against a slight overestimation of 1.7% by SCAN. Overall the c parameter, *i.e.* the spatial period along the chain direction, is satisfyingly described with all methods. The closest geometry to experiment is the one calculated with HSE06-GD3 with less than one percent deviation in absolute value.

However, the choice of methodology to describe the two materials would not be complete without taking into consideration the bandgap prediction. The bandgap of β -Se ring-like structure is reported experimentally at 2.53 eV.[341] The chain-like structure γ -Se has a smaller bandgap reported between 1.83 and 2.00 eV in the literature.[336, 337, 347]

Before comparing the bandgap values for the different density functionals, we comment on the electronic band diagrams of the two structures as it is an important electronic ground state characteristic of the compounds. As mentioned in the introduction, the direct or indirect nature of the bandgap varies from one allotropic form to the other. Moreover, as highlighted beforehand, the γ -phase is strongly anisotropic. It is thus of interest to study the electronic band diagram of the relaxed structures before further investigations.

The electronic band structure of both β - and γ -Se computed with the SCAN functional are reported in Figure 4.4. Both compounds are semiconductors. The gap values are discussed more in details hereafter, however it should be mentioned here that the

Table 4.4: γ -Se structure parameters calculated using different methodologies compared with experimental data. The van der Waals distance d_{vdW} corresponds to the inter-chain distance, while $d_{\text{Se-Se}}$ corresponds to closest neighbour distances (bonds within the same chain).

Source	$a = b$ (Å)	c (Å)	$d_{\text{Se-Se}}$ (Å)	d_{vdW} (Å)
ICSD 40018[346]	4.368(3)	4.958(4)	2.375	3.438
PBE	4.475	5.052	2.407	3.533
PBE-GD3	4.173	5.132	2.432	3.291
PBE-GD3-BJ	4.058	5.138	2.446	3.190
SCAN	4.443	4.987	2.379	3.509
SCAN-GD3	4.218	5.057	2.389	3.337
HSE06	4.785	4.892	2.345	3.799
HSE06-GD3	4.334	4.964	2.361	3.423
	Δa	Δc	$\Delta d_{\text{Se-Se}}$	Δd_{vdW}
PBE	2.40%	1.90%	1.3%	2.8%
PBE-GD3	-4.50%	3.50%	1.0%	-4.3%
PBE-GD3-BJ	-7.10%	3.60%	0.6%	-7.2%
SCAN	1.70%	0.60%	-2.7%	2.1%
SCAN-GD3	-3.43%	2.00%	0.4%	-2.9%
HSE06	9.50%	-1.30%	-1.8%	10.5%
HSE06-GD3	-0.80%	0.10%	0.7%	-0.4%

existence of an electronic gap is preserved with all the functionals tested, even uncorrected GGA-PBE. β -Se (rings) exhibits a direct bandgap of 1.74 eV on the $\Gamma - Y$ segment while γ -Se shows an indirect $L - H$ bandgap of 1.29 eV. The electronic bands of β -Se are quite flat, which translates as high charge carrier effective masses and low mobility. This can be understood as the electronic states are localised onto a Se_8 ring and the inter-ring interaction is weak and of van der Waals nature. The flatness of the bands can be correlated to the pseudo-0D character of the structure which exhibits separate moieties. On the contrary, the dispersion of the electronic bands of γ -Se is much more important due to its pseudo 1D structure.

A parabolic fit of the vicinity of the band extrema yield the effective mass values reported in Table 4.5. They are used as input parameters for the computation of the defect concentrations.

The most substantial modification of the band diagram when changing the approximation for the electronic exchange correlation is the opening of the gap when climbing Jacob’s ladder of *ab initio* simulations. Now the quality of the gap simulation is discussed with respect to the choice of functional. The experimental and computed DOS gap values are reported in Table 4.6.

The well-known bandgap problem at the GGA level is visible with a bandgap underestimation of $\simeq 40\%$ for β -Se and 50% for γ -Se. In the case of the GGA description of β -Se, the closer to experiment the cell parameters are, the more underestimated the bandgap is. At the meta-GGA level, pure SCAN is in both cases closer to the experimental value than SCAN-GD3 with a $\simeq 30\%$ gap underestimation. The addition of the laplacian term in the Taylor expansion of the electronic density (kinetic term) is not enough to recover entirely the localised character of the chemical bonds from the semi-local GGA description, but provides a fair improvement at negligible computational cost. The HSE06 geometries being very distorted compared to the experimental ones,

they will not provide suitable models for these materials, even if the bandgap can be by coincidence quite close to the experimental one, as is the case for β -Se. The HSE06-GD3 gap simulation is quite good with an 8% underestimation in the case of β -Se and 6% overestimation in that of the γ -phase. The introduction of 25% of Hartree-Fock exchange allows to recover the gap, along with a structure closer to experiment thanks to the GD3 scheme.

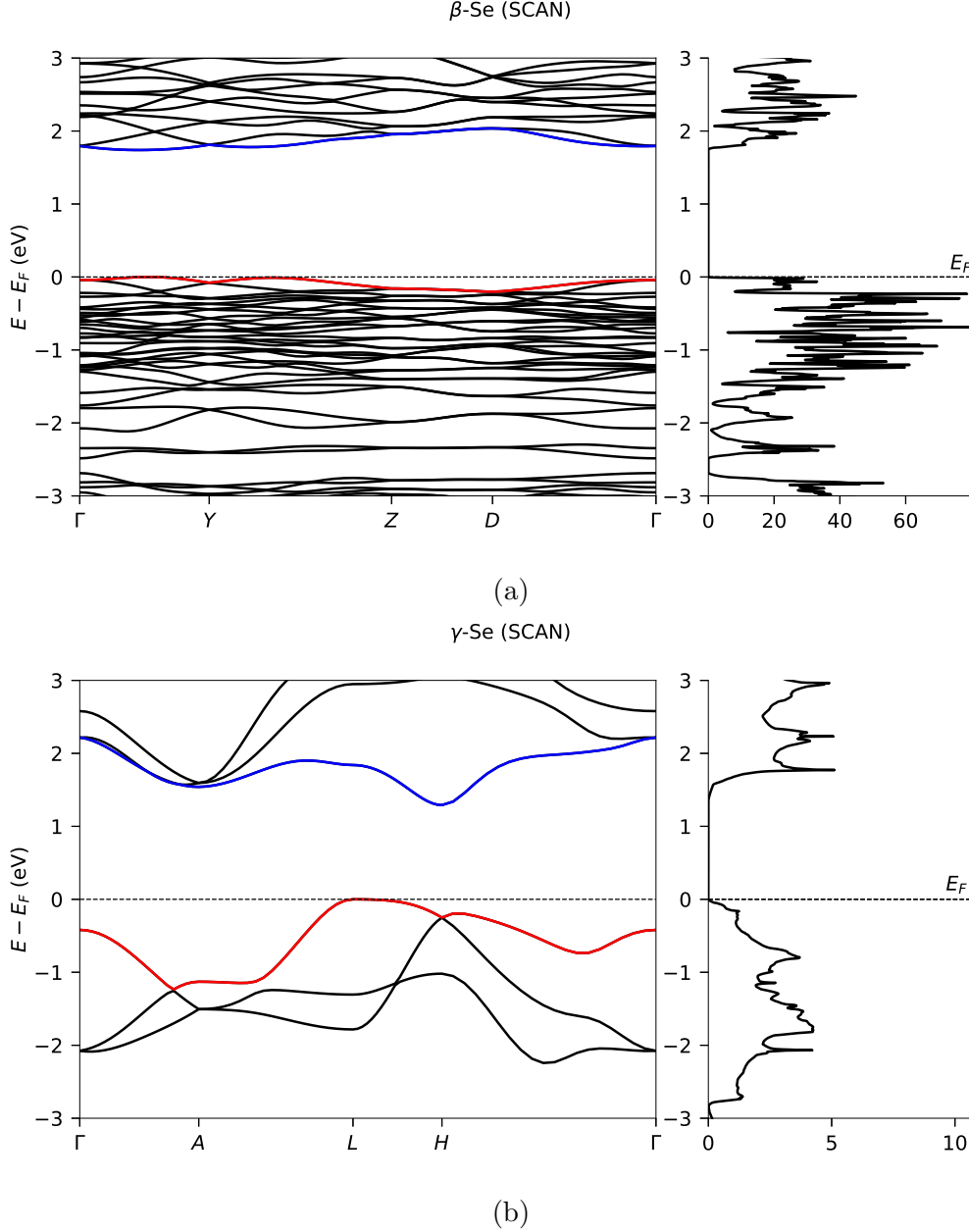


Figure 4.4: Electronic band structure and DOS computed using meta-GGA SCAN functional for a) β -Se exhibiting a direct bandgap of 1.74 eV on the $\Gamma - Y$ segment (Γ (0,0,0), Y($\frac{1}{2}$,0,0), Z(0, $\frac{1}{2}$,0), D(0, $\frac{1}{2}$, $\frac{1}{2}$)) and b) γ -Se showing an indirect $L - H$ bandgap of 1.29 eV. (Γ (0,0,0), A(0,0, $\frac{1}{2}$), L($\frac{1}{2}$,0, $\frac{1}{2}$), H($\frac{1}{3}$, $\frac{1}{3}$, $\frac{1}{2}$)).

HSE06-GD3 provides the most reliable structural and electronic description combined for both compounds and are thus retained as the reference calculations to position the band-edges in the later defect study. However, relaxing the faulted supercells at this level of approximation would be too cumbersome and a less demanding func-

tional is required for the defect study. SCAN provides a convenient way to describe reliably both compounds using state-of-the-art functional of affordable computational cost, thus is retained for the defect study.

4.2.3 Defect formation energies

Then, point defects are investigated in both β - and γ -phase in order to understand the origin of the conductivity of the materials and explore potential dopants which may prove useful for their application in optical devices. The SCAN functional is used throughout the defect study as mentioned previously. Note that in addition to the SCAN lattice parameters being in good agreement with the experimental ones, the interatomic distances are also very well reproduced, with a deviation with respect to experiment inferior to 3%. As summarised in Table 4.2, a $2 \times 2 \times 1$, $3 \times 3 \times 3$, supercell is used for β -, γ -Se, respectively.

Computational studies allow to screen the periodic table for dopants in an affordable and efficient way, prior to experiment in order to give valuable insights to guide synthesis. In that spirit, the following extrinsic defects were also considered. It is useful to make an analogy with Si, the most studied elemental material, in order to choose relevant dopants. Aliovalent doping in Si usually relies on boron substitutions to induce p -type and phosphorus for n -type doping, as B possesses one less valence electron than Si and P one more. Following the same line of thoughts, any V (VII) element substitution to Se should induce p -type (n -type) doping. Due to prior investigation of Sb_2Se_3 , Sb was selected over P and As. Bromine was considered for electron doping. Due to the similarities with the study of Sb_2Se_3 , where copper interstitial, among others, was potentially an electron donor defect, it was also investigated to dope selenium. Copper having a $3d^{10}4s^1$ electronic configuration, it appears as a potential n -type dopant, giving an electron to the system to reach the $3d^{10}4s^0$ full electronic layer configuration.

β - and γ -Se are unary compounds, so the chemical potential of selenium is taken as the energy per atom, and only one synthesis condition is represented in the in-

Table 4.5: Effective masses obtained by fitting parabola onto SCAN band extrema displayed in Figure 4.4 following equation 1.35.

	β -Se (rings)	γ -Se (chains)
$\frac{m_e^*}{m_e}$	1.8	0.6
$\frac{m_h}{m_e}$	1.3	0.6

Table 4.6: β - and γ -Se electronic DOS bandgap (eV) calculated using different methodologies compared with experimental data.

	β -Se (rings)	γ -Se (chains)
ICSD 280666[340]/40018[346]	2.53[341]	1.83-2.00 (1.91)[336, 337, 347]
PBE	1.55 (-39%)	0.96 (-50%)
PBE-GD3	1.29 (-49%)	0.57 (-70%)
PBE-GD3-BJ	1.07 (-58%)	0.45 (-76%)
SCAN	1.75 (-31%)	1.32 (-31%)
SCAN-GD3	1.62 (-36%)	1.00 (-48%)
HSE06	2.75 (9%)	2.58 (35%)
HSE06-GD3	2.33 (-8%)	2.02 (6%)

trinsic defect model. The difference in selenium chemical potential between the two phases is small (9.0 meV/atom), highlighting the fact that the two coexist at ambient temperature and pressure. The chemical potential values are available in Table 4.7.

Only the total energy of one binary needs to be computed for each dopant considered in order to obtain the maximum possible dopant chemical potential value. The binary compound with the lowest dopant content will set this limit. This is verified with copper by comparing the values obtained for μ_{Cu} with $CuSe_2$ ($\mu_{Cu} = -15.437$ eV), $CuSe$ ($\mu_{Cu} = -15.433$ eV) and Cu_2Se ($\mu_{Cu} = -15.139$ eV). Thus, $CuSe_2$ ($Pnnm$, no 58), Sb_2Se_3 ⁴ ($Pnma$, no 62) and $SeBr_4$ ($P31c$, no 159) were considered for copper, antimony and bromine, respectively.

Table 4.7: Chemical potential values in electronvolts, as computed with the SCAN functional. The competing binary phase limiting the stability domain of the selenium phase is indicated in brackets.

	β -Se (rings)	γ -Se (chains)
μ_{Se}	-20.076	-20.085
μ_{Cu} ($CuSe_2$)	-15.455	-15.438
μ_{Sb} (Sb_2Se_3)	-37.873	-37.860
μ_{Br} ($SeBr_4$)	-19.548	-19.546

In this unary compound, only two types of intrinsic defects can be considered, namely vacancies and interstitials. β -Se exhibits 8 distinct crystallographic sites, however they are very similar in terms of environment, all being bicoordinated. As our previous work has shown that the environment is the driving force for important vacancy DFE difference, only one vacancy was considered in β -Se. The structure of γ -Se offers only one crystallographic position, so there is no ambiguity on the vacancy position. A Frenkel defect ($Se_i + V_{Se}$) was build for the γ -phase, but could not be stabilised. This relaxation leads the displaced atom back to its initial position within the ideal arrangement.

Two different initial positions were considered for the Se_i in β -Se, both in low electronic density regions found through charge density plots. The first position corresponds to the barycentre of a Se_8 ring and the second is initialised between two rings. The total energy difference between both supercells is 0.13 eV in favour of the in-ring initialisation. Although the difference is small, only this first initial position was retained in order to alleviate the computational burden.

As far as γ -Se is concerned, the charge density plot confirms the intuition of the shape of the charge density and the interstitial initial position is set in the middle of the interchain region.

Let us examine the DFE of the intrinsic defects, as reported in Figure 4.5. In both cases, V_{Se} is lower in enthalpy than Se_i , and both defects exhibit quite low enthalpy of formations, inferior to 2 eV. However, the negative U behaviour of the chalcogen vacancy⁵ observed in the other chalcogen compounds studied (In_2S_3 , Sb_2Se_3 , TiS_2 , $CsCu_5Se_3$) is found only in the γ -phase. V_{Se} is potentially an electron donor defect, however the formation enthalpies of the non-zero charge states are too high for the transition level $+2/+1$ in β -, $+1/0$ in γ -Se, to be above the VBM. Interestingly, there is only a 0.05 eV difference between the transition level $\epsilon_{+2/+1}^\beta = -0.07$ eV and $\epsilon_{+1/0}^\gamma =$

4. This is the only binary compound in the Sb-Se system anyway.

5. $+2/0$ charge transition with the intermediate $+1$ charge not thermodynamically stable.

-0.12 eV. The $\epsilon_{+1/0}^\beta$ transition level is located 0.015 eV above the VBM, *i.e.* 2.25 eV under the CBM. Consequently, V_{Se} is totally unable to give any electron to the CB. However, it may act as a hole killer, a recombination site, and may be detrimental to the hole conductivity.

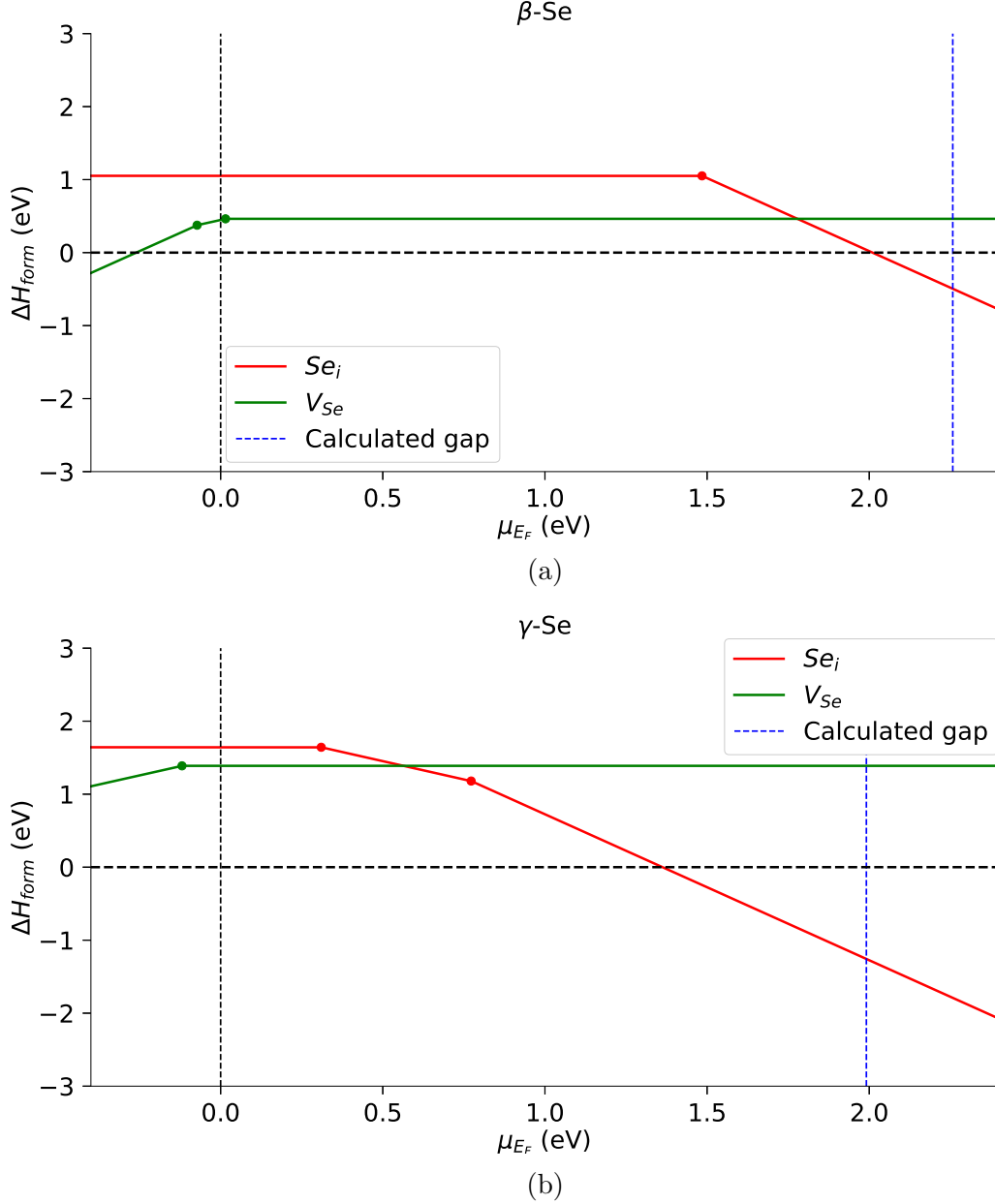


Figure 4.5: DFE of intrinsic defects plotted against Fermi level μ_{E_F} a) in β -Se b) in γ -Se. The vertical black and blue dotted line stand for the VBM and CBM, respectively.

The energetic cost associated to the creation of a selenium vacancy in the two phases is quite different. For the neutral state of charge, it is of 0.46 eV in β -Se against roughly three times more in γ -Se, more precisely 1.39 eV. Counterintuitively, it cannot be directly related to the bond lengths. Indeed, the Se-Se interatomic distance is 2.345 Å (2.335 - 2.358 Å) in β -Se, 1.4% shorter than 2.378 Å in γ -Se. The strength of the chemical bond is expected to increase when the interatomic distance decreases. Thus, the vacancy is lower in formation enthalpy in the allotropic form with the stronger Se-Se bonds (β -Se). The comparison between perfect and faulted geometries provides an

interesting insight into reason for the DFE difference for V_{Se} between the two allotropic forms. They are represented in Figure 4.6. The variation in interatomic distance after introduction of the vacancy is presented in Figure 4.6. Although the Se-Se distance is shorter in β -Se indicating stronger chemical bonding than in γ -Se, the relaxation of the structures after the vacancy formation occurred leads to two very distinct situations. Atoms are arbitrarily numbered starting at zero for the atom missing as shown in Figure 4.6. In β -Se, once the two chemical bonds $\text{Se}_0\text{--Se}_1$ and $\text{Se}_0\text{--Se}_7$ and the Se_0 atom gone, the structure is able to recover a ring shape. In doing so, the $\text{Se}_1\text{--Se}_7$ is now 5% longer than $\text{Se}_0\text{--Se}_1$ was, and $\text{Se}_1\text{--Se}_2$ 2.4% shorter than in the ideal Se_8 ring. The impact on the second neighbours and following is less than 1.5% variation in interatomic distances. On the other hand, in γ -Se the infinite chain is broken. The covalent bond $\text{Se}_0\text{--Se}_1$ is replaced by a long range interaction $\text{Se}_1\text{--Se}_8$ with a distance between nuclei of 2.784 Å. $\text{Se}_1\text{--Se}_2$ shrinks by 2.4%. Thus, Se_1 in γ -Se in the final configuration exhibits a radical change in environment, with one covalent bond replaced by a long range interaction. This configuration is energetically very unfavoured. This explains why, in spite of stronger Se-Se bonds in β -Se, it is easier to create a vacancy in β - than in γ -Se.

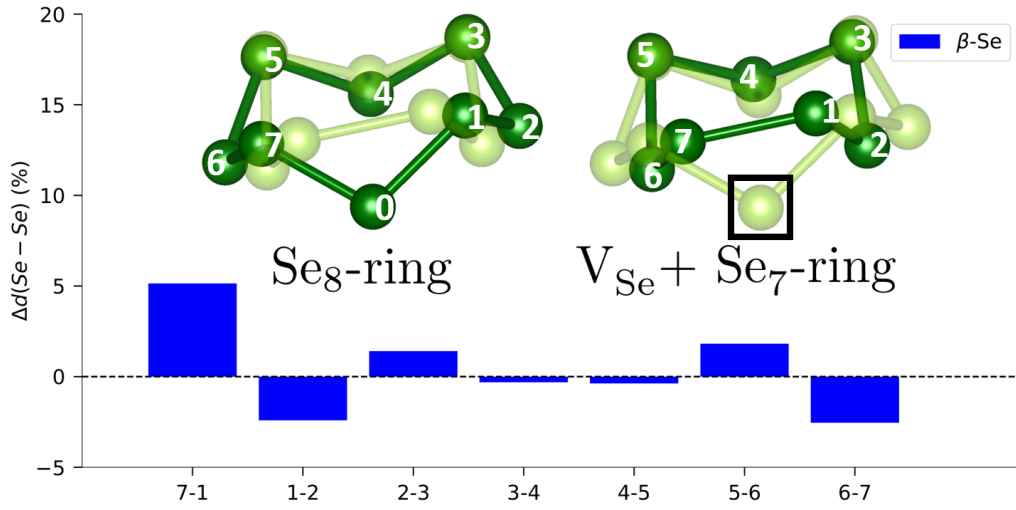
As the γ -Se phase is very anisotropic and periodic boundary conditions are applied, the DFE of V_{Se} was validated against another supercell ($2 \times 2 \times 7$) to ensure the quality of the result.

The behaviour of Se_i however is very different between the two phases. In β -Se, the $-2/0$ transition level stands far above the VBM at 1.48 eV, whereas in γ -Se $\epsilon_{0/-1}$ exists and is located only 0.31 eV above it. $\epsilon_{-1/-2}$ sits 0.77 eV above the VBM. Thus, the self-interstitial is expected to be electrically inactive in the ring form while being a fair acceptor defect in the linear allotropic form. The DFE also varies significantly from one structure to the other. While the DFE of Se_i in the neutral state of charge is only of 0.45 eV in β -Se, it is 1.64 eV in γ -Se, roughly three times higher. It is very clear that the ring structure is far more prone to intrinsic defects than the linear one. However, the very concentrated defects of β -Se are very deep defects and do not give rise to free charge carriers, while Se_i in γ -Se is a fair acceptor.

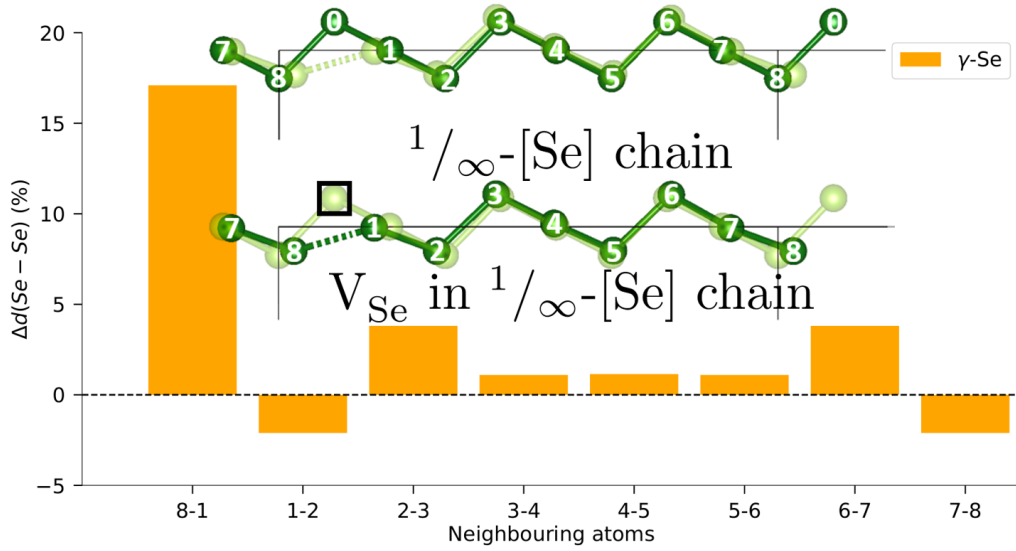
Although the Fermi level μ_{E_F} is often taken as a variable, it is important to keep in mind that for an isolated material⁶, the charge neutrality imposes one single possible value for the Fermi level at a considered growth temperature. As mentioned in Chapter 1, it is necessary to calculate the effective masses of the charge carriers. By fitting a parabolic model onto the band extrema, the effective masses summarised in Table 4.5 are obtained for the two phases. For β -Se, a difficulty emerges. The N prefactor in the expression of the defect concentration, as written in equation 1.31 of Chapter 1, is the number of available sites for the defect. Although its value is obvious in the case of vacancies, it is much more ambiguous in the case of an interstitial in β -Se for two reasons discussed hereafter. In the materials investigated so far (In_2S_3 , TiS_2), unoccupied crystallographic sites provide potential host sites for interstitials which are both obvious to the physico-chemist's eye and prove significantly (several tenth of electronvolts) lower in energy than other potential interstitial sites in DFT calculations. In β -Se, due to the flexibility of the structure which can be seen as a very soft/flat potential energy surface, the energy difference between different interstitial sites is much lower, making it harder to discriminate between sites. The second reason is that the structure is usually quite "rigid", *i.e.* the environments are maintained after relaxation in the presence of an additional atom. The neighbouring atoms are locally

6. Particularly, in the absence of an electric potential.

slightly displaced, but the global structure is preserved even if locally the symmetry is broken.



(a)



(b)

Figure 4.6: Relative variations of closest-neighbours' interatomic distances after introduction of V_{Se} in a) β -Se b) γ -Se. Atoms are arbitrarily numbered from 0, the atom which will be missing. The position of the vacancy is highlighted with a black square. The cell borders appear in solid lines.

For interstitial selenium atoms in γ -Se, N_{sites} was considered equal to one per conventional cell ($N = 27$ for the $3 \times 3 \times 3$ supercell). This allows the determination of the Fermi level at growth temperature and after quenching at room temperature, as well as the defect concentrations, as presented in Chapter 1. The simulation results are summarised in Table 4.8. The Fermi level during crystal growth is one third of the bandgap above the VBM, near the crossing point of the formation enthalpy curves of the two intrinsic defects (0.66 eV for $T_{growth} = 500$ K, which corresponds to the synthesis temperature of Todorov *et al.*).[317] Then, once the defect concentrations are frozen to model a quenching of the material, the Fermi level is dragged down towards the VBM. This is due to the following mechanism. The charge neutrality condition during synthesis imposes the 0.66 eV value for E_F^{growth} . Then the point defect concentrations are kept constant. As the number of free charge carriers is the product of the distribution and the DOS, the Fermi level is bound to come closer to the band-edges, as discussed in Chapter 1. Here, the p -type behaviour of the material due to the selenium interstitial is reproduced for the Fermi level as well. It highlights the fact that increasing the synthesis temperature will increase the concentration of charge carriers and by extension the conductivity, as the concentration of charged point defects increases with temperature. Note that the maximum hole concentration is quite low (10^{14} cm^{-3} for $T_{growth} = 1000\text{K}$). This calculated value is in perfect agreement with experimental data.[348] Interestingly, whereas at low synthesis temperature interstitials are more concentrated than vacancies, for growth temperatures above $\simeq 570\text{K}$, vacancies become the major defect in pure γ -Se. Defect concentrations are calculated to be inferior to 10^{15} cm^{-3} , comparably to In_2S_3 . [159]

Table 4.8: Fermi level (eV) at growth temperature (K) and after quenching at room temperature (300K), free hole and electron concentrations at room temperature and intrinsic defect concentrations (cm^{-3}) in γ -Se with respect to growth temperature.

T_{growth}	E_F^{gr}	E_F^{room}	n_h	n_e	$[V_{Se}]$	$[Se_i]$
500	0.66	0.37	$1.0 \cdot 10^9$	$1.6 \cdot 10^{-12}$	$3.6 \cdot 10^8$	$1.0 \cdot 10^9$
800	0.49	0.15	$7.3 \cdot 10^{12}$	$2.3 \cdot 10^{-16}$	$6.3 \cdot 10^{13}$	$7.3 \cdot 10^{12}$
1000	0.38	0.07	$1.5 \cdot 10^{14}$	$1.1 \cdot 10^{-17}$	$3.5 \cdot 10^{15}$	$1.5 \cdot 10^{14}$

Now that intrinsic defects properties have been thoroughly investigated, the potential dopants mentioned previously are discussed (Cu, Sb, Br). The extrinsic DFE curves are reported in Figure 4.7. Copper interstitial proves to be a deep-defect for both phases, with a +1/0 CTL 0.68 eV (0.92 eV) below the CBM for the β -phase (γ -phase). Once more, β -Se proves quite defect tolerant with low (1-2 eV) DFE for all considered defects, except for antimony interstitial. Antimony ($4d^{10}5s^25p^3$) can both exhibit the cationic form Sb^{3+} emptying the 5p orbitals as in Sb_2Se_3 and the anionic form Sb^{3-} saturating the same orbitals, as in AlSb . Thus, six different non neutral states of charge were considered for Sb_i . The transition levels unfortunately are buried deep inside the gap. The -2/-3 transition level of Sb_i is only 0.25 eV below CBM in β -Se but is an acceptor level, not a donor one. Its position should thus be considered with respect to the VBM and not the CBM. Bromine can lead to Br_i acceptor and Br_{Se} donor defects. In β -Se, both are deep defects. In γ -Se, the +1/0 CTL of Br_{Se} is 1.62 eV below the CBM and is thus very deep. The 0/-1 CTL of Br_i makes it a good acceptor, however it is more than 0.9 eV higher in formation enthalpy than deep donor Br_{Se} . Br_{Se} is expected to act as a “hole killer” defect as it is much more concentrated than Br_i . To summarise, no efficient dopant for β -Se was found in the list of chemical

species we selected. Copper and bromine doping of γ -Se are ineffective with respect to the improvement of the conductivity. Sb_{Se} in γ -Se is the lowest enthalpy defect in a γ -Se material containing antimony. Its DFE of 1.14 eV in the neutral state of charge, and its 0/-1 transition level 0.10 eV above the VBM makes it a far better acceptor defect than the intrinsic Se_i .

From those calculations, it can be concluded that the formation of the metastable phase β -Se should be avoided because of its extremely poor conductivity. It appears that Sb-doping of γ -Se may be an efficient way to improve the conductivity of selenium layers in optoelectronic devices. The other two species tried out, namely bromine and copper, seem irrelevant for such purpose.

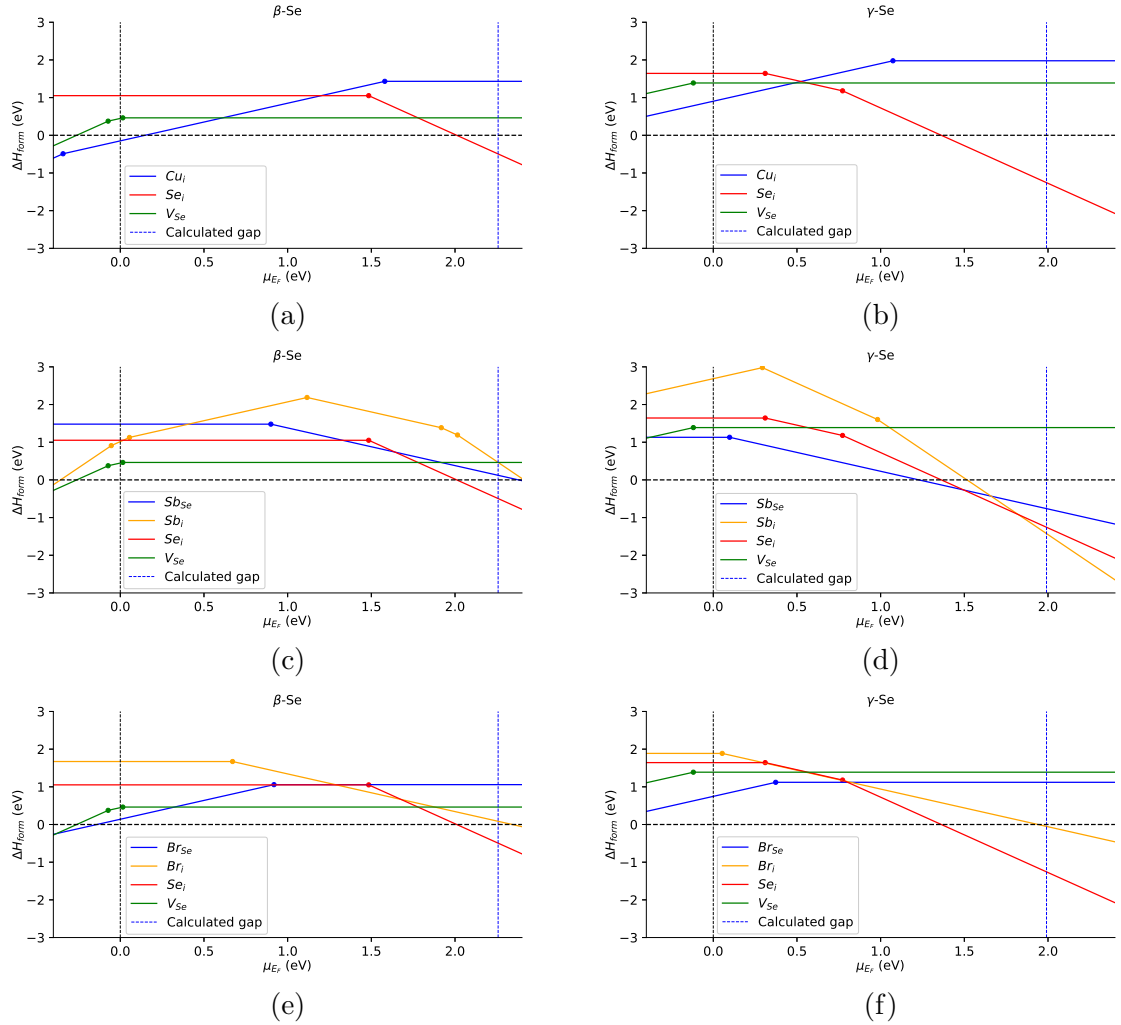


Figure 4.7: DFE plotted against Fermi level μ_{E_F} for intrinsic defects and a) Cu_i in β -Se b) Cu_i in γ -Se c) Sb defects in β -Se d) Sb defects in γ -Se e) Br defects in β -Se f) Br defects in γ -Se.

The relative simplicity of the two selenium phases studied (only one chemical species involved) offers the opportunity to try to go beyond the static model at zero temperature. This would allow to link the simulated variables to experimentally relevant macroscopic quantities, here pressure and temperature. The state function to simulate is no more the enthalpy but the free energy, as discussed hereafter.

4.3 Free energies

As discussed in Chapter 1, including the entropy allows to calculate the free energy $F = E - T \times S$ and considering both pressure/volume effects and temperature to go up to the Gibbs' energy G of the system, the thermodynamic quantity which should ideally be evaluated. The relative simplicity of the systems considered provides the opportunity to check the amplitude of the entropic and volume terms ignored in the model. The Gibbs' energy for the two ideal structures is calculated first, followed by the free energy of formation of intrinsic defects in γ -Se.

4.3.1 Computational details

To take into account the effect of pressure, a series of 6 additional cells with different $\frac{V}{V_0}$ ratios were built from the relaxed structure of volume V_0 (PBE-GD3-BJ for β -Se and PBE-GD3 for γ -Se). They were optimised at constant volume. The values reported in Tables 4.3 and 4.4 show that these functionals can be satisfactorily used for such purpose. The $E(V)$ data was fitted using Birch-Murnaghan equation of state 1.3 as implemented in PyDEF[117] and described in Chapter 1.

Density Functional Perturbation Theory (DFPT)[349] could not be used to calculate the phonon properties as the dispersion corrections are not included yet in the Hessian matrix in VASP. Thus, the finite-displacement method was used with $2 \times 2 \times 2$ supercells. The related post-treatment was performed using the phonopy code.[177]

4.3.2 Pressure and temperature effects

In order to calculate the Gibbs' energy G for the determination of pressure and temperature dependent phase diagram of crystalline selenium, both pressure and temperature contributions to G , namely $P \times V(P)$ and $T \times S(T)$, must be calculated. It is assumed that at low pressure and temperature, the two variables P and T can be decorrelated so that the two dependencies can be studied separately. The results are then linearly extrapolated to complete the *ab initio* data determined at $P(T = 0)$ and $T(P = 0)$.

To take into account pressure effects, Birch-Murnaghan equation of states was fitted on a series of energy *vs.* pressure *ab initio* data points. They were obtained by relaxing at constant volume and calculating the energy of compressed/dilated models with PBE-GD3. It was chosen to use the same dispersion scheme for both allotropic forms to enable comparison of the obtained energies. The fit is shown in Figure 4.8. Birch-Murnaghan equation of state has been previously used for high-pressure phases of Se.[335] Young modulus B_0 and its derivative with respect to pressure B'_0 are extracted from the fit. B_0 is found to be 3 times bigger for the β - than for the γ -phase. As only the total energy from the *ab initio* simulation is extracted to fit the equation of state, PBE-GD3 ought to provide reliable data.

Then, in order to reflect temperature effects, phonon properties are investigated within the harmonic approximation. In the ideally ordered structures, the configurational entropy is zero as there is only one possible configuration for the atoms within each structure. The only configuration is the crystallographic arrangement, where all atoms sit at their equilibrium position. Thus, the entropy in the ideal systems only consists in the vibrational entropy. Of course, the situation is fairly different when considering possible crystallographic point defects as will be discussed in the next section.

Thus, computing phonon properties of the ideal cells is enough to obtain the entropy of such ordered system. Due to overdelocalisation, GGA phonon frequencies are usually underestimated.[350]

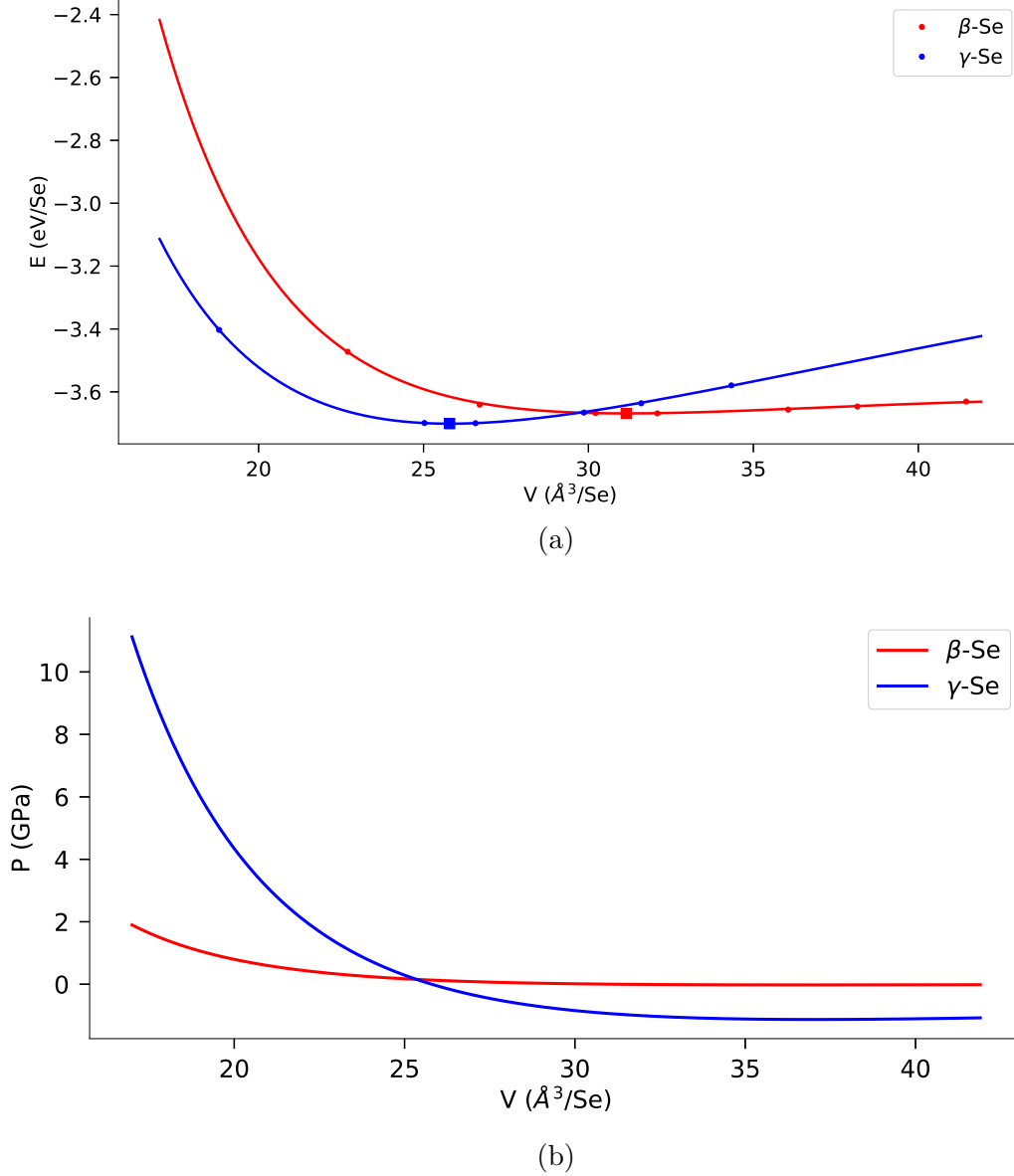


Figure 4.8: Birch-Murnaghan equation of state fitted onto PBE-GD3 calculation series. a) $E(V)$ curve for β -Se yields $B_0 = 0.16$ GPa and $B'_0 = 5.51$. $E(V)$ curve for γ -Se yields $B_0 = 0.05$ GPa and $B'_0 = 8.08$. Data points correspond to *ab initio* results while solid lines correspond to fitted Birch-Murnaghan equation of state. The square corresponds to the (V_0, E_0) minimum obtained without pressure. b) $P(V)$ curves for β - and γ -Se.

Phonon band structure and DOS are presented in Figure 4.9. As expected from theory,[351] $3N$ acoustic phonon branches and $3N - 3$ optical branches are obtained, where N stands for the number of atoms in the conventional cell. Acoustic phonon branches reach zero frequency within the infinite wavelength limit, *i.e.* the Γ -point of the first Brillouin zone, corresponding to rigid body translation of the whole crystal without deformation of the crystal lattice. They exhibit a linear behaviour in the vicinity of the Γ -point as expected. They decompose into one longitudinal and two

transverse modes. Vibrational frequencies of the acoustic modes are lower for the β -phase ($< 25 \text{ cm}^{-1}$) than for the γ -phase ($< 80 \text{ cm}^{-1}$). It means that the chemical bond in the chain-like structure is more “rigid” than in the ring-like one. This is coherent with the previous interpretation of β -Se being the most flexible structure of the two. The forbidden frequency gap in the infinite wavelength limit (Γ -point) is computed to be 21 cm^{-1} in β -Se and 113 cm^{-1} in γ -Se. The DOS gap between the medium- and high-frequency optical phonons is three times more important for the β - than for the γ -phase ($\simeq 60 \text{ cm}^{-1}$ *vs.* $\simeq 20 \text{ cm}^{-1}$). Finally, β -Se exhibits phonon modes of frequencies higher than 250 cm^{-1} while γ -Se does not. All these distinctive features can help identify the allotropic form of Se using Raman spectroscopy.

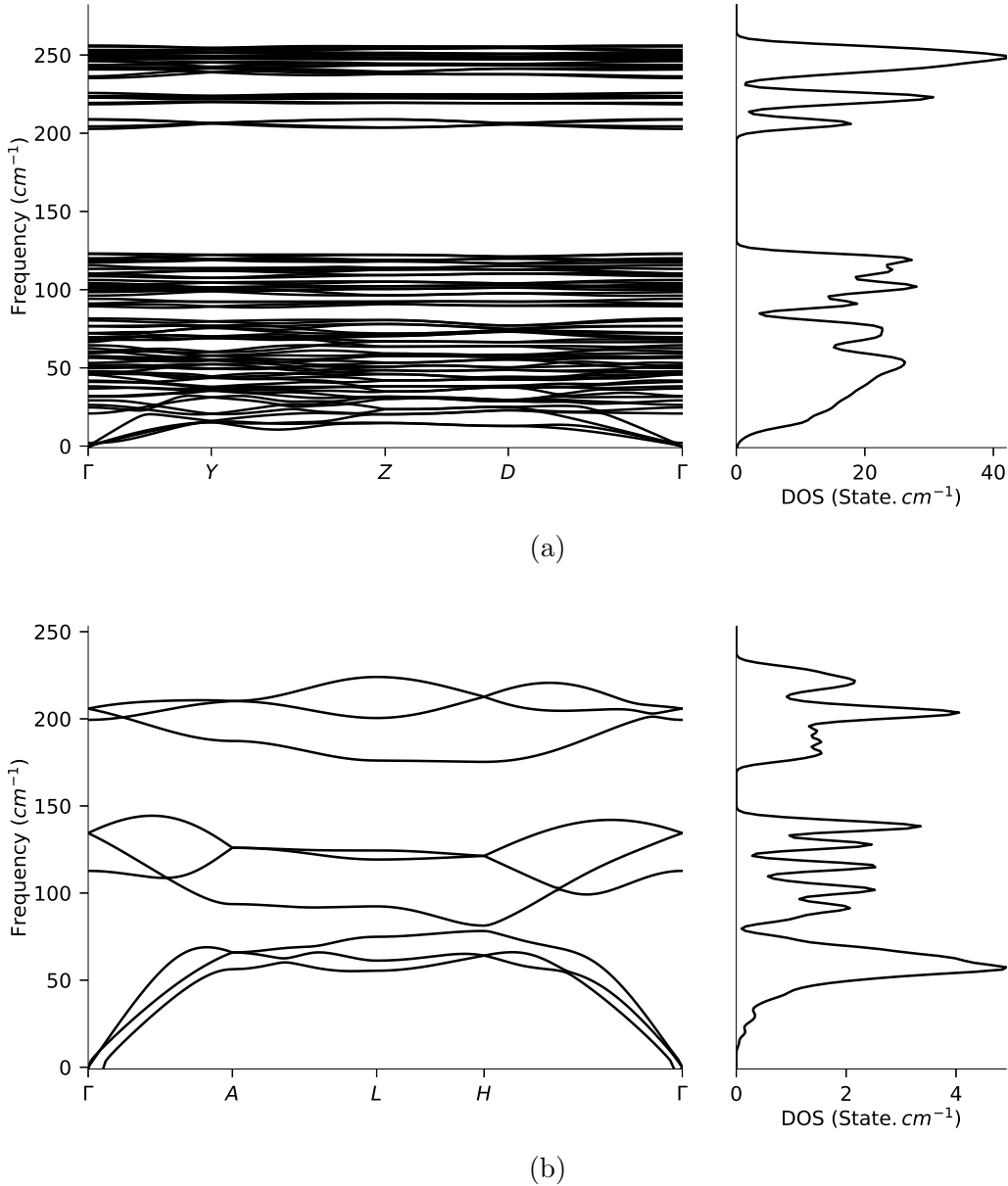


Figure 4.9: Phonon band structure and DOS for a) β -Se (Γ (0,0,0), Y($\frac{1}{2}$,0,0), Z(0, $\frac{1}{2}$,0), D(0, $\frac{1}{2}$, $\frac{1}{2}$)) computed with PBE-GD3-BJ and b) γ -Se (Γ (0,0,0), A(0,0, $\frac{1}{2}$), L($\frac{1}{2}$,0, $\frac{1}{2}$), H($\frac{1}{3}$, $\frac{1}{3}$, $\frac{1}{2}$)) computed with PBE-GD3.⁷

7. 3 negligible imaginary frequencies at $2.5 \cdot 10^{-6} \text{ eV}$ (doubly degenerated) and $7.6 \cdot 10^{-7} \text{ eV}$ were

This allows us to obtain free energy dependency with respect to temperature, as depicted in Figure 4.10. The entropic contribution is more important for β -Se. This may be due to the fact more degrees of freedom are available for the vibrations of the ions as the rings are roughly free to vibrate independently from one another, whereas the chain structure of γ -Se constrains the vibrations in the c crystallographic axis.

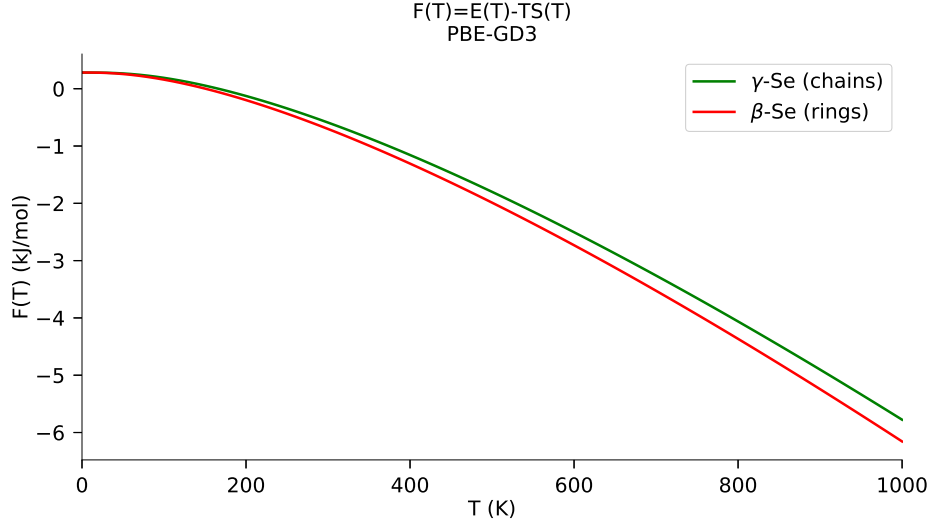


Figure 4.10: Free energy of each phase, in electronvolts, plotted against temperature.

The dependency in temperature and pressure of the ideal structures Gibbs' energies can be extrapolated from the obtained data, following equation 4.1. The thermal dependency is modelled *via* the simulation of phonons. Expressions of $E(T)$, $S(T)$ and free energy $F(T) = E(T) - T \times S(T)$ can be found in reference [177] (equations 8, 10 and 11). The inversion of the $V(P)$ relation from Birch-Murnaghan EOS as expressed in Chapter 1 equation 1.3. Of course, this is appropriate far below the melting point, near melting point studies would require molecular dynamic simulations.

$$G(P, T) \simeq \underbrace{E(T) - T \times S(T)}_{\text{Phonons}} + \underbrace{P \frac{\partial E}{\partial P} \Big|_{T=0}(P) + P \times V(P)}_{\text{Birch-Murnaghan}} \quad (4.1)$$

The Gibbs' energy difference gives the calculated pressure-temperature phase diagram presented in Figure 4.11. The 1D phase γ -Se is the low-temperature phase, as observed experimentally.[353] This is consistent with the fact that thin film synthesis, during which temperature is typically of a few hundreds of degrees, always lead to the formation of γ -Se.[322, 323] It should be noted that due to the strong assumptions made to come to such result, the absolute values of pressure and temperature should be considered with care. Only the studied phases are represented in Figure 4.11. As mentioned previously, a phase transition towards a monoclinic system is expected at a few dozen GPa, as reported in the experimental literature. However, the exact structure as well as the pressure at which the transition occurs remains a matter of debate.

found in the finite difference VASP/phonopy process. This is a known issue related to numerical interpolation in the vicinity of the Γ high symmetry K -point of no physical importance. It might be eliminated when using other implementations such as ABINIT.[352]

Note that the entropic contribution to the Gibbs' energy is more important than the volume term here. It may explain why, counterintuitively, the low-pressure phase γ -Se has a slightly higher density of 4.80⁸ than that of 4.61 of β -Se.

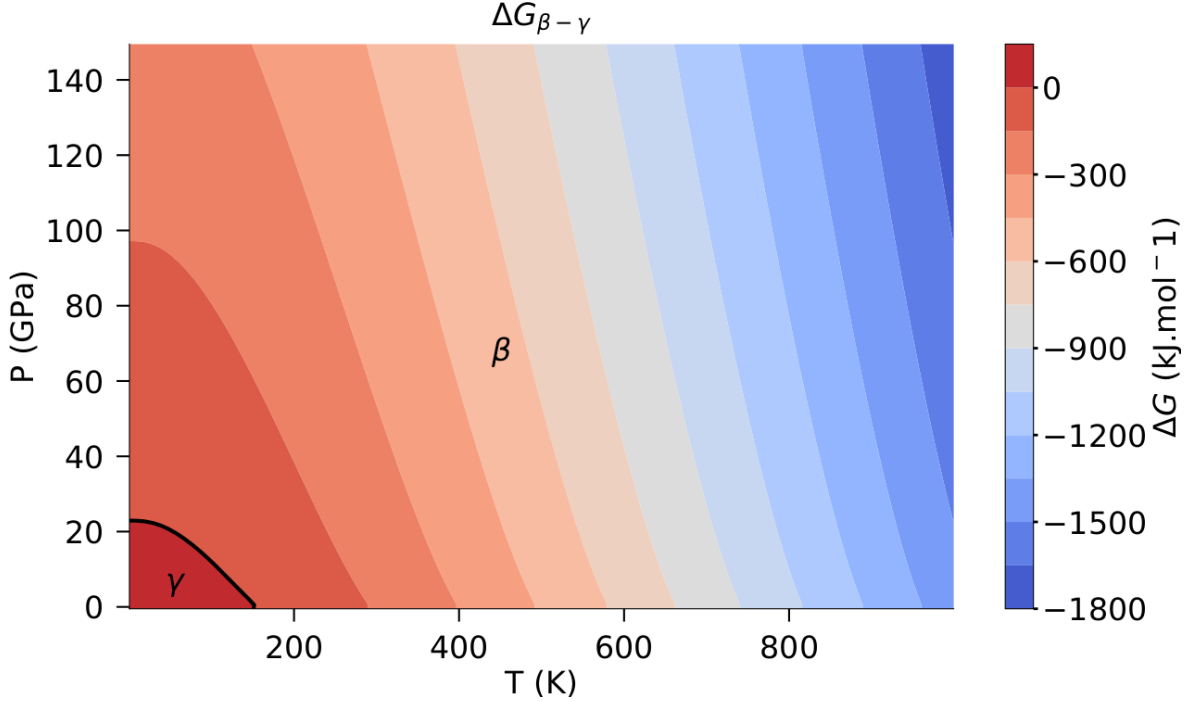


Figure 4.11: Calculated phase diagram of crystal selenium against pressure and temperature. $\Delta G_{\beta-\gamma}(T, P) = G_{\beta}(T, P) - G_{\gamma}(T, P)$.

4.3.3 Free formation energies of intrinsic interstitial defect of γ -Se, the standard phase of Se

The relative simplicity of the structures offers the opportunity to test the model further and to get closer to the Gibbs' free energy of formation which is rigorously the thermodynamic quantity to aim for. This will allow us to check the validity of the approximation made in Chapter 1 which consists in ignoring the entropic contribution. In the dilute defect limit, volume change due to the defect is supposed to be zero. Hence, so is the change in the volume term of the Gibbs' energy $\Delta(P \times V)$. In any case, it could hardly be taken into account using our methodology. Thus, the free formation energy of formation $\Delta F_f^{D,q}(\mu_{EF}, T)$ is computed, in order to quantify the error made by ignoring the entropic part. In the following discussion, T always refers to the crystal growth temperature noted T_{growth} previously. The notation is simplified to lighten the expressions. As noted by Freysoldt *et al.*, [48] it is rigorously the thermodynamic quantity to calculate. In metals, where the bandgap problem does not occur, and subsequently avoids the determination of the Fermi level at growth temperature, free energy of defect creation has been calculated for systems such as Al and Cu, taking into account both configurational and vibrational entropies. [97, 354] Similar studies in semiconductors remain scarce and limited to well-known materials such as Si, diamond, Ge and GaN. [355, 356]

8. As calculated from the XRD structure.

The computation of the configuration entropy requires no additional DFT calculation compared to a standard DFE study but only a refinement of the post-treatment step, while accounting for the most important part of the entropy. Thus, first only the configurational entropy will be taken into account, not the vibrational entropy. The treatment of the disordered (faulted) system is very different from that of the ordered (ideal) system regarding the computation of entropy. Only the configurational entropy as expressed in equation 1.6 of Chapter 1 needs to be taken into account in a first approximation. As expressed in the system of equations 4.2, the free energy depends on the entropy among other things. In turn, the configurational entropy is a function of the defect concentration, which is a function of the free energy among other things. This triangular dependency causes a practical difficulty. It can be overcome by solving the first equation of 4.2 of unknown quantity ΔF using a standard root-finding algorithm. It implies that the fundamental quantity in the model is no more determined in a single step from μ_{E_F} but using a self-consistent loop.

$$\begin{cases} \Delta F_f^{D,q}(\mu_{E_F}, T) &= \Delta E_f^{D,q}(\mu_{E_F}) - T \Delta S_{conf}(\Delta F_f^{D,q}) \\ \Delta S_{conf}([D^q]) &= k_B([D^q] - [D^q] \ln[D^q] + [D^q] \ln(N^{sites})) \\ [D^q](\Delta F_f^{D,q}) &= N_D^{sites} \cdot (1 + e^{\frac{\Delta F_f^{D,q}}{k_B T}})^{-1} \end{cases} \quad (4.2)$$

In Chapter 1, the configurational entropy was plotted against the defect concentration (ratio). Here, it is applied first to Se_i in $\gamma\text{-Se}$ and plotted against volume defect concentration in Figure 4.12a. Let one keep in mind that the expression of $\Delta S_{conf}([D^q])$ used in equation 4.2 is obtained by considering the possible configurations of a system containing n defects and N atoms, then by simplifying the obtained expression using the Stirling approximation $\ln N! \simeq N \ln N - N$ and exploiting $\frac{n}{N} \ll 1$. Furthermore, for high defect concentrations, the dilute defect model becomes irrelevant as the system tends to become a solid solution. This is a different problem which should be addressed using an appropriate methodology which differs from the one used in this work. Thus, the model employed here becomes gradually irrelevant as the defect concentration in the system reaches the solid-solution domain.⁹ Of course, above a defect ratio of 100% represented by the dotted blue line in Figure 4.12a, the model loses any physical meaning. For realistic defect concentrations, the $T \times \Delta S$ product is inferior to 0.10 eV for temperatures up to 1250 K. The range of growth temperatures considered (500 - 1250 K) corresponds to typical temperatures encountered in different growth/deposition processes. Low temperatures would be employed in vacuum processes such as PVD and high temperatures in ceramic routes. So far, merely by looking at the expression of the configurational entropy used in the model, one can see that in the most extreme limit the $T \times \Delta S$ product would weight no more than 0.10 eV. One would like to go further and estimate the actual dependency in Fermi level μ_{E_F} and see whether this value is actually met. Note that the very low maximum values for the configurational entropy validate the assumption that the vibrational entropy associated to the defect creation can be safely ignored.

Then, the system of equations 4.2 is solved self-consistently to obtain the variations of entropy with respect to the position of the Fermi-level μ_{E_F} . The weight of the product of the temperature by the configurational entropy $T \times \Delta S$ is inferior to 5 meV

9. The value at which a solid-solution should be considered is a matter of discussion and depends both on the physical system investigated and the research communities. For certain, a defect concentration above 10% is definitely not a mere perturbation of the ideal host lattice.

throughout the bandgap, far below the maximum 0.10 eV noticed during the previous analysis of $S([D])$. As the formation enthalpy of Se_i in β -Se, which is the main term of the free energy, decreases with increasing Fermi level, the calculated defect concentration increases with the Fermi level. It leads to an increase in the entropic term. Although it is experimentally known that the real γ -Se material is a p -type one, it is still interesting to look at the range of Fermi level values for which the entropic term would weight the most. For values of the Fermi level within the bandgap, the entropic term is of the order of magnitude of the millielectronvolt or less. The approximation of the free energy by the enthalpy of formation appears thus entirely justified for this defect. It is only for very high values of μ_{E_F} that the DFE of Se_i becomes low enough for the entropic term to increase significantly. Let one keep in mind that the formation enthalpy of this defect is quite high, $\Delta H^{\text{Se}_i^{-2}}(\mu_{E_F} = 0) = 3.02 \text{ eV}^{10}$.

Thus, one can wonder under which formation enthalpy value the configurational entropy becomes substantial. This is investigated by considering hypothetical defects of constant charge -2 and increasing formation enthalpy within the range 0 to 3 eV¹¹. Let us arbitrarily fix this criteria as $T \times \Delta S \geq 0.10 \text{ eV}$. The N_{sites} prefactor is set to one in the defect concentration expression. Note that as the defect concentration is necessarily inferior to one (100%), the $[D] \ln[D]$ term dominates in the expression of the configurational entropy. The dependency in Fermi level is computed and shown in Figure 4.13. Figure 4.13 can be read as an abacus showing the importance of the entropic term with respect to the Fermi level for different DFE and constant charge $q=-2$. The curves are slightly distorted Fermi-Dirac distribution, as derived from 4.2. Increasing the defect formation enthalpy shifts them up towards the CB. The opposite charge would reverse the picture, with a maximum value near the VB and a transition to negligible $T \times \Delta S(\mu_{E_F})$ in the gap. The maximum value is 0.11 eV for $N_{\text{sites}} = 1$. Depending on the crystallography, this curve is scaled by N_{sites} . In short, the configurational entropy ought to be taken into account for defects exhibiting both low formation enthalpies and high N_{sites} . It shows the importance which must be taken in the evaluation of N_{sites} to decide whether the entropy is needed. It also maps the values for which the configurational entropy becomes significant.

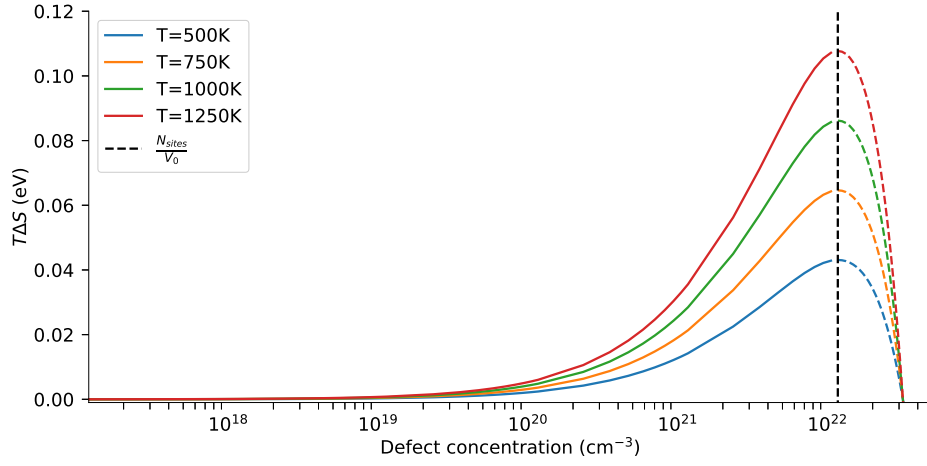
4.4 Partial conclusion on selenium

Ab initio simulations on two allotropic forms of selenium encountered at ambient pressure and temperature were performed. Birch-Murnaghan equation of state fitted onto series of ideal models and phonon calculations allowed to get the contribution to the Gibbs' free energy of pressure and temperature, respectively, for the ideal structures. It shows that the infinite chains of γ -Se are favoured over the metastable ring structure β -Se at low pressure and temperature.

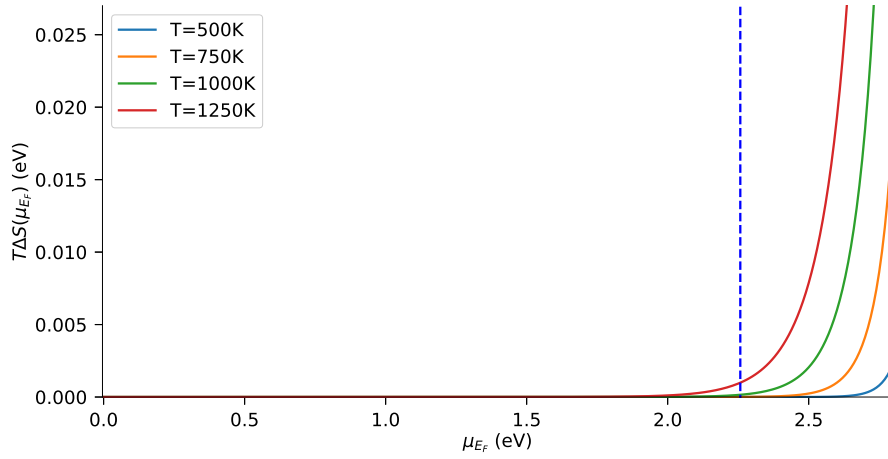
Then, intrinsic point defects of both phases were investigated, revealing that β -Se has practically no conductivity while the fair hole conductivity of γ -Se originates from selenium interstitials. Geometric modifications induced by selenium vacancies were studied in detail. It was shown that the ability of the rings to relax to a structure relatively close in terms of environment after the introduction of the vacancy compensates

10. The DFE value at the top of the VBM is the intercept of the $\Delta H^q(\mu_{E_F})$ line. For Se_i in the $q=-2$ state of charge, it can be obtained by prolonging the red line of slope -2 in Figure 4.5 and reading the enthalpy value at the intersection with the vertical black dotted line of equation $\mu_{E_F} = 0$.

11. A 0.01 eV shift is added to the $k \times 0.5 \text{ eV}$, $k \in 0, 6$ energy values to avoid numerical divergence for $\Delta H = 0$.



(a)



(b)

Figure 4.12: Se_i in $\beta\text{-Se}$ $q=-2$ a) Product of the configurational entropy and crystal growth temperature with respect to defect concentration as obtained from the second equation in 4.2. The blue dotted line stands for $\frac{N_{\text{sites}}}{V_0}$, the maximum possible limit for the defect ratio (100% faulted). b) Product of the configurational entropy and crystal growth temperature with respect to Fermi level μ_{E_F} obtained by self-consistently solving the system of equations 4.2.

the energy required to break two Se-Se chemical bonds. Comparatively, breaking two such bonds in the chains is easier but results in a very different structure, replacing a covalent bond by a long range interaction, which is not favoured energetically. These considerations provide an explanation for the lower V_{Se} DFE in $\beta\text{-Se}$ than in $\gamma\text{-Se}$ despite stronger Se-Se bonds (shorter Se-Se distances).

The problem of counting potential interstitial sites in $\beta\text{-Se}$ was discussed and it was preferred not to calculate the Fermi level in this phase. In $\gamma\text{-Se}$, such issue does not appear and the simulations were performed, exhibiting a typical p -type behaviour.

Then, antimony, bromine and copper doping were investigated. All proved ineffective in $\beta\text{-Se}$, whereas antimony was found to improve significantly the hole conductivity in $\gamma\text{-Se}$ *via* the creation of Sb_{Se} substitutional defects. Given these results, one can

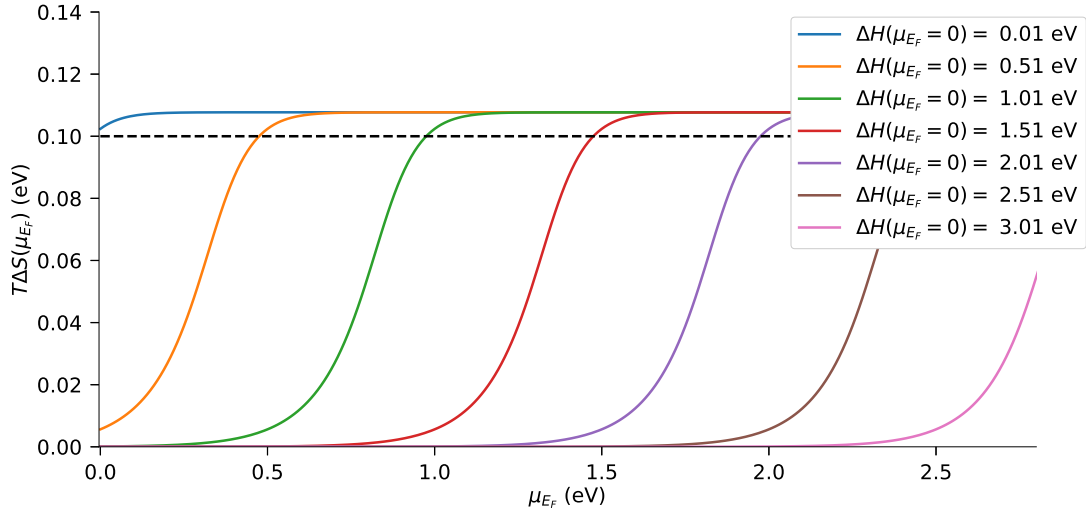


Figure 4.13: Product of the configurational entropy and crystal growth temperature with respect to Fermi level μ_{E_F} obtained by self-consistently solving the system of equations 4.2 for hypothetical defects of charge $q=-2$ with increasing formation enthalpies. The black line marks the 0.1 eV, arbitrarily considered as significant. The N_{sites} prefactor is set to one in the defect concentration expression.

advise for selenium used in optoelectronic devices to be grown rather at high temperature as long as the γ -phase can be maintained, and conductivity improved by antimony doping.

Pressure and temperature effects were taken into account for the phase diagram based on the ideal structures. Se_i provided a test case to investigate the impact of configurational entropy. The calculation proves that for selenium, it can be safely neglected. An abacus of configurational entropy values is calculated to provide the quantitative data needed for the decision on the need for the configurational entropy in a defect study.

Conclusion

As exposed in introduction, lattice defects are ubiquitous in real materials and have a strong impact on their properties. Mechanical properties are driven mostly by line defects, while the optoelectronic ones arise from point defects. The present work focuses on the impact of the latter on the optoelectronic properties of materials. Thus, it is necessary to identify the nature and role of each defect in applicative compounds in order to design a device fabrication process which favours the desired defects to optimise performances. Herein, the focus was set on chalcogenide PV solar cells, in which the conductivity of the absorber and buffer layers composing the p - n junction and the identification of potential recombination centres is key. However, the microscopic scale of point defects and indirect measurement techniques make them difficult to study comprehensively through experiments. Thus, *ab initio* simulations appear as a tool of choice to complement the experimental process. By extension, their reliability means that this method can now also be used prior to experiment in order to envision the feasibility of some concepts.

This methodology is applied to investigate the native and extrinsic point defects in β - In_2S_3 , a buffer material for chalcopyrite solar cells, as reported in Chapter 2. The interstitial indium atom in tetrahedral environment is the main driver of the n -type conductivity of the material, along with a sulphur vacancy to a lower extent. Given our simulation results, sulphur-poor synthesis conditions appear more suited to enhance the concentration of free electrons within the layer. Then, the impact of alkali-doping on the host is investigated. On the computational side, this case highlights the necessity for the competing binary and ternary compounds involving the dopant to be taken into account into the computation of the chemical potentials. Gathered evidence show that the observed positive impact of alkali on the conversion efficiency of PV cells is most probably due to the formation of AInS_2 ($A = \text{Na}, \text{K}, \text{Rb}, \text{Cs}$) rather than the stabilisation of extrinsic alkali defects in the In_2S_3 lattice due to the large amount of alkali introduced. The mass balance of the In_2S_3 host reacting with the alkali element to form AInS_2 is probably guaranteed by the co-formation of InS . The main approximations in this model are the thermodynamic limit which may not be reached in the real system and the absence of any interface, as all calculations were conducted on bulk structures. The destabilisation of the host In_2S_3 by the insertion of incoming alkali A in the vacant tetrahedral site leads to the formation of a new phase AInS_2 and subsequently of an interface between the remaining host in excess In_2S_3 and the newly formed phase. It can be imagined that this discontinuity leads to a situation where the chemical potentials cannot anymore be considered as single-valued throughout the system which is now constituted of at least two different grains. The chemical potentials can undergo a brutal shift when considering two points on both sides of this interface. It seems possible that due to the continuing diffusion of alkali atoms, the situation inside the remaining host grain is so that the chemical potential of the dopant is lower than the calculated limit and some alkali atoms can be stabilised

as interstitials in the remaining host grain. In any case, the major change which the system has underwent after exposure to large amounts of alkali is the apparition of the AlInS_2 phase. One intuition is that the absolute limit value of dopant chemical potential found through the computation of the stability domain prior to defect studies may give a clue *a priori* on the difficulty to achieve doping. This is confirmed by experimental means.

A material of fundamental interest, TiS_2 , is presented in Chapter 3. Large intrinsic defect concentrations are suspected to be responsible for the controversy on the semi-metallic or semiconducting character of this transition-metal dichalcogenide. Prior to studying defects, the difficulties to find a relevant methodology to describe the properties of the ideal material are discussed. The importance of long-range interactions in such a layered compound and the need for the use of a hybrid electronic density functional are highlighted. The intrinsic point defects of the material are studied using PBE0-GD3-BJ. It shows that regardless of the growth conditions, titanium interstitials stabilised in octahedral environment in the interlayer structural gap are the major defects. Based on our computations, titanium interstitial do not adopt the tetrahedral configuration. Most importantly, in sulphur-poor conditions, the interstitial Defect Formation Enthalpy is so low that the Fermi level must enter the CB to satisfy the charge equilibrium, leading to a semimetallic behaviour. Conversely, in sulphur-rich atmosphere, it lies under the CBM, sign of a semiconducting character. This shift in behaviour between the two limits of the stability domain remains unchanged if the hypothetical phase Ti_7S_{12} is not considered. Indeed, considering the S-poor/Ti-rich end of TiS_2 stability domain as fixed by Ti_7S_{12} or TiS only changes the chemical potentials of a few tenths of electronvolt. The simulated transition obtained *via* a slight change in growth conditions explains the controversy around the semimetallic/semiconductor property of the material.

Finally, due to the current surge in interest for elemental selenium for its potential use as an active layer in next generation chalcogenide PV cells, be it as an absorber or a hole conductive layer, this material is investigated. More broadly, the importance of the chemical species of selenium in the field of chalcogenides for PV make it a relevant compound to investigate. The complexity of the phase diagram, even at ambient pressure, is discussed, and two allotropic forms are chosen for the study, namely 0D β -Se consisting in Se_8 rings and 1D γ -Se of infinite helical chains. Intrinsic and extrinsic point defects are studied within the meta-GGA approximation through the SCAN functional. The difficulty to model interstitial defects within such low-density and versatile structures is addressed. The 0D form proves to have no shallow defect, with V_{Se} and Se_i showing a deep Charge Transition Level. For the 1D form, neutrally charged selenium vacancies, irrespective of the position of the Fermi level in the electronic bandgap, do not affect the electronic properties, while acceptor defect Se_i possesses a 0/+1 Charge Transition Level close to the VBM. Thus, the native *p*-type conductivity in γ -Se is due to selenium interstitials. Then, the apparent simplicity of those elemental compounds is exploited to test the capacity to take into account entropy in the model. By performing Birch-Murnaghan Equation of States fits and phonon studies, the pressure and temperature impact on the two ideal structures is modelled. Then, the point defect model is refined to include configurational entropy. Calculating the defect configuration entropy does not require any supplementary *ab initio* calculation and the post-treatment was refined to include it. In the light of those calculations, the general assumption that the defect configurational entropy is negligible seems valid in most cases, provided that the Defect Formation Enthalpy is

not too low (≥ 1 eV). An abacus is also computed in order to get an idea of the order of magnitude of this quantity with respect to different variables (Defect Formation Enthalpy, Fermi level). It also strengthens the confidence regarding the reliability of the results obtained previously on the other materials studied.

This research work allowed our group to acquire the knowledge necessary to handle the supercell approach to point defects, especially regarding the meaning and impact of the different energetic corrections. Appropriate tools gathered in the PyDEF 2 program were developed and deployed. Additional hindsight on the model was gained through the constitution of a portfolio of material test cases. The methodology was applied to identify the key intrinsic point defects, screen extrinsic dopants and evaluate their impact on the opto-electronic properties of applicative materials for the field of photovoltaics, β - In_2S_3 , Sb_2Se_3 , β - and γ -Se, CsCu_5Se_3 ¹², and also reveal some peculiar defect-related properties in compounds of fundamental scientific interest, namely TiS_2 and ZrSe_2 ¹³. In addition to following the now well-established framework to obtain Defect Formation Enthalpies, the limits of the model were tested when possible. In particular, Fermi level positioning and defect concentrations were simulated when relevant. Problematic cases such as TiS_2 were investigated. The configurational defect entropy was quantified for selenium.

In the light of the different results obtained throughout this work and also gathered from the literature, it appears that the supercell approach towards point defects is now a mature methodology which can provide reliable results complementary to experiment and even forecast trends *in silico*. The computational load, mainly due to the high number of *ab initio* calculations to conduct, requires adequate power to carry out.¹⁴ Care and organisation is necessary for the post-treatment step, which is now made easier by the aforementioned tools. Based on our experience, the study of the intrinsic and a few extrinsic point defects of a non-problematic material can reasonably hope to get reliable results within a handful of months. This should be compared to the few years require to conduct and analyse Positron Annihilation Spectroscopy experiments. The quantities routinely *via* the supercell framework assessed are Defect Formation Enthalpies and concentrations in the dilute approximation and thermodynamic limit. Great care should be taken in the systematic investigation of all possible intrinsic point defects, considering when possible for instance all different crystallographic sites. When not, the influence of the chemical environment should at least be taken into account. The example of tetrahedral and octahedral indium environments in β - In_2S_3 proves this. This is of particular importance when investigating doping, as intrinsic defects, or at least the most concentrated ones, should not be forgotten in the model. They will always be present in the real material and influence the Fermi level position. It is quite clear that the approach can only give results on the defects investigated. The unusual self-substitutions in Sb_2Se_3 are a great example for this. All the other more conventional intrinsic defects fail to explain the conductivity of the material. Not considering them would not allow to understand the origin of this property. Also, the importance of correctly describing the physics of the system has extensively been illustrated through the example of TiS_2 . In particular, small bandgap semiconductors may require the mandatory use of hybrid functionals. In the same spirit, long-range interactions in

12. Not described in the present manuscript see reference[118] for more details.

13. Not described in the present manuscript, undergoing experimental investigation prior to publication.

14. In our case, supercell calculations were performed using typically 3 computing nodes of Xeon dual-processors XE340 of 6 cores (12 cores per node in total) working at 2.66 GHz frequency.

van der Waals compounds must be addressed. Semi-empirical schemes appropriately chosen case-specifically can handle this. The corollary for these remarks is that GGA energy differences with band positions corrected with higher levels of theory is often sufficient to quickly provide useful insights for materials with high-enough bandgaps. This is quite logical as the methodology is based on thermodynamics and GGA is most of the time appropriate to calculate total energies. Lastly, this method is appropriate to study point defects. Studies were conducted in the bulk in this work. A parent framework can be derived for interface defects,[357] a subject of interest to raise the barriers in electronic device operations. Higher-dimensionality defects require of course different and appropriate approaches and must be considered as a different problem from a simulation point of view, although they probably appear simultaneously in the real material. Finally, only ground state properties are investigated in the version of the methodology proposed herein.

Defect physics and chemistry is a field of current interest for its vast implications on both fundamental and applicative research. Crystallographic defects of all dimensionalities exist, from point to volume defects. They have an impact on different types of material properties. Hence, depending on the application desired, researchers in different fields will focus on defects of different dimensionalities. On the subject of electronics, in particular solar photovoltaics, point defects especially are of vital importance, due to their dramatic impact on the electronic and optical properties of materials. Simulations in the form of DFT within the supercell approach offers a mature and powerful method complementary to experiments to investigate them. Although this methodology is now well established to investigate the thermodynamics of both intrinsic and extrinsic point defects, some exciting challenges remain. The methodology used in this work has already been employed to investigate the deep defects which could potentially be responsible for the luminescence of some compounds, such as ZnO,[88] when electron-trapping mechanisms are involved. In particular, trap depth can be estimated by positioning transition levels within the bandgap. One more refinement has been proposed on ZnS which allows the computation of emitting energies by simulating a charge transfer.[358] However, on-site transitions remain elusive for these methods. The use of constrained DFT has recently been successfully employed to lift this limitation and simulate the $4f \rightarrow 5f$ excitations,[359, 360] paving the way for further theoretical investigations. Another challenge is the simulation of doping of amorphous materials which is of particular interest in the field of optics. Amorphous silica for instance, is of great importance in the fabrication of optical fibres, and coloured glasses are often found in optical devices. Traditionally, amorphous materials are apprehended *via* (often classical) molecular dynamics, which does not include any electronic property, or the polymeric chains studied separately. With the increase in computational power, building large supercells of realistic structural models coherent with Pair Distribution Function analysis for instance would become affordable. This would allow the determination of preferred oxidation states of dopants and help to understand and predict optical properties of disordered systems.[361, 362] Finally, the current excitement around high-throughput simulations[237, 363, 364] may lead to the increase in reliability needed for systematic and automatic defect investigations[167] to accelerate discoveries of properties of potential interest within the next one or two decades. Dedicated databases should logically become one additional tool for the community in the next decades.

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Titre : Modélisation *ab initio* des défauts ponctuels chargés et de leur impact sur les propriétés opto-électroniques de matériaux semiconducteurs cristallins.

Mots clés : DFT, défauts ponctuels, semiconducteurs, simulations *ab initio*

Résumé : Les défauts cristallographiques sont à l'origine de nombreuses propriétés d'intérêt pour les matériaux applicatifs. Dans le domaine de l'électronique, et du solaire photovoltaïque en particulier, un grand nombre de propriétés opto-électroniques (conductivité électronique, nature et concentration des porteurs de charges...) sont pilotées par les défauts cristallographiques ponctuels dans les matériaux mis en jeu et aux interfaces. Aussi il est crucial de caractériser les défauts prépondérants et leur impact sur les propriétés recherchées afin de pouvoir améliorer les performances des dispositifs. L'étude expérimentale des défauts, objets microscopiques, étant complexe et ne donnant qu'une image partielle et sujette à interprétations, les méthodes de simulation *ab initio* apparaissent comme un outil puissant pour la compléter.

Une approche dite de supercellules permet avec l'aide de la théorie de la fonctionnelle de la densité (DFT) d'étudier un à un chaque défaut dans tous ses états de charge, et au moyen du calcul de son enthalpie de formation en fonction du niveau de Fermi d'établir sa concentration et son impact sur la conductivité. Ainsi l'origine du type *n* du matériau β - In_2S_3 étudié au laboratoire comme potentielle couche tampon dans des cellules photovoltaïques de deuxième génération est déterminée. Le problème d'intérêt fondamental du caractère semimétallique/semiconducteur de TiS_2 est élucidé. Enfin, les limites de la méthode sont éprouvées par l'étude de l'entropie dans différentes formes de sélénium cristallin

Title: *Ab initio* modeling of charged point defect and their impact on opto-electronic properties of crystalline semiconductor materials

Keywords: DFT, point defects, semiconductors, *ab initio* simulations

Abstract: Numerous applicative properties of materials originate from crystallographic defects. In the field of electronics and solar photovoltaic in particular, several opto-electronic properties (electronic conductivity, nature and concentration of the charge carries...) are driven by point defects in the different materials in place and at the interfaces. Thus, it is crucial to characterise the most concentrated defects and their impact on the targeted properties in order to enhance the device performances. Studying microscopic defects experimentally is a complex task which only brings partial answers requiring interpretation. *Ab initio* simulation techniques appear as a powerful tool to complete experiments.

The supercell approach along with Density Functional Theory (DFT) allows to study each defect in all its states of charge. Evaluating the formation enthalpy of defects with respect to the Fermi level allows to obtain its concentration and impact on the conductivity. This way, the origin of the *n*-type conductivity of β - In_2S_3 , a buffer material for 2nd generation photovoltaic solar cells studied at the laboratory, is determined. The problem of fundamental interest of whether TiS_2 is a semiconductor or a semimetal is elucidated. Finally, the limits of the method are tested by studying entropy in different allotropic forms of crystalline selenium.