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ELECTRONIC STRUCTURE OF DEFECTS IN III-VI AND II-VI SEMICONDUCTORS AND NOVEL Yb-BASED INTERMETALLICS

By

Zsolt Rák

A DISSERTATION

Submitted to Michigan State University in partial fulfillment of the requirements for the degree of

DOCTOR OF PHILOSOPHY

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Physics and Astronomy

2009

ABSTRACT

ELECTRONIC STRUCTURE OF DEFECTS IN III-VI AND II-VI SEMICONDUCTORS AND NOVEL Yb-BASED INTERMETALLICS

By

Zsolt Rák

In recent years there has been a revival of interest in the III-VI family of semiconductors (GaS, GaSe, GaTe and InSe) due to their exciting nonlinear optical properties and their possible application in detector devices. These materials crystallize in layered crystal structure and their physical properties display a quasi two-dimensional character. An important characteristic of these systems is the existence of Ga-Ga (or In-In) dimers. It is well known that defects control the physical properties of semiconductors. In this thesis, we have carried out electronic structure calculations to study the nature of defect states in these materials. The defects we have studied include substitutional impurities at the cation and the anion sites as well as cationic and anionic vacancies. The failure of the hydrogenic effective mass approximation (EMA) to reproduce the experimental binding energies for the substitutional Cd and Sn defect states in GaSe, indicates the presence of large central cell corrections and the necessity of incorporating short range interactions in the calculation of defect binding energy. This has been done using a supercell model and self-consistent ab initio electronic structure method within density functional theory (DFT), which is known to be quite successful in tackling the problem of defects in semiconductors. Analyzing the defects from first-principles, we have been able to explain the detailed microscopic mechanism of the formation of Ga-site defects in GaSe and GaTe. When Ga is replaced by an impurity or when it is removed from the system to create a vacancy, the Ga dimer states can be strongly perturbed and this perturbation can give rise to defect states in the band gap.

Defect formation energy calculations, based on total energy differences between

the pure and defect containing systems, can give valuable insight into the solubility of different impurities in a host compound. The formation energies of Ge and Sn impurities reveal that under Ga-rich growth conditions it is easier to incorporate Sn in GaTe, whereas in the Te-rich limit Ge becomes more soluble than Sn. This information can be used to reduce the large leakage current due to the presence of native acceptors (Ga vacancies) in GaSe and GaTe by Ge or Sn doping. Furthermore, the formation energy calculations provide information about the preferred location of an impurity inside the host lattice. Using this idea, we developed a model which explains the experimentally observed improvement in the mechanical properties of In doped GaSe. In p-type GaSe, In becomes positively charged and can occupy an interstitial site, improving drastically the shear rigidity of the layered material.

Using the same theoretical methods we have investigated the nature of H defects in CdTe. The formation energy calculations indicate that the ground state position of H inside the CdTe lattice depends on the charge state: the lowest energy positions for H^0 and H^+ is at the bond center site, while H^- prefers the low electron density site surrounded by Cd cations. H in CdTe acts as an amphoteric impurity as expected. In the case of H on Cd site, the system undergoes Jahn-Teller distortion, due to the presence of a partially occupied degenerate t_2 state at the top of the VB. The symmetry of the system is lowered (the H atom moves closer to one of the four nearest neighbor Te atoms) and the t_2 level is split by ~74 meV at the Γ -point.

In order to study the properties of strongly correlated systems, one has to go beyond the local density approximation (LDA)to the DFT and take into consideration the strong Coulomb interaction within the localized electronic shell. In this thesis we have used the LDA+U formalism to investigate the electronic, magnetic and structural properties of several Yb-base systems, which involve highly localized and strongly correlated f electrons. We find that the configuration of the f shell plays a crucial role in the physical properties of many Yb containing intermetallics.

DEDICATION

To my lovely wife, Enikő, who kept my spirits up.

ACKNOWLEDGMENT

Foremost, I would like to express my sincere gratitude to my advisor Prof. S. D. Mahanti for the continuous support of my Ph.D study and research, for his patience, motivation, enthusiasm, and immense knowledge. His guidance helped me in all the time of research and writing of this thesis. I could not have imagined having a better advisor and mentor for my Ph.D study.

My sincere thanks go to Dr. K. C. Mandal form EIC Laboratories, with whom we collaborated and worked on diverse exciting projects, most of which are included in my PhD thesis.

Special thanks also go to Prof. Stuart Tessmer, Dr. Alecsandra Tomic and Josh Veazey for the interesting discussions and the collaboration on CeTe₃ system.

I would like to thank the rest of my thesis committee: Prof. Ruby Ghosh, Prof. Carlo Piermarocchi and Prof. Pavel Danielewicz for their encouragement and insightful comments and questions during the Guidance Committee Meetings.

I thank my former and present group mates: Dr. Daniel Bîlc, Dr. Salameh Ahmad, Dr. Khang Hoang, Dr. Mal-Soon Lee and Dat Than Do for the stimulating discussions.

Last but not the least, I want to thank my parents István and Juliánna and my brother István who encouraged me during all these years.

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Chapter 1

Introduction

1.1 The III-VI layered semiconductors: GaS, GaSe, GaTe, InSe

The layered III-VI semiconductors GaS, GaSe, GaTe and InSe form a quite remarkable class of materials. They have long been studied not only because of fundamental interest in their electronic structure, but also due to their possible application in nonlinear optics [1–3], detector devices [1–4], solar cells [5–8] and solid state batteries [9]. They crystallize in quasi two-dimensional layered structure and exhibit interesting optical, electronic and mechanical properties. Each atomic layer is composed of four hexagonally arranged monoatomic sheets of anion-cation-cation-anion. Because of the strong, covalent intralayer interaction and weak, van der Waals type interlayer coupling, most of the physical properties display anisotropic, two-dimensional characters. In this context, the early theoretical investigations, in the 1960's, using the tight-binding approach considered the III-VI materials as being two-dimensional in nature, and totally neglected the interlayer interaction [10, 11]. However, despite the fact that the interlayer coupling in the layered III-VI compounds is small, it is much greater than in typical layered materials such as graphite, and it cannot be neglected. For instance, in the case of ε -GaSe, the ratio between the elastic constants C_{33}/C_{11} in the directions perpendicular and parallel to the layers is ~15 times greater compared to graphite [12], and only ~3 times smaller compared to three-dimensional (3D) materials. Moreover, the interlayer interaction can also influence the optical properties of the crystal. Thus, the theoretical investigation of this class of materials requires models which are capable of describing electronic interactions of rather different nature (covalent, ionic) within the same system.

The first electronic structure calculations, which took into account the interlayer interaction, emerged in the 1970's and used the empirical pseudopotential approach [13]. Later, 3D calculations of the electronic structure of InSe [14, 15] and GaSe [15, 16] were performed, based on parametrized tight-binding method using s and p orbitals as basis $(sp^3 \mod e)$. A significant improvement of the tight-binding formalism was achieved in the 1980's, when an additional s^* orbital was introduced in order to mimic the effect of the d orbitals lost in the truncation of the tight binding Hamiltonian matrix. The s^* orbital allowed the sp^3s^* model to reproduce the electronic structure and band gaps of semiconductors [17]. The first band structure calculations of GaSe and InSe in the framework of the tight-binding approach with sp^3s^* model, again considered the interlayer interaction as being of purely van der Waals type, i.e. the III-VI materials were regarded as 2D [18–21]. Only in a recent theoretical study the sp^3s^* tight-binding model was adjusted such that the interlayer interaction was taken into account [22]; consequently the band dispersion ($\epsilon_{n\vec{k}}$ vs. \vec{k} , where \vec{k} is the wave vector and $\epsilon_{n\vec{k}}$ is the energy of the nth band for \vec{k}) determined by empirical pseudopotential methods for the valence band (VB) and the lower conduction band (CB) of the GaSe and InSe (to foit the experimental data) was well reproduced by this extended tight binding method.

In the late 1990's, with the increase in the computational power and the development of the modern electronic structure packages based on *ab initio* density functional theory (DFT), the understanding of the III-VI semiconductors reached a whole new level. Very good agreement has been found between the *ab initio* results and angleresolved photoemission measurements performed on GaSe [23]. The evolution of the band structures of the GaSe and InSe under pressure has also been investigated, using pseudopotential methods within DFT, to explain the behavior of hole transport parameters under compression [24]. First-principles investigations of the lattice dynamics and elastic constants of GaSe has revealed that the dynamical properties of the GaSe(0001) surface are very similar to those of the bulk, supporting the fact that only weak interaction exists between the atomic layers [25, 26].

Despite the development of the modern electronic structure methods, one had to wait until the early 2000's to find theoretical calculations involving the least studied member of the III-VI family: GaTe [27, 28]. Among the III-VI layered compounds GaTe occupies a special place because it has a more complex crystal structure with higher anisotropy. Unlike GaS, GaSe or InSe in which all the cation-cation bonds are perpendicular to the atomic layers, in GaTe one-third of the Ga-Ga bonds are parallel to the layers. Partly because of its more complex crystal structure, GaTe has not been studied experimentally and theoretically as extensively as the other members. Consequently the optical properties and even the band structure of GaTe are less well known.

Modern electronics and optoelectronics rely heavily on semiconductors. The property of semiconductors that makes them so unique and most useful for constructing electronic devices is that their conductivity can be easily modified by introducing impurities into their crystal lattice. Defects in semiconductors can significantly enhance the performance of the host; they can introduce electronic states in the vicinity of the band edges and therefore can control the electronic and optical properties of the material. As a result, understanding and controlling the origin and nature of the electronic states introduced by various impurities and defects is crucial in improving the efficiency of the semiconductors in high quality device applications. In the case of the III-VI layered family most of the attention has been concentrated on the experimental investigation of the defect levels in GaSe. Numerous authors have investigated the electrical and optical properties of GaSe and InSe doped with different elements (such as Cu, Cd, Zn, Sn, Mn, Cl, In, As, Bi Sb, Te, Si, Ge) and many impurity levels have been detected [8, 29–41]. The number of experimental studies related to defects in GaTe, however, is much less. Cui et al. [42] measured the levels associated native defects, several defect complexes and indium impurities in GaTe using deeplevel transient spectroscopy (DLTS). Further defect levels in unintentionally doped p-GaTe have been measures by Shigetomi et al. [43, 44] and Zubiaga et al. [45].

Despite the large amount of experimental effort devoted to investigate the electronic and optical properties of defects in III-VI semiconductors, there is significant lack of theoretical studies concerning the impurities in this class of materials. Theoretical investigations are very important because they not only help interpreting experimental data about the origin and nature of the defect levels, but also predict the solubility, ionization energies, electrical activity and the lattice relaxation associated with various impurities and defects in semiconductors and insulators.

To our knowledge at this point, there are no theoretical studies in the scientific literature on the electronic structure of defects and impurities in III-VI layered semiconductors. This thesis is a serious attempt to address this issue. In Chapters 3, 4 and 5 of the this thesis we present theoretical electronic structure results and the energetics obtained for several defects and defect complexes in GaSe and GaTe. In addition, we also investigate the effect of doping on the structural and elastic properties of GaSe. This is an important problem, because certain type of defects dramatically increase the shear rigidity of the layered solids, thereby improving its applicability in device fabrication.

1.2 The II-VI wide band gap semiconductors: CdTe and CdZnTe

Research in cadmium telluride (CdTe) dates back to the 1950's when it was identified as having a band gap (~1.5 eV) almost perfectly matched to the distribution of photons in the solar spectrum in terms of optimal conversion to electricity. A simple heterojunction design was developed in which *p*-type CdTe was matched with n-type cadmium sulfide (CdS) and the cell was completed by adding top and bottom contacts. During the last several decades CdTe, cadmium zinc telluride (CZT) and related II-VI compounds have been subjected to a tremendous amount of experimental and theoretical research. These semiconductors possess many attractive properties such as sufficiently wide band gap, good carrier mobility, large atomic numbers of Cd and Te, which makes them promising materials for room temperature x-ray and γ -ray detector applications [46, 47].

The performance of CdTe and CZT in radiation detector devices and solar cells are often limited by the presence of localized defect states in the band gap, which act as electron or hole trapping centers and thus reduce the efficiency of free charge carrier collection. Furthermore, the required high resistivity $(>10^9 \ \Omega \text{ cm})$ for a detector-grade semiconductor is difficult to reach due to the excess holes and electrons originating from the native defects. The principal intrinsic defect in CdTe and CZT is the cation vacancy $(V_{Cd/Zn})$, which introduces acceptor states in the band gap, close to the valence band maximum (VBM). It has been proposed that the excess holes originating from $V_{Cd/Zn}$ can be compensated by introducing donor impurities in the crystal; however an exact compensation of the shallow donors and acceptors is impossible. Numerous models involving point defects and defect complexes have been suggested and studied using experimental [48–52] and theoretical [53–56] methods in order to understand the carrier compensation and the semi-insulating behavior of CdTe and CZT. Clearly understanding the carrier compensation in CdTe is an important step towards the further improvement of detector and solar cell performance.

The passivation of the electrically active defects can also be achieved in principle by hydrogenation [57]. Hydrogen is a very reactive element, it can easily form hydrogen-defect complexes in bulk materials. Theoretical studies performed on a large number of semiconductors such as Si, Ge, GaAs, GaN, ZnSe have shown that hydrogen typically takes a charge state counteracting the prevailing type of conductivity in the system: in p-type materials acts as a donor and in n-type materials acts as acceptor [57–61]. Detailed *ab initio* theoretical studies of H in CdTe have not been made. In this thesis we have attempted to address this problem. In Chapter 6 we discuss the *ab initio* modeling of hydrogen in CdTe, we describe the electronic structure associated with the H impurity located at different lattice site, and from total energy calculations we identify the most stable position of the H defect in different charge states.

1.3 Ytterbium containing intermetallics

Ytterbium (Yb) is one of the most fascinating element of the periodic table. Ytterbium based systems display a great variety of unusual physical properties, related to the presence of the localized Yb 4f states, which can hybridize with the conduction band states. The Yb ion usually exists in two valence states: trivalent magnetic (Yb^{3+}) and divalent nonmagnetic (Yb^{2+}) . Depending on the electronic and crystallographic environment of the Yb-ion, the two valence states can be energetically almost degenerate, giving rise to a rich variety of unusual magnetic and transport properties such as mixed-valency, valence fluctuation, heavy fermion behavior, Kondo effect, charge density wave (CDW) instability and even superconductivity [62–69]. A large amount of experimental and theoretical studies have been carried out in recent years, which show that equiatomic or even isostructural Yb-systems can display very different ground state and low energy excitations. One such isostructural series is the extensively investigated YbMCu₄, with M = Ag, Au, Pd, In, Cu, Cd, Mg, Tl and Zn [63,70–77]. The compounds with M = Ag, Au, Pd are heavy-fermion systems with approximate electron effective masses of 60 m_e [74]. The ground state of YbAgCu₄ is nonmagnetic, while $YbAuCu_4$, $YbPdCu_4$ display long-range magnetic order below the temperatures 0.6 K and 0.8 K respectively [74,77]. YbInCu₄ shows a first-order isostructural valence transition at 40 K from trivalent Yb state to a mixed valence state [71, 73, 75]. The compounds with M = Cd, Tl, Mg and Zn display a variety of magnetic properties depending on the degree of hybridization between the 4f and the band states [72, 76]. Experimental investigations of the equiatomic ternary series YbTX (T = transition metal, X = Sn and Bi) reveal a wealth of interesting physical properties [78-80]. The compounds YbTBi (T = Cu, Ag, Au) and YbTSn (T = Ag, Au, Zn) have non-magnetic ground state due to divalent Yb ions, whereas in YbRhSn and YbPtSn the valence state of Yb it is trivalent. In YbPdBi the Yb display mixed valent character.

A fundamental theoretical description of such systems is extremely difficult due to the mixing between the two valence configurations of the RE ions (interconfiguration fluctuation) [81–83] at certain atomic sites. However, before any attempt to understand these complex mixing processes, a deeper understanding of the ground state electronic structure these systems, within the effective mean field approximation (LDA or LSDA) is extremely important, not only from material science standpoint, but also from fundamental point of view.

A proper *ab initio* theoretical description of strongly correlated electrons still represents a serious challenge. It is well known that the local (spin) density approximation L(S)DA fails to describe the correct ground state of systems containing transition metal or rare-earth metal atoms. L(S)DA always puts the partially filled d or f bands right at the Fermi level E_F , predicting metallic character with itinerant d or f electrons, which is obviously not always correct. Strong Coulomb repulsion (U) between localized d (or f) electrons, when two electrons are present at the same state, suppresses the charge fluctuations inherent in an itinerant system. In order to describe correctly the ground state of such systems, one has to go beyond the standard L(S)DA, and add the effects of strong electron-electron repulsion. One of the most successful approaches is the L(S)DA+U method [84–87], in which the localized d or f electrons and the delocalized s and p electrons are treated differently. The orbital-dependent Coulomb potential (U) is only taken into account for the localized states, while the delocalized states are treated by orbital-independent L(S)DA type potential. The L(S)DA+U method has been successfully applied to many binary and ternary rare earth (RE) systems with a diversity of physical properties like heavy fermion behavior, Kondo effect, mixed valency and valence fluctuation, long range magnetic order and superconductivity [62–69]. However, not many quaternary systems have been studied using this approach.

In recent years a large number of RE-containing multinary phases have been discovered, partly due to a continuous effort to enhance magnetic, thermoeletric, transport and structural characteristics of the materials. New synthetic methods and crystal growth techniques have been developed to explore novel intermetallic phases. The use of molten Al, Ga or In as solvents has contributed to the discovery of many ternary and quaternary systems. Examples of such materials are REAu₃Al₇ [88], RENiGe₂ [89,90], Yb₈Ge₃Sb₅ [91], RECo₄Si₁₄ [92], RENiAl₄Ge₂ [93], Yb₅Pt₆In₁₆Bi₂ [94], just to name a few. As discussed in the previous paragraph, electronic structure calculations on numerous RE-containing binaries and ternaries have been reported in the literature, however there are only a few examples where the electronic structure of quaternary systems has been theoretically investigated. The quaternary compounds do possess a more complex crystal structure and the RE

ions can occupy several inequivalent sites. Depending on the local coordination of each RE ion, the position of the f level with respect to the Fermi energy can change, and one can have different valence states: 2+, 3+ or mixed valency. The system can simultaneously exhibit homogeneous mixed-valent and inhomogeneous mixed-valent behavior [83].

In the last chapter of the present thesis we address some of the issues associated with the valence state of the Yb in several intermetallic compounds along with the electronic structure calculation of the ternary YbAuIn, Yb₃AuGe₂In₃ and quaternary Yb₇Co₄InGe₁₂ and YbNiFeAl₈.

Chapter 2

Defects in Semiconductors

2.1 Crystal defects: classification and basic concepts

A perfect crystalline solid is a material whose constituent atoms, molecules, or ions are arranged in an orderly repeating pattern extending in all three spatial dimensions. Such a crystallin solid is described in principle by a *many-body* Hamiltonian, which describes the correlated motion of all electrons and nuclei in the material. A convenient way to reduce the complex electron-ion problem to a tractable form is to use the Born-Oppenheimer approximation, that is to separate the motion of the nuclei from the electronic motion and neglect the nuclear kinetic energy. After this approximation we obtain a simpler (but still too difficult to solve) many-body Hamiltonian, in which the nuclear positions enter as parameters, so that the only players left are the electrons. The electron-nucleus interactions are not removed, therefore the electrons feel the Coulomb potential of the nuclei fixed at certain positions in space. From this Hamiltonian one can deduce an effective one-electron Hamiltonian, which describes in approximate way the behavior of each electron in the field created by the nuclei and all other electrons. Several methods exist to solve the one-electron (single-particle) Schrödinger equation, and they will be presented later in this chapter.

In a perfect crystal, due to the periodicity, the single-particle wave functions of all the states extend over the entire crystal, localized states does not exist. However, when the periodicity of the crystal lattice is disrupted by a defect or impurity, localized states are allowed, precisely states whose wave functions decay with distance outside the unit cell containing the defect (or a finite set of unit cells) can appear. In the case of semiconductors, two types of defect-induced localized states may exist: (i) those with energy within the allowed energy bands of the perfect crystal (resonant states) and (ii) those with energy within the fundamental band gap (bound states). The defect-induced states can have a dramatic effect on the electronic, optical and even on the mechanical properties of the semiconductors.

Since there is a large variety of imperfections that can be present in an otherwise periodic crystal and these imperfections can impact the properties of the material in many different ways, we begin by classifying the typical defects. They can be classified, on the one hand, in terms of the modifications they produce in the lattice geometry and on the other hand, in terms of the changes they generate in the electronic properties of the host semiconductor. For instance, some of them produce donor or acceptor states, others introduce carrier trapping centers, still others are responsible for carrier scattering and recombination.

2.1.1 Point defects

In terms of the geometrical changes induced by the defects in the host lattice we distinguish *point defects*, such as vacancies or misplaced atoms, *line defects*, which correspond to misplaced lined of atoms, also known as dislocations, *surface defects* such as stacking faults and *volume defects*, which are related to small inclusions and precipitations inside the crystal. In this thesis we only study the electronic structure of point defects and simple defect complexes, which are formed by a combination of

at most two point defects.

There are two main classes of point defects: (i) intrinsic or native lattice defects and (ii) foreign atoms or impurities present inside the lattice. Within the class of intrinsic point defects we distinguish vacancies (missing atoms), self-interstitials (extra host atom occupying an interstitial site) and antisite defects in compound semiconductors (in an AB compound atom A occupies site B). The defects associated with foreign atoms can be classified in terms of their physical location inside the host lattice. The case when a single foreign atom occupies the site of a host atom, is called a substitutional impurity, whereas the case when the impurity is located at an interstitial site is knows as a simple interstitial. Further, the special case when a host atom is replaced by two symmetrically displaced atoms is called split-interstitial. Finally, in terms of the geometrical arrangement with respect to each other, the point defects can form simple defect complexes such as pairs (two impurity atoms are located at neighboring lattice sites), impurity-vacancy complexes (vacancy and impurity at the neighboring sites) and divacancies. Evidently, the formation of more extended defect complexes is also possible but their characterization becomes more difficult.

2.1.2 Donors and acceptors

Substitutional impurities are often classified in terms of their position in the periodic table relative to the host elements. Impurities from the same column as the host atom are identified as isovalent impurities, because they have the same number of valence electrons as the host atoms. Non-isovalent impurities are frequently referred to as acceptors or donors, depending if the impurity is located to the left or to the right of the host atoms in the periodic table of elements. Acceptors/donors have less/more valence electrons compared to the host atoms, therefore they must accept/donate electrons from/to the host, in order to fulfill the local bonding requirements.

The definition of donor and acceptor impurities given above, is somewhat confus-

ing, because in principle an impurity can introduce, both donor and acceptor states in the electronic structure of a semiconductor, in which case the impurity is called amphoteric. For instance, hydrogen in most semiconductors acts as amphoteric impurity, as it counteracts the prevailing type of conductivity in the system [57]. Furthermore, it is known that isovalent impurities, which have the same number of valence electrons as the host atoms, can introduce defect states in the band gap [95], thus the above definition of donors and acceptors cannot be applied. A more general and unambiguous definition for donors and acceptors can be given by the charged state of the defect: we define a positively charged defect states as donors and the negatively charged states as acceptors. This definition allows for a defect to have one or more acceptor or donor states, and also allows for the possibility that a particular impurity can introduce both donor and acceptor states, and therefore acts as an amphoteric impurity. According to this definition one can describe the donor and acceptor states associated with the isovalent impurities as well.

2.1.3 Shallow versus deep defects

Another criterion which can be used for the classification of defects is related to the degree of localization of the eigenfunction of the defect-induced electronic state. Generally, if the energy of the defect state is close to the VBM or CBM, the defect state is referred to as shallow acceptor or donor, whereas if the state is located close to the mid-gap, it is called deep defect state. This definition however, implies that the binding energy (energy of the defect state measured from the band extrema) of a deep defect level necessarily has to be large, and that the energy position of the deep level in the gap has to be far from the band edges. However, it is known that deep levels also appear in narrow-gap semiconductors [96, 97] or close to the band edges [98]. Therefore a better and more general way of classification is needed: one which is related to the fundamental nature of the shallow and deep defect states. The shallow defects states are dominated by long-range Coulomb potentials, therefore their wavefunctions extend over several unit cells in the crystal. Deep defect states, on the other hand, are dominated by short-range potential and the corresponding wavefunctions are highly localized, and usually do not extend beyond one or two unit cells.

In the next subsections we will present some of the basic characteristics of the shallow and deep defects states. The detailed theoretical description of the models and methods used for analyzing defects will be addressed in later sections.

2.1.4 Shallow defects in semiconductors

From theoretical point of view the description of shallow defect states is quite straightforward. For instance a shallow donor can be regarded as a hydrogen atom with a positive nucleus binding an electron. In order to understand the elementary aspect of the hydrogenic model, we can start from the electronic band structure of a perfect solid. In the case of semiconductors and insulators there is a valence band followed by the band gap and the conduction band. At 0K, the valence band is completely occupied while the conduction band is completely empty. If an extra electron is introduced in the system, at 0K it will occupy the lowest energy state available, which is the bottom of the conduction band. In the case of simple, parabolic bands the energy of the states in the vicinity of the conduction band minimum (CBM) is given by:

$$E(k) = E_{CBM} + \frac{\hbar^2 k^2}{2m_e^*}$$
(2.1)

where E_{CBM} is the energy of the CBM and m_e^* is called *effective mass*. The comparison between Eq. (2.1) and the corresponding relation for a free electron characterized by the same wave vector \vec{k} :

$$E\left(k\right) = \frac{\hbar^2 k^2}{2m_0} \tag{2.2}$$

where m_0 is the free electron mass, justifies the terminology for the constant m_e^* . The effect of the crystal potential is included in the effective mass in an average way, such that the dynamical behavior of an extra electron in the conduction bands resembles to that of a free electron with a mass m_e^* .

To illustrate the basic concept behind the hydrogenic model, we will describe, as an example, the case of a single substitutional donor. This means that a host atom in a perfect crystal is replaced by an impurity from a column in the periodic table located to the right of the host atom. This impurity contains one extra electron compared to the host and becomes positively charged after it has given its electron to the system. If we imagine that somehow we keep the extra electron out of the crystal, then the crystal has the same number of valence electrons as it had before, so that the valence band is completely filled and the conduction band is still completely empty. Although at this point it appears that there is no change in the occupation of the bands, there is a significant modification in the crystal potential. Since the impurity is necessarily positively charged, it introduces a Coulomb field in addition to all crystal fields that were present before the introduction of the impurity. Due to the dielectric medium the impurity-induced Coulomb potential is given by $U = +e/\varepsilon r$, where ε is the dielectric constant of the material. Now if we introduce the extra electron into the system, according to the above discussion, it can be regarded as a free electron with mass m_e^* , which moves in a Coulomb potential $e/\varepsilon r$. It is now clear that the whole picture is analogous to the hydrogen atom, except that the nucleus has a charge equal to e/ε and the mass of the electron is m_e^* . Therefore, by analogy with the ionization energies of the hydrogen atom $\left(E_n^H = -e^4 m_0 / 2\hbar^2 n^2, n = 1, 2, 3, ...\infty\right)$, we conclude that the shallow donor introduces bound state below the conduction band, whose energies are

given by:

$$E_n = E_{CBM} - \frac{e^4 m_e^*}{2\hbar^2 \epsilon^2 n^2}$$
(2.3)

or

$$E_n = E_{CBM} - E_n^H \left(\frac{m_e^*}{m_0 \varepsilon^2}\right) \tag{2.4}$$

In eqs. (2.3) and (2.4) m_e^* is given in units of m_0 and the principal quantum number is $n = 1, 2, 3, ...\infty$. Equation (2.4) can be used to obtain an estimate of the ionization energies of shallow donor levels: if we consider that the typical value of ε is 10 and the value of m_e^* ranges from $0.1 m_0$ to $0.5 m_0$, than the binding energy (E_1) of a shallow donor ranges from about ~10 meV to ~70 meV. These binding energy values represent a small fraction of the typical bandgap (~1 eV), therefore such a shallow donor is intimately related to the conduction band. Furthermore, we can also estimate the quasi-Bohr radius associated with the shallow defect in the hydrogenic model:

$$a_n = \frac{\hbar^2 \varepsilon}{m_e^* e^2} n^2 = \varepsilon a_0 \left(\frac{m_0}{m_e^*}\right) n^2 \tag{2.5}$$

where a_0 is the Bohr radius. Using equation (2.5) with the above mentioned typical values of ε and m_e^* , we obtain a range for the quasi-Bohr radius of ~50 Å to ~10 Å. These values are larger compared to the typical lattice constant of a semiconductor.

The qualitative picture for a shallow acceptor is similar to that for donors. First we remove an electron from the perfect crystal, which corresponds to the creation of a hole at the top of the valence band. The dynamics of the hole at the near the top of the valence band can be described by an equation similar to (2.1):

$$E(k) = E_{VBM} - \frac{\hbar^2 k^2}{2m_h^*}$$
(2.6)

where E_{VBM} is the energy of the VBM, and m_h^* is the effective mass of the hole. If an impurity, with fewer valence electrons than the host, is introduced in the otherwise perfect crystal, it will capture an electron and will create a negatively charged center. This impurity-induced Coulomb potential will act upon the positively charged hole, again creating a picture similar to the hydrogen atom. The energy levels introduced in the band gap, now are located close to the valence band and they are given by:

$$E_n = E_{VBM} + E_n^H \left(\frac{m_h^*}{m_0 \varepsilon^2}\right) \tag{2.7}$$

The numerical estimates for the shallow acceptor states are similar to those given in the case of shallow donors.

The use of hydrogenic model is justified when the impurities introduce approximately Coulombic potentials in the crystal. Its quantitative success depends on the complexity of the band structure and on the values of the dielectric constant (ε) and the effective mass $\left(m_{e/h}^*\right)$. It gives good results for single donors and acceptors, when the band extrema have simple form and the quasi-Bohr radius is large compared to the lattice constant. The hydrogenic model can be extended to double donors and acceptors, by simply using the screened Coulomb potential of two charges, so that the energy levels are four times deeper. However, it has been found that the quantitative agreement between the binding energies calculated this way and the experimental results is not very good [99]. Despite its striking simplicity, the hydrogenic model of shallow-level impurities has been confirmed by a large number of electrical and optical studies in a vast number of semiconductors and insulators [100].

2.1.5 Deep defects in semiconductors

In contrast to shallow-level impurities, which are quite well understood, it is much more difficult to describe theoretically the electronic behavior of deep-level centers.


Figure 2.1: Rectangular, one-dimensional well of depth V_0 and width d

They are dominated by short-range potentials and the wavefunctions remain localized close to the core of the defect. Deep levels are usually connected to more than one band edge (may be connected to both VB and CB), and in the case of some external perturbation, they do not follow a specific band edge. States from both VB and CB may be necessary to construct the ground state eigenfunction of such a deep center and in addition the deformed lattice environment also has to be considered. The resulting deep defect levels communicate with both bands and act as charge carrier trap or recombination center. Several good reviews about deep defects can be found in references [99, 101–103].

To illustrate the substantial difference between the eigenvalue spectrum of the shallow and deep defect centers, we can consider the very simple case of a onedimensional, deep potential well. The chemical identity of the center is introduced, by assuming a square-well potential of depth $-V_0$ and width d, as represented in Fig. 2.1 (referred to as central cell potential).

In general, the stationary electronic states in such a quantum well are described by Schrödinger equation:

$$\frac{d^2\psi}{dx^2} - k^2\psi = 0$$
 with $k = \sqrt{\frac{2m\left[E - V(x)\right]}{\hbar^2}}$ (2.8)

After simple calculations, for $-V_0 < E < 0$, $(V_0 > 0)$ it can be shown that the solutions of the Eq. (2.8) exist for k values that satisfy the following transcendental equations:

$$\sqrt{\kappa^2 + k^2} = k \tan\left(\frac{kd}{2}\right) \quad \text{or} \quad \sqrt{\kappa^2 + k^2} = -k \cot\left(\frac{kd}{2}\right)$$
(2.9)

where

$$\kappa^2 = \frac{2mV_0}{\hbar^2} \tag{2.10}$$

Equations (2.9) can be solved graphically, and for the discrete values obtained for k, the values of E inside the well are also discrete:

$$E_n = \frac{\hbar^2 k_n^2}{2m_0} - V_0 \tag{2.11}$$

where $k_n \simeq n\pi/d$ for the lower values of $n \neq 0$. In Eq. (2.11), the electron rest mass was used, because in a deep-level center, the electron remains close to the core of the defect. Therefore the eigenvalues can be written as:

$$E_n = \frac{\hbar^2 \pi^2}{2m_0 (d/2)^2} n_q^2 - V_0 \quad \text{where} \quad n_q = 1, 2, \dots$$
 (2.12)

From Eq. (2.12) we see that the eigenstates increase quadratically with n_q . In contrast, according to Eq. (2.3), the eigenstates of the simple hydrogen-like defect decrease as $1/n^2$. The electron eigenstates for the two simple potentials are represented schematically in Fig. 2.2.

We have used the simple example of the square well potential as a tool to illustrate the difference between the spectrum of shallow and deep defect centers. However, for a realistic description of the deep defect states, a better central cell potential, V(r), is required. Furthermore, as we have mentioned earlier in this section, a deep defect



Figure 2.2: Electron eigenstates (a) in a one-dimensional square well potential and (b) in a Coulomb potential

state is usually connected to more than one band, therefore the inclusion of additional bands in the model of the deep center is very important. In addition, along with the central cell potential, we also have to consider the long-range Coulomb potential of the charged deep center as it describes the higher excited states of such a center [103].

Deep defects also present a challenge from experimental point of view. In semiconductors and insulators a great variety of deep centers exist, and their identification and chemical origin is not always an easy task. However, by intensive experimental efforts it is possible to identify unambiguously some of the deep centers [101,104]. The experimental methods include optical absorption, luminescence emission and excitation spectroscopy, electron-spin resonance, optical detection of magnetic resonances, extended X-Ray absorption fine structure (EXAFS), deep-level transient spectroscopy (DLTS). Despite all the efforts put into understanding deep-centers, some of them seem to escape the generally accepted identification methods.

2.1.6 The role of defects in semiconductors

The role played by defects and impurities in semiconductors depends on the nature of the localized levels (shallow or deep) that are introduced in the band-gap and on the concentration in which they can be incorporated into the crystal. The most important role of shallow donors and acceptors is to control conductivity. This is because at room temperature the ionization energies of shallow defects are comparable to k_BT (k_B is the Boltzmann's constant and T is the temperature) and therefore almost all such shallow levels are ionized and contribute to conductivity. A very important aspect of the semiconductor doping is that the impurities can be incorporated in arbitrary concentrations, up to 10^{20} cm⁻³. By controlling the impurity concentration, the conductivities can be varied over a range of twelve orders of magnitude: from approximately $10^{-9} (\Omega \text{ cm})^{-1}$ to about $10^3 (\Omega \text{ cm})^{-1}$. To appreciate the benefits of semiconductor doping, these values should be compared with the conductivity in metals $(10^6 (\Omega \text{ cm})^{-1})$ and insulators $(10^{-22} (\Omega \text{ cm})^{-1})$. Furthermore, in most semiconductors, the conductivity can be dominated either by electrons (n-type), or holes (p-type).

The most important feature of semiconductor doping is that, by carefully controlled ways, the concentration of shallow donors and acceptors can be made nonuniform within a sample. The inhomogeneities of electron and hole densities can be exploited to produce a variety of effects useful for device applications. A simple example of such an inhomogeneous semiconductor is the well known p-n junction, which consists of a region doped with acceptors (p-type) adjacent to a region doped with donors (n-type). Such a p-n junction permits the flow of electrical current in only one direction and it can also act as radiation emitter in a light emitting diode (LED). Other devices such as transistors, modulators, detectors, photocells, etc. consist of more complicated structures of p- and n-type regions of different acceptor and donor concentrations.

Deep defect states play an entirely different role. They are incorporated in semiconductors in smaller concentrations $(10^{12} - 10^{13} \text{ cm}^{-3} \text{ in Si})$ and their contribution to conductivity is usually negligible. In most cases they act as traps and recombination centers for electrons and holes. For an electron and hole to recombine, that is, an electron from the CB to drop into the VB, an amount of energy equal to the band gap must be dissipated. The recombination is going to be more likely if this energy can be dissipated in smaller fractions, and this can be precisely accomplished by a deep-level present somewhere in the middle of the band-gap. The electron from the CB can first drop to the deep-level and then to the VB, by losing energy (emitting photons) in smaller quantities at a time. and the second statement of th

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The most important role of the recombination centers introduced by deep defects is to control the lifetime of carriers. When a device (such as a photovoltaic) needs long carrier life-times, then deep defects have to be avoided. On the other hand, when a device calls for short carrier lifetime, deep defects must be incorporated carefully in the semiconductor. An example of such a case is a photocell which is used as a fast switch, where the current generated by the electron-hole pair must last only a short period of time.

2.2 Theoretical methods to analyze defects

we will approach the defect problem within an effective single-particle model.Even within the approximation the theoretical methods are based on different approximations for solving Schrödinger equation associated with the defect. Schrödinger equation can be solved using any electronic structure methods. The defect in the crystal environment can be modeled by a considering only the atoms surrounding the defect, thus defining a *cluster* or by using the *supercell* technique, in which periodic boundary conditions are applied to the surface of a cluster. The potential of the defect Hamiltonian can be constructed using empirical (or semiempirical) parameters or by self-consistent methods.

In this section we will address some of the issues associated with the approxima-

tions used for solving Schrödinger equation. We will describe the hydrogenic model, which is used to treat the shallow defects and then, in subsequent sections, we will talk abut theoretical methods applicable to deep defects as well. First we discuss general, elementary formulation of the quantum mechanical problem associated with crystal defects.

2.2.1 Basic quantum mechanics

After mapping the many-body ground-state problem onto single-particle problems, we end up with a set of eigenvalue equations of the following type:

$$H\psi_{\nu} = \left[-\frac{\hbar^2}{2m}\nabla^2 + V\right]\psi_{\nu} = E_{\nu}\psi_{\nu} \qquad (2.13)$$

If we start from the premise that the electronic structure of the perfect host solid is known then the total crystal potential and the Hamiltonian of the system can be written as:

$$V = V^0 + U$$
 with $H = H^0 + U$ (2.14)

where H^0 is the Hamiltonian of the unperturbed lattice and U is the perturbation introduced by the defect. By using the term "perturbation" we do not imply that we use the well known perturbation theory (based on a power series in the perturbation U), but rather that we want to calculate the changes produced by the perturbation.

The corresponding eigenvalue problem which has to be solved is given by:

$$H\psi_{\nu} = \left(H^0 + U\right)\psi_{\nu} = E_{\nu}\psi_{\nu} \tag{2.15}$$

Equations identical to Eq. (2.15) can be written down whether the above quantities are regarded as true, pseudo, or model. The eigenvalues E_{ν} and the eigenfunctions ψ_{ν} can be determined by using the secular matrix method, that is expanding ψ_{ν} in terms of a complete set of functions ϕ_{λ} :

$$\psi_{\nu} = \sum_{\lambda} F_{\lambda} \phi_{\lambda} \tag{2.16}$$

where we have omitted the index ν in the F_{λ} coefficients. By substituting (2.16) in (2.15), multiplying on the left by ϕ_{λ}^* and integrating over all space, we get a set of coupled linear equations:

$$\sum_{\lambda} \left[\left\langle \phi_{\lambda'} \middle| H^0 \middle| \phi_{\lambda} \right\rangle + \left\langle \phi_{\lambda'} \middle| U \middle| \phi_{\lambda} \right\rangle - E_{\nu} \left\langle \phi_{\lambda'} \middle| \phi_{\lambda} \right\rangle \right] F_{\lambda} = 0$$
(2.17)

If the basis set is orthonormal, that is $\langle \phi_{\lambda'} | \phi_{\lambda} \rangle = \delta_{\lambda'\lambda}$, than the energies E_{ν} are just the eigenvalues of the secular matrix:

$$H^{0}_{\lambda'\lambda} + U_{\lambda'\lambda} = \langle \phi_{\lambda'} | H^{0} | \phi_{\lambda} \rangle + \langle \phi_{\lambda'} | U | \phi_{\lambda} \rangle$$
(2.18)

The set of functions ϕ_{λ} can be chosen to be Bloch functions, Wannier functions or other orthonormalized functions, such as simple exponentials of Gaussian orbitals. In many cases one of the most natural choices for ϕ_{λ} is the set of Bloch functions $\psi_{n\vec{k}}^{0}$, which are eigenfunctions of H^{0} and are orthonormal. In this case (2.16) becomes:

$$\psi_{\nu}\left(\vec{r}\right) = \sum_{n\vec{k}} F_{n\vec{k}} \psi_{n\vec{k}}^{0}\left(\vec{r}\right)$$
(2.19)

and the set of coupled equations (2.17) is:

$$E_{n\vec{k}}^{0}F_{n\vec{k}} + \sum_{n'\vec{k'}} \left\langle \psi_{n\vec{k}}^{0} \middle| U \middle| \psi_{n'\vec{k'}}^{0} \right\rangle F_{n'\vec{k'}} = E_{\nu}F_{n\vec{k}}$$
(2.20)

The secular matrix which needs to be diagonalized is:

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$$E^{0}_{n\vec{k}}\delta_{nn'}\delta_{\vec{k}\vec{k}'} + \left\langle \psi^{0}_{n\vec{k}} \Big| U \Big| \psi^{0}_{n'\vec{k}'} \right\rangle$$
(2.21)

The size of this matrix is equal to the product between the number of k-point in the BZ and the number of bands included in the expansion (2.19). Since in a practical implementation the sampling of the BZ is necessarily finite, this method is not very useful for states for which $F_{n\vec{k}}$ varies rapidly with k.

Different methods have been developed, in an effort to reduce the size of the secular matrix which has to be diagonalized. Simple models, specially designed for cases when the range of perturbing potential is short, have been constructed by Koster and Slater, using Wannier basis functions and other localized representations [105, 106].

2.2.2 Hydrogenic-model (effective mass approximation)

Shallow defect states are described by the hydrogenic model or effective mass approximation (see also section 2.1.4). As an example we will discuss the electronic states associated with a shallow, hydrogen-like donor (such as a substitutional phosphorus atom in the silicon lattice). In this case the Hamiltonian of the defect containing crystal can be written as:

$$H = H_0 - \frac{e^2}{\varepsilon r} \tag{2.22}$$

where H_0 is the Hamiltonian of the host lattice, to which the attractive Coulomb potential of the defect, which is added as a perturbation to H_0 . The static dielectric constant ε is introduced in the expression of the Coulomb potential, because of the screening action of the host. The eigenfunctions of H near the defect can be constructed, using the Bloch functions $\psi_c(\vec{k}, \vec{r}) = u_c(\vec{k}, \vec{r}) e^{i\vec{k}\cdot\vec{r}}$ of the nearest band (which is the conduction band in the case of a shallow donor):

$$\psi \simeq \sum_{\vec{k}} c_c \left(\vec{k}\right) \psi_c \left(\vec{k}, \vec{r}\right)$$
(2.23)

As we have mentioned in Section 2.1.4, the eigenfunctions of a shallow-state extend over several lattice constants, therefore the values of \vec{k} are restricted close to the center of the Brillouin zone (BZ). Since $u_c(\vec{k})$ changes slowly with \vec{k} , we can extract $u_c(\vec{k} = \vec{k}_0, \vec{r})$ as a constant from the summation in Eq. (2.23). \vec{k}_0 is the value of the wavevector at which $E(\vec{k})$ reaches its minimum. We have:

$$\psi = u_c \left(\vec{k}_0, \vec{r}\right) \left\{ \sum_{\vec{k}} c_c \left(\vec{k}\right) e^{i\vec{k}\cdot\vec{r}} \right\}$$
(2.24)

For $\vec{k}_0 = 0$ (Γ -point) we have: $\psi_c \left(\vec{k}_0 = 0, \vec{r}\right) = u_c \left(0, \vec{r}\right) e^{i0 \cdot \vec{r}} = u_c \left(\vec{k}_0 = 0, \vec{r}\right)$. Therefore Eq. (2.24) can be written as:

$$\psi = \psi_c \left(\vec{k}_0, \vec{r}\right) \left\{ \sum_{\vec{k}} c_c \left(\vec{k}\right) e^{i\vec{k}\cdot\vec{r}} \right\} = F(\vec{r})\psi_c \left(\vec{k}_0, \vec{r}\right)$$
(2.25)

where $\psi_c(\vec{k}_0, \vec{r})$ is the Bloch function in the minimum of $E(\vec{k})$ and $F(\vec{r}) = \sum_{\vec{k}} c_c(\vec{k}) e^{i\vec{k}\cdot\vec{r}}$ is an envelope function, which satisfies the modified Schrödinger equation for the hydrogenic-model:

$$\left(-\frac{\hbar^2}{2m_e^*}\nabla^2 - \frac{e^2}{\varepsilon r}\right)F\left(\vec{r}\right) = \left(E - E_c\right)F\left(\vec{r}\right)$$
(2.26)

Equation (2.26) is identical to the Schrdinger equation for the hydrogen atom, but with an electron with effective mass m_e^* in a medium with dielectric constant ε . In particular the envelope eigenfunction of the 1s ground state is given by:

$$F(r) = \frac{1}{\sqrt{\pi a_{qH}^3}} \exp\left(-\frac{r}{a_{qH}}\right)$$
(2.27)

where the effective Bohr radius a_{qH} is given by:

$$a_{qH} = \frac{\hbar^2 \varepsilon}{m_e^* e^2} = \varepsilon a_0 \left(\frac{m_0}{m_e^*}\right) = 0.529 \times \varepsilon \left(\frac{m_0}{m_e^*}\right) \tag{2.28}$$

In Eq. (2.28) the electron effective mass m_e^* is given in units of free electron mass m_0 . The eigenstates of the envelope function are bound states located below conduction band minimum (CBM) and the energy eigenvalues are given by the quasi-hydrogen energy spectrum:

$$E_{qH} = E_c - \frac{e^4 m_n^*}{2\hbar^2 \varepsilon^2} \left(\frac{1}{n^2}\right)$$
(2.29)

Equations (2.28) and (2.29) are identical to (2.5) and (2.3) respectively, which were derived from the qualitative picture of shallow defects in Section 2.1.4.

In our description of the hydrogenic model, so far, we have considered that the defect potential is spherically symmetric. In this case the entire energy spectrum of the hydrogen-like defect (Eq. (2.29)) is described by the principal quantum number n, and all the states characterized by the same quantum number are degenerate. However, when the defect potential deviates from the spherical symmetry, the degeneracy of the hydrogenic levels is lifted and the energies of the s, p, d,... states are shifted. We will discuss this case in more detail in Chapter 3 (Section 3.4.2), when we apply the hydrogenic-approximation to the highly anisotropic compound GaSe.

2.2.3 Green's function methods

The first theoretical method which addressed the problem of deep defect states in semiconductors was the *Green's functions* method [103, 105, 107, 108]. In this method the defect free host crystal with Hamiltonian H^0 is perfectly described. The localized defect is represented by the Hamiltonian H, which includes the defect potential V. The Green's function calculations determine the differences between the ideal crys-

tal and the changes introduced by the defect. The Green's function is defined by G(E) = 1/(E - H), so that the perturbed energies E are given by its poles. The new eigenvalues contain the gap levels of the defect, while the corresponding eigenfunctions are the defect wave functions. If the new eigenvalues overlap the eigenvalues of the unperturbed Hamiltonian H_0 , then one has resonant states. Despite the fact that Green's functions, in principle provide a near ideal description of the defect in a crystal, their implementation is difficult, especially when it comes to defects that induce large relaxations and distortions in the otherwise perfect crystal. There are difficulties associated with the construction of the defect potential and with the eigenfunctions of the perfect crystal that can be used as basis set for the defect calculation [107,109]. In recent years, due to their computational complexity, there has been a decrease in the use of the Green's function calculations, particularly for complex systems. However, their revival within the GW formalism [110] is probable, if one wants to go beyond an effective single particle model for describing the defect states.

2.2.4 Scattered wave method

Another method to solve the general eigenvalue problem (2.13), is the $X\alpha$ -scattered wave method, which is a particular technique for small collection of atoms. The potential is calculated self-consistently for the entire system, including the core electrons, using Slater's $X\alpha$ exchange [111]. The approximation used in this method is that the potential is spherically averaged within atom centered, muffin-tin spheres and volume averaged within the interstitial region. The eigenvalue problem is then solved by scattering methods [111,112]. The $X\alpha$ -scattered wave method has been successful in describing the one-electron spectra of molecules, and it has also been applied to study interstitial transition metal impurities and hydrogen-alkali metal complexes [113,114]. Despite its relative success, it was difficult to bring the method to self-consistency and the rather arbitrarily chosen muffin-tin spheres made it unsuitable for calculation of atomic positions by minimizing total energies.

2.2.5 Partial retention of diatomic differential overlap method

A successful self-consistent Hartree-Fock method in the mid-1980s was the partial retention of diatomic differential overlap (PRDDO) [115,116]. It contained no empirical parameters, allowed for geometry optimizations to be performed without symmetry constraints, the convergence was efficient. This method was implemented using a cluster model (see below) and relatively large clusters could be used (44 atoms). It has been used to study defects in diamond and silicon, and it was the first theoretical tool which demonstrated the stability of hydrogen at the bond-centered site in Si. It was unexpected and surprising that H could occupy the site between two Si atoms and force the Si-Si bond by more than 1 Å [117,118]. On the negative side, PRDDO is a minimal basis-set technique and ignores electron-electron correlation.

2.2.6 Atomic cluster models

The eigenstates of a defect center can be described by considering only a few host atoms in its neighborhood, thus defining an atomic cluster [119]. The first *cluster calculations* were performed using basis sets consisting of linear combination of atomic orbitals (LCAO) [119,120] or other localized functions such as Gaussians. The early work was empirical or semiempirical, that is the potential V was not calculated explicitly, but instead a basis set was chosen and the matrix elements of H were determined from a direct fit to experiment or evaluated using a well-tested prescription.

A very simple LCAO method for the determination of energies of molecular orbitals of π -electrons in conjugated hydrocarbon systems was the Hückel method, proposed by Erich Hückel in 1930. The extended Hückel theory (EHT) is a semiempirical quantum chemistry method, develedoped by Hoffmann since 1963 [121]. It is based on the Hückel method but, while the original Hückel method only considers π -orbitals, the extended method also includes the σ -orbitals. The extended Hückel method can be used for determining the molecular orbitals, but it is not very successful in determining the structural geometry of an organic molecule. It can however determine the relative energy of different geometrical configurations. It involves calculations of the electronic interactions in a rather simple way where the electron-electron repulsions are not explicitly included and the total energy is just a sum of terms for each electron in the cluster.

The usefulness of the cluster models is reflected by the numerous theoretical studies within Hartree-Fock or density functional theory, which use the cluster model.

Although, the implementation of the cluster calculations is straightforward, they converge slowly with the size of the cluster and they suffer from a variety of problems such as cluster size, surface effects, basis-set limitations, lack of electron correlation. Furthermore the adjustable parameters are very sensitive to the conditions at the cluster surfaces. The finite size of the cluster confines the wavefunction, which affects charged defects the most, as the charge tends to distribute at the surface of the cluster.

2.2.7 The supercell model

In order to overcome the surface problem in the cluster calculations, the supercell technique was designed, which replaces the problematic boundary conditions for clusters with less problematic Born-von-Kármán periodic boundary conditions. We will describe the supercell technique in more detail in subsequent sections, as it is the principal approach which has been used throughout this thesis.

The great progress in the theory of defects in semiconductors occurred in the mid-1980s with the introduction of the theoretical approach known as "first-principles". In general the first principles methods use a combination of ab-initio pseudopotentials for the electronic core region and density functional theory (DFT) for the valence region. These methods use periodic supercells to represent both the host crystal and the crystal with defect. The parameters in this approach include the size of the supercell, k-point sampling of the Brillouin zone (BZ) in carrying out summation over wave vectors \vec{k} , size of the basis set and other parameters associated with the pseudopotentials. However, these parameters are not fitted to an experimental data, but rather determined self-consistently from first-principles.

Since the results presented in this thesis have been obtained using DFT in combination supercell technique in the next two sections we will provide brief descriptions of the DFT and supercell approach to solve the defect problem.

2.3 Density functional theory (DFT)

For *ab initio* electronic structure calculations in solids, the overwhelming method of choice is Density Functional Theory (DFT) due to Kohn, Hohenberg and Sham [122, 123]. The greatest simplification introduced by this theory is that it replaces the ground state problem of a complicated many-body system and the associated many-particle Schrödinger equation, with the single-particle density, which is a function of position. We review for completeness the description of DFT with the presentation of two important theorems proved by Hohenberg and Kohn [122]. In this presentation we follow the same line of development as in Ref. [124].

2.3.1 The theorems of Hohenberg and Kohn

The first theorem of Hohenberg and Kohn states that the external potential, $v(\vec{r})$ acting on a fully interacting many-particle system in its ground state is determined within an additive constant by the electron density $n(\vec{r})$. To prove this theorem let us consider the Hamiltonian of an N-electron system moving in some external potential $v(r)^1$:

$$\hat{H} = \sum_{i=1}^{N} \left(-\frac{1}{2} \nabla_i^2 \right) + \sum_{i=1}^{N} v\left(\vec{r_i} \right) + \sum_{i(2.30)$$

The first term in Eq. (2.30) is the kinetic energy operator and the last term describes the Coulomb interaction between the electrons, with $r_{ij} = \left| \vec{r_i} - \vec{r_j} \right|$. The second term can be considered, for instance, to be the potential $v(\vec{r_i}) = -\sum_{\alpha} Z_{\alpha}/r_{i\alpha}$ acting on an electron located at $\vec{r_i}$ due to the presence of the nuclear charges Z_{α} at position \vec{R}_{α} , with $r_{i\alpha} = \left| \vec{r_i} - \vec{R}_{\alpha} \right|$. After applying the Born-Oppenheimer approximation, this potential created by the fixed nuclei becomes external to the electron cloud. Let us suppose that there are two different external potentials $v(\vec{r})$ and $v'(\vec{r})$ corresponding to the same ground state density $n(\vec{r})$. Also let \hat{H} and \hat{H}' be the corresponding many-body Hamiltonians, with ψ and ψ' the associated ground state wavefunctions. If E_0 and E'_0 are the ground state energies of the N-electron system in the presence of $v(\vec{r})$ and $v'(\vec{r})$ we can write:

$$E_{0} = \langle \psi | \hat{H} | \psi \rangle \langle \psi' | \hat{H} | \psi' \rangle = \langle \psi' | \hat{H}' | \psi' \rangle + \langle \psi' | \hat{H} - \hat{H}' | \psi' \rangle$$

$$= E_{0}' + \int n(\vec{r}) \left[v(\vec{r}) - v'(\vec{r}) \right] d^{3}r$$
(2.31)

The integral in Eq. (2.31) comes from the second term in Eq. (2.30) and describes the interaction of the charge distribution with the external potential. Similarly, if we take ψ as a trial wavefunction for the system described by \hat{H}' , we have:

¹In order to simplify the notations throughout this section, we use atomic units in which the unit of length is the first Bohr radius of the hydrogen atom $a_0 = 0.529$ Å, the unit of mass is the mass of the electron, and the unit of charge is the electronic charge. We also set $\hbar = 1$.

$$E_{0}^{\prime} = \langle \psi | \hat{H} | \psi \rangle < \langle \psi | \hat{H}^{\prime} | \psi \rangle = \langle \psi | \hat{H} | \psi \rangle + \langle \psi | \hat{H}^{\prime} - \hat{H} | \psi \rangle$$

$$= E_{0} - \int n \left(\vec{r} \right) \left[v \left(\vec{r} \right) - v^{\prime} \left(\vec{r} \right) \right] d^{3}r \qquad (2.32)$$

Adding Eq. (2.31) and Eq. (2.32) we get:

$$E_0 + E'_0 < E_0 + E'_0 \tag{2.33}$$

which is clearly a contradiction. Therefore there cannot be two different external potentials that give the same ground state density for the system. This implies that there is a one-to-one correspondence between the ground state density and the external potential of a many-electron system. On the one hand, a given many-electron system has a unique external potential which gives, by the Hamiltonian (2.30) and corresponding Schrödinger equation, a unique ground state many-particle wave function, from which the ground state density is easily calculated. An external potential, therefore leads in a well defined way to a unique ground state density. On the other hand the first theorem of Hohenberg and Kohn states that the density $n(\vec{r})$, of a many-particle system contains exactly as much information as the wave function; that it is possible to find a unique external potential if only the ground state density is given. The ground state observables can be obtained uniquely way from the density alone, since they can be written as functionals of the density.

Among the ground state properties of the many-particle system, the total energy and the different contributions to the total energy are of particular interest. Thus the kinetic energy, T[n], the potential energy, V[n], and the total energy, E[n] are determined as functional of the density $n(\vec{r})$:

$$E[n] = T[n] + U_{ext}[n] + U_{ee}[n]$$

= $\int n(\vec{r}) v(\vec{r}) d^3r + F_{HK}[n]$ (2.34)

Here the integral describes the interaction between the electron cloud and the external potential and:

$$F_{HK}[n] = T[n] + U_{ee}[n]$$
(2.35)

is the exact functional representing the kinetic part and the mutual interaction between the electrons. All the ground state many-body effects are incorporated in this functional. The second term in Eq. (2.35) contains the classical repulsive interaction of a charge distribution with itself (Hartree term) as well as the contributions arising from the fact that the electrons are indistinguishable particles which obey Fermi-Dirac statistics. We can write:

$$U_{ee}[n] = J[n] + (non - classical \ terms)$$
(2.36)

where

$$J[n] = \frac{1}{2} \int \frac{n(\vec{r_1}) n(\vec{r_2})}{|\vec{r_1} - \vec{r_2}|} d^3 r_1 d^3 r_2$$
(2.37)

The non-classical term in Eq. (2.36) is of extreme importance and although its exact form is not known, it contains a major contribution to the exchange-correlation energy. In principle, both exchange and correlation is included in a self-interaction of the form:

$$U_{ee}[n_2] = \frac{1}{2} \int d^3 r_1 \int d^3 r_2 \frac{n(\vec{r_1}, \vec{r_2})}{|\vec{r_1} - \vec{r_2}|}$$
(2.38)

where $n(\vec{r_1},\vec{r_2})$ is the exact two-particle density, giving the number of particles in

unit volume simultaneously at $\vec{r_1}$ and $\vec{r_2}$. Formally, the non-classical term in (2.36) includes the difference between J[n] and $U_{ee}[n_2]$.

The second theorem of Hohenberg and Kohn provides a variational principle for the energy. It can be formulated as follows: For a trial density $\tilde{n}(\vec{r})$ such that $\tilde{n}(\vec{r}) \ge 0$ and $\int \tilde{n}(\vec{r}) d^3r = N$,

$$E_0 \le E\left[\tilde{n}\right] \tag{2.39}$$

where $E[\tilde{n}]$ is the energy functional in Eq. (2.34). This theorem can be proved based on the first theorem of Hohenberg and Kohn according to which each $\tilde{n}(\vec{r})$ determines its own $\tilde{v}(\vec{r})$ and wave function $\tilde{\psi}$. For a system described by the Hamiltonian \hat{H} and with external potential $v(\vec{r})$, we can write:

$$\langle \tilde{\psi} | \hat{H} | \tilde{\psi} \rangle = \int \tilde{n} \left(\vec{r} \right) v \left(\vec{r} \right) d^3 r + F_{HK} \left[\tilde{n} \right]$$

= $E \left[\tilde{n} \right] \ge E \left[n \right] = E_0$ (2.40)

In Eq. (2.40) n is the correct ground state density, therefore by definition $E[n] = E_0$, which proves the theorem. According to this second theorem, out of the infinite number of possible densities, the one which minimizes E[n] is the ground-state density corresponding to the external potential $v(\vec{r})$.

We note that the functional $F_{HK}[n]$ defined in Eq. (2.34) is a universal functional of n. It does not contain any information about the external potential (e.g. nuclei and their positions) therefore it is universal to any many-electron system. This means that in principle an expression for $F_{HK}[n]$ exists, which can be used for every atom, molecule or solid. However, an explicit expression for the functional $F_{HK}[n]$ is not known. One approximate approach has been to use the form of $F_{HK}[n]$ appropriate to a uniform electron gas, but with the constant density replaced by the local, varying density of the interacting electron system at position \vec{r} . This local approximation, referred to as Local Density Approximation (LDA), has proven to be a very successful approach for describing the properties of numerous systems.² At the same time, the existence of an exact functional has given a momentum to ongoing work for the development of more accurate forms of $F_{HK}[n]$.

2.3.2 The Kohn-Sham equations

In the previous section we have seen that the theorems of Hohenberg and Kohn guarantee that the ground state energy of an interacting many particle system is the minimum of the energy functional defined by Eq. (2.34). Although the theorems provided an exact treatment for the interacting electron system, the numerical implementation of the theory was not obvious until Kohn and Sham published in 1965 a set of equations, which turned DFT (LDA) into a practical tool to obtain the ground state density and energy [123].

Kohn and Sham proposed a method in which the kinetic energy component of the total energy is replaced by the kinetic energy functional $T_0[n]$ of a non-interacting electron gas. Any difference between the exact kinetic energy T[n] and $T_0[n]$, along with any difference in the energy due to exchange and correlation effects (see Eqs. (2.37) and (2.38) for J[n] and $U_{ee}[n_2]$) are treated as a separate contributions to the energy. Therefore we have:

$$F_{HK}[n] = T_0[n] + J[n] + E_{xc}[n]$$
(2.41)

where J[n] defined in Eq. (2.37), is the classical interaction of the electron-cloud with itself (commonly known as Hartree term). The last term $E_{xc}[n]$, usually referred to as the exchange-correlation energy, contains the difference $T[n] - T_0[n]$, and any

²For a large class of materials, commonly referred to as strongly correlated systems, LDA fails. One method to overcome this problem is the LDA+U approach, discussed in Section 2.3.3 and Chapter 7.

difference between the exact self-interaction $U_{ee}[n_2]$, defined by Eq. (2.38) and its classical approximation J[n]. Using (2.41), we have a new expression for the energy functional:

$$E[n] = T_0[n] + J[n] + U_{ext}[n] + E_{xc}[n]$$
(2.42)

We can now interpret the expression (2.42) as the energy functional of a noninteracting electron-gas, subject to two external potentials: one external potential such as due to the nuclear charges and another due to exchange and correlation effects. The corresponding single-particle Hamiltonian is called Kohn-Sham Hamiltonian and has the form:

$$\begin{aligned} \hat{H}_{KS} &= \hat{T}_0 + \hat{J} + \hat{U}_{ext} + \hat{E}_{xc} \\ &= -\frac{1}{2} \sum_i \nabla_i^2 + \frac{\delta J [n]}{\delta n} + \frac{\delta U_{ext} [n]}{\delta n} + \frac{\delta E_{xc} [n]}{\delta n} \\ &= -\frac{1}{2} \sum_i \nabla_i^2 + \int \frac{n (\vec{r'})}{|\vec{r} - \vec{r'}|} d^3 r' + v (\vec{r}) + v_{xc} (\vec{r}) \end{aligned}$$
(2.43)

Now we can state that the ground state density $n(\vec{r})$ of an interacting many-electron system is:

$$n(\vec{r}) = \sum_{i=1}^{N} \phi_i^*(\vec{r}) \phi_i(\vec{r})$$
(2.44)

where the single particle wave functions $\phi_i(\vec{r})$ are the N lowest-energy solutions of the Kohn-Sham equation

$$\hat{H}_{KS}\phi_i = \varepsilon_i\phi_i \tag{2.45}$$

As a result, to find the ground state density, all we have to do is to solve the Schrödinger-like noninteracting single-particle equations. We note that the singleparticle wave functions, $\phi_i(\vec{r})$, are not the single-particle electronic wave functions; they describe mathematical "single-particles states", without any direct physical meaning. The only thing we know is that the density associated with these "singleparticles" is guaranteed to be equal to the exact electron density. Also the singleparticle energies, ε_i are not the singe-electron energies.

In the expression of Kohn-Sham equations, both J[n] and $E_{xc}[n]$ operators depend on the density $n(\vec{r})$, which in turn depends of $\phi_i(\vec{r})$ which are being searched. This means that we are dealing with a self-consistent problem, which can be solved using an iterative process. Some starting density n_0 is guessed, and a Hamiltonian H_{KS1} is constructed with it. The eigenvalue problem is solved and using the resulting set of ϕ_1 , a new density n_1 can be derived. If n_0 differs from n_1 , then n_1 is used to construct H_{KS2} which will give n_2 etc., and the is repeated until the convergence of the density is reached. This final density is consistent with the Hamiltonian.

Kohn-Sham equations accomplish a remarkable thing: in principle, they allow an exact treatment of the ground state of the many-body problem. However, in reality the exact treatment is not possible, because the exchange-correlation functional is not known exactly.

2.3.3 The exchange-correlation functional

The solution of the Kohn-Sham equations requires an explicit form of the exchangecorrelation term. A widely used approximation, called Local Density Approximation (LDA, briefly mentioned at the end of the Section 2.3.1), is to postulate that the exchange-correlation functional has the following form:

$$E_{xc}^{LDA}\left[n\right] = \int n\left(\vec{r}\right) \varepsilon_{xc}\left[n\left(\vec{r}\right)\right] d^{3}r.$$
(2.46)

The function $\varepsilon_{xc}(n)$ for the homogeneous electron gas is numerically known. This postulate implies that the exchange-correlation energy associated with a particular density $n(\vec{r})$ can be found by dividing the material in infinitesimally small volumes with uniform densities, and then the exchange-correlation energy is calculated by summing the contributions of all the small volume over all space. By construction, LDA is expected to perform well for systems with slowly varying densities, but surprisingly, it gives very accurate results in many realistic cases too.

In order to improve on LDA, one can consider the dependence of the exchangecorrelation energy on the density of the neighboring infinitesimal volumes as well. In other words, the gradient of the density can also be taken into account. This approximation is therefore called Generalized Gradient Approximation (GGA). Within GGA, the exchange-correlation is a functional not of the density alone, but also of its local spatial variations:

$$E_{xc}^{GGA}\left[n\right] = \int n\left(\vec{r}\right) \varepsilon_{xc}^{GGA}\left[n\left(\vec{r}\right), \nabla n\left(\vec{r}\right)\right] d^{3}r.$$
(2.47)

Despite the fact that in general GGA performs slightly better than LDA, there are situations when LDA is preferred over GGA. As we will see in Chapter 3, GGA has the tendency to underestimate the binding between atoms and as a result it usually overestimates the lattice constants. This effect of GGA is especially problematic in the case of layered crystals, such as the III-VI family of semiconductors, where due to the weak interlayer interaction the lattice constant becomes highly overestimated in the direction perpendicular to the atomic layers.

One of the classic and well known failures of the LDA is the underestimation of band gaps in semiconductor. There are two origins of this failure: (i) the selfinteraction error inherent in LDA potential, and (ii) the vanishing discontinuity of the LDA exchange-correlation potential as a function of occupation at the Fermi level. They lead to wrong absolute energy positions and too small or entirely absent bang gap for many materials. This failure is not corrected by GGA, where the discontinuity also vanishes. In fact it has been found that in many cases, due to the above mentioned under-binding tendency of GGA, it produces even smaller band gaps than LDA.

Another deficiency of LDA and GGA is related to the description strongly correlated materials. Such systems usually contain transition metal (TM) or rare earth (RE) elements, with partially filled d or f electronic shells. When we apply a oneelectron method with orbital-independent potential such as LDA, to TM or RE systems, the result is partially filled d or f band with metallic type electronic structure and itinerant d or f electrons. This is a definitely wrong description of transitionmetal-oxides and RE metal compounds, where the d and f electrons are well localized. with a large energy separation between the occupied and unoccupied bands. One way to overcome this deficiency of LDA (and GGA) is to take into account the strong Coulomb repulsion within the localized shells. This has been done in the LDA+U method [84–87], in which the orbital dependent Coulomb interaction is considered for localized electrons by the addition of the Hubbard-like term $1/2U \sum_{i \neq j} n_i n_j$ (n_i) are orbital occupancies), while the delocalized electrons are treated by the usual orbital-independent, one-electron LDA functional. In order to avoid double counting one has to subtract from the LDA functional the corresponding Coulomb d-d (or ff) interaction energy. As a result (neglecting the exchange), we have the following functional:

$$E = E_{LDA} - UN(N-1)/2 + \frac{1}{2}U\sum_{i\neq j}n_in_j$$
(2.48)

where N is the total number of electrons in the localized shell. The above energy functional allows us to calculate orbital energies and orbital dependent one-electron potentials, which reproduce qualitatively the correct physics for many TM and RE systems.

2.4 The supercell technique for defect calculations

2.4.1 Introduction

The supercell method is a widely used approach to calculate properties associated with the presence of defects in solids. In this method the defect and the surrounding atoms are placed in a suitably chosen box, which is repeated infinitely in one or more spatial directions. Therefore this box becomes the new unit cell for the system and periodic boundary conditions are applied. The supercell method transforms an isolated point defect or defect complex in a three dimensional periodic array of defects. For surface calculation the system becomes a repeating array of slabs separated by vacuum regions. In each case, one has to be careful about how to choose of the size of the supercell (separation between the slabs), so that the effect of impurityimpurity (or surface-surface) interaction is reduced. Typical sizes of the supercells are 64-atoms, however, the increasing computational power has allowed for supercells with several hundred atoms.

Using supercells in combination with periodic boundary conditions allow the exploitation of many techniques derived for the quantum physics of periodic systems. The wave vectors of the BZ in the reciprocal space of the periodic supercell are good quantum numbers, thus the standard band structure methods can be applied. Furthermore the supercell method enables the full relaxation of the crystal structure by minimizing the total energy. Defect formation energies and migration barriers can be calculated as a function of Fermi level position of the host material and as a function of chemical potentials of the atoms which form the material. Using supercell calculations, useful physical properties can be extracted such as probabilities of certain type of defect to form under particular thermodynamical growth conditions, basic nature of the defect state (acceptor, donor, deep, shallow), local vibrational modes (LVM), hyperfine fields, and other ground state properties and optical properties.

2.4.2 Defect formation energies and ionization levels

In first-principle total energy calculations, the defect formation energies are usually described as a function of atomic chemical potentials of the constituent elements [125, 126] and Fermi energy, which is the chemical potential of the electrons [127]. To understand the dependence of the formation energy on the chemical potential and Fermi level, we give some simple and illustrative examples of defects. First, let us consider a charge-neutral cation vacancy (denoted as V_C^0) in a binary compound. In order to form such a defect one cation must be removed from the compound and place in an atomic "reservoir" of energy equal to the chemical potential of the cation in its bulk form, μ_C . Therefore the formation energy of the cation vacancy is:

$$\Delta H_f \left(V_C^0 \right) = E_{tot} \left(V_C^0 \right) - E_{tot} \left(0 \right) + \mu_C \tag{2.49}$$

where $E_{tot} \left(V_C^0 \right)$ is the total energy of the crystal with the vacancy present and $E_{tot} \left(0 \right)$ is the total energy of the pure host material. The chemical potential μ_C in Eq. (2.49) is kept as a parameter, and it can vary over a certain range, depending on the growth conditions. If the crystal is grown under cation-rich conditions (μ_C is high), the formation energy of cation vacancy according to Eq. (2.49) will increase, so that it will be less probable for the cation vacancy to form. Therefore, in order to avoid the formation of an undesired defect it is useful to prepare the growth conditions such that the formation energy of that defect is maximized.

The dependence of the formation energy on the Fermi level can be understood as follows. In order to create a positively charged defect (D^+) we have to remove an electron from the corresponding neutral defect (D^0) and place it in an electronic reservoir of energy equal to the Fermi energy (E_F) . Thus the formation energy of (D^+) is equal to the formation energy of (D^0) , minus the energy $\varepsilon (0/+)$ required to ionize (D^0) , plus the energy of the electron reservoir (E_F) :

$$\Delta H_f \left(D^+ \right) = \Delta H_f \left(D^0 \right) - \varepsilon \left(0/+ \right) + E_F \tag{2.50}$$

Equation (2.50) shows that the higher the E_F , the more energy is required to form a positively charged defect. This makes sense because in electron-rich materials (ntype or with high E_F) it is more difficult to create donors (which produce even more electrons by: $D^0 \rightarrow D^+ + e^-$). In the case of acceptors, on the other hand, the formation energy decreases with the increase of E_F :

$$\Delta H_f\left(A^{-}\right) = \Delta H_f\left(A^{0}\right) + \varepsilon\left(-/0\right) - E_F \tag{2.51}$$

Equation (2.51) shows that it is more difficult to create acceptors in hole-rich (p-type) materials.

In general, the formation energy of a defect X in charge state q is given by:

$$\Delta H_f \left(X^q \right) = E_{tot} \left(X^q \right) - E_{tot} \left(0 \right) + \sum_i n_i \mu'_i + q E'_F$$

$$= \underbrace{E_{tot} \left(X^q \right) - E_{tot} \left(0 \right) + \sum_i n_i E_i + q E_{VBM}}_{\Delta E(X^q)} + \sum_i n_i \mu_i + q E_F \quad (2.52)$$

$$= \Delta E \left(X^q \right) + \sum_i n_i \mu_i + q E_F$$

In Eq. (2.52) $E_{tot}(X^q)$ and $E_{tot}(0)$ are the total energies of the defect containing and defect free supercells, n_i indicates the number of atoms added $(n_i < 0)$ or removed $(n_i > 0)$ from the supercell and μ'_i denote the corresponding chemical potentials.

They represent the energies of the reservoirs with which atoms are exchanged when assembling the crystal. Usually the chemical potential (μ'_i) can vary over a certain range, with the upper limit being the energy (E_i) of the elemental solid or gas. This happens because if $\mu'_i > E_i$ then the elemental solid will form, which will prevent the further increase of the chemical potential. For convenience, in Eq. (2.52), we have set $\mu'_i = E_i + \mu_i$ so that the upper limit to the newly defined chemical potentials μ_i is zero $(\mu_i \leq 0)$. Similarly we have set $E'_F = E_{VBM} + E_F$, where E_{VBM} is the energy of the VBM of the bulk material as calculated using the defect free supercell. The VBM of the defect containing supercell must be aligned with that in the pure supercell. The importance of this alignment will be discussed in Section 2.4.4.

Following Eq. (2.50) and (2.51) we can define the defect transition level or ionization level $\varepsilon (q/q')$, as the Fermi energy at which two charge states q and q', of the same defect X have the same formation energy, $\Delta H_f(X^q) = \Delta H_f(X^{q'})$. Thus

$$\varepsilon\left(q/q'\right) = \frac{\left[\Delta E\left(X^{q}\right) - \Delta E\left(X^{q'}\right)\right]}{q' - q}$$
(2.53)

If the total energy of the final state q' is calculated after allowing the atomic positions in the supercell to relax, then the transition level given by Eq. (2.53), is the one observed in DLTS experiments or as thermal ionization energies derived from temperature-dependent conductivity or Hall effect data. If the energy of the final state with charge q' is calculated using the geometry of the initial state q, then the level given by Eq. (2.53) corresponds to the optical level observed in "vertical" absorption experiments, where the final charge state cannot relax to equilibrium. In emission experiments, however the initial excited state has evolved towards its equilibrium configuration thus the emitted photon has less energy than the absorbed one. Therefore the peak positions of the optical absorption and emission spectra of the same electronic transition are separated. This separation, the so-called Stokes shift, poses challenges to both the experimental assignment of the peaks and the theoretical analysis.

2.4.3 Equilibrium growth conditions

We have mentioned in the previous section that the atomic chemical potentials of the host elements and impurities can vary over certain range. The achievable values of the chemical potential are determined by the *equilibrium growth conditions* [55, 128]. First, as explained in Section 2.4.2, in order to avoid precipitations, the atomic chemical potentials of the constituent and dopants are bound by the total energies of the constituents in their bulk metallic (or gaseous) form. For example if we consider a ternary compound $A_l B_m C_n$, and for convenience we set the total energies of the constituents as reference, we have:

$$\mu_A \le 0, \ \mu_B \le 0, \ \mu_C \le 0 \tag{2.54}$$

For instance, if the chemical potential of component A is greater than zero, than the component A will form rather the compound $A_l B_m C_n$.

Second, the chemical potentials are limited to those values that maintain a thermodynamically stable host $A_l B_m C_n$ compound:

$$l\mu_A + m\mu_B + n\mu_C = \Delta H \left(A_l B_m C_n \right) \tag{2.55}$$

where $\Delta H (A_l B_m C_n)$ is the heat of formation (enthalpy of formation) of host solid $A_l B_m C_n$. In first-principles calculations the heat of formation can be calculated from:

$$E\left(A_{l}B_{m}C_{n}\right) = lE\left(A\right) + mE\left(B\right) + nE\left(C\right) + \Delta H\left(A_{l}B_{m}C_{n}\right)$$

$$(2.56)$$

where the E's are the total energies of the host and the constituent in their bulk (solid or gas) form.

Finally, to avoid the formation of secondary phases between a dopant X and a host element H, the chemical potentials are limited by:

$$m\mu_X + n\mu_H \le \Delta H \left(X_m H_n \right) \tag{2.57}$$

In Eq. (2.57), $\Delta H(X_m H_n)$ is the heat of formation of the secondary phase $X_m H_n$.

The above discussion demonstrates that by changing the chemical potentials of the host and impurity elements or the Fermi energy, one can control the dopant solubility. It is well known that there are intrinsic thermodynamic limitations to the ability to dope semiconductors, such as p-type doping in wide gap semiconductors. To overcome these fundamental limitations, first-principles simulations can be used to design new materials with desired doping properties. One such example is the recent success in fabricating p-type transparent conductive oxides (TCOs), where the mechanism that led to p-type conductivity was explained by Nie et al [129].

2.4.4 Energy-level reference and valence band alignment

It is obvious that from Eq. (2.52), that an important parameter in supercell calculations is the position of VBM. Usually in almost all theoretical calculations the VBM is considered to be the reference for the electron chemical potential (cf. Eq. (2.52)). However an important issue is how to find the energy of the VBM in a finite size supercell, where the eigenvalues of the bulk could be strongly perturbed by the presence of a periodic array of defects. One method of valence band alignment was proposed by Zhang and Northrup [126]: a region of the supercell was chosen away from the defect to represent the bulk and the average self-consistent potential calculated for this region was aligned with the average potential of the same region in the defect free supercell. Consequently the magnitude of the correction to the VBM can be written as:

$$\Delta E_{VBM} = E_{VBM}^D - E_{VBM}^H = \left\langle V^D \right\rangle - \left\langle V^H \right\rangle \tag{2.58}$$

where E_{VBM}^{D} and E_{VBM}^{H} are the energies of the VBM calculated in the defect containing and defect free supercells, respectively. A widely applied practice in defect calculations is to assign $E_{VBM}^{D/H}$ to the single-particle VBM eigenvalue, which is often located at the Γ -point. However, it has been suggested that within the framework of supercell approach, it is often better to calculate the energies E_{VBM} and E_{CBM} as averages of the band edges over the special k-point used in total energy calculation [130].

Other energy references are also possible: in all electron calculations, one can align the electronic core or semicore level energy, or define all energy references with respect to the so-called crystal zero, the potential energy at the surface of a neutral Wigner-Seitz cell.

2.4.5 Summary and conclusions

First-principles calculations within DFT and supercell method enable us to quantitatively estimate the defect formation energies, diffusion barriers, structural parameters, detect ionization levels in semiconductors. However, the desired accuracy in totalenergy calculations is not always easy to achieve. In particular, the calculation of the energy position of the defect induced states in the semiconducting band gap can be quite challenging and requires careful considerations of possible sources of error. One possible source of error can be related to the underlying theory, because of the treatment of electronic exchange and correlation. As mentioned in Section 2.3.3, local and semilocal approximations contribute to the underestimation of the fundamental band gap. The second source of error is associated with the finite-size effects inherent in the supercell approach. These errors include spurious defect-defect interaction which leads to dispersion of the defect related electronic states, incomplete sampling of the reciprocal cell, and the constrained relaxations of the atoms surrounding the defects. The third source of errors is related to the approximations needed for specific implementations such as generation of pseudopotentials, construction of basis sets and numerical accuracy of the algorithms.

The superiority of the DFT methods consists in revealing systematic trends in the electronic and structural properties of defects in semiconductors. These include the nature of the defect levels (donor, acceptor, deep, shallow), their spin structure, point symmetry, energetics.

Obtaining quantitatively accurate results using supercell calculations is an extremely difficult task and requires significant computational resources. As a result, many confusing and seemingly contradictory results have been published in the scientific literature. However, over the time the computational methods have matured, and with the significant increase in the computational power available for such calculations it is possible to perform calculation with critical predictive power.

Chapter 3

Electronic structure of non-isovalent impurities in GaSe

3.1 Introduction

Gallium Selenide (GaSe) is a wide band-gap semiconductor that has been studied for a long time due to its unique properties associated with different layered structures. Strong covalent bonding within the layers and weak bonding between them (van der Waals and small ionic-covalent component) make GaSe highly anisotropic. Because of its large nonlinear optical coefficient ($d_{22} = 75 \text{ pm/V}$), GaSe has been investigated as a non-linear optical material [131]. One of the important applications of nonlinear optical effects is the generation of broadband mid-infrared electromagnetic waves and detection of coherent broadband THz radiation.

Another important application of GaSe is in the area of radiation detectors. Since the first report by Manfredotti et al., in 1974, GaSe has been studied by several groups due to easy fabrication, high resistance for radiation damage, and high temperature operation [29, 132–136]. It has room temperature resistivity of 103-109 Ω cm [132]. The large leakage current for pure GaSe made it unsuitable for efficient radiation detectors. However doping GaSe with Ge or Sn gives rise to high resistivity by reducing the leakage current [137]. In a different experiment, Yamazaki et al. reported 3-7 orders of magnitude decrease in leakage current and dramatic improvement in energy resolution of GaSe detectors by doping with 0.005-0.1 at.% Ge [29, 136].

Since defects play a dominant role in the ultimate performance of a semiconductor, it is extremely important to understand the nature of the impurity-induced states. As we described in the previous chapter, defect states in semiconductors can be broadly classified as shallow defect states (SDS) and deep defect states (DDS). These are of course two extremes and one can have defect states somewhere in between. SDS in wide band gap semiconductors associated with donors or acceptors are well described by effective mass approximation (EMA) with small central cell corrections associated with deviations from the hydrogenic potential in the impurity cell and its immediate neighborhood. On the other hand DDS cannot be described adequately by the EMA. Also the EMA has difficulties when the central cell corrections are large or comparable to the EMA binding energy(BE).

In this chapter we discuss the nature of the defect states in GaSe when Ga is substituted by impurities of different nominal valence. The impurities we have considered are Cd (divalent), and Sn (tetravalent). Cd gives rise to acceptor state(s) whereas Sn gives rise to a donor state. The experimental values of the Cd acceptor binding energies (BEs) are 0.13 eV and 0.18 eV [41] while the Sn donor BE is 0.36 eV [34]. From these BE values it appears that the donor state introduced by Sn is more likely a deep defect state whereas the acceptor states due to Cd are somewhere between a shallow and deep defect state [99]. In addition to the above substitutional defects we have also looked at the electronic structure of Ga and Se vacancies. Micocci et al. [138], have found a localized level at ~0.2 eV above the valence band from their hole trapping measurement which they have assigned to Ga vacancy. Also they find another defect level at ~0.8 eV above the valence band maximum. The latter was assigned to some extended defect region. Micocci et al. [34] have also argued that Se vacancies produce electron trapping centers at ~ 0.52 eV below the conduction band minimum. All these defect levels assigned to vacancies in GaSe appear to be of deep defect type.

To understand the nature of the defect states mentioned above we first used EMA in the case of substitutional defects to see how large the central cell and nonparabolic corrections are [99]. We then used *ab initio* methods and supercell model to calculate the defect state energies (defect bands) and also looked at the degree of localization of the defect states. A comparison of the results obtained with these two extreme approaches can help us to get a better understanding of the nature of defect states in GaSe. For the vacancies we only use the supercell model. It is well known that due to the underestimation of the band gap by GGA and due to the limitations of the supercell model, accurate calculations of defect BE represents a serious challenge [139]. However, in the case of acceptor states, derived mostly from the valence band, their position relative to the valence band maximum (VBM) can be obtained more reliably and with reasonable accuracy.

3.2 Method of calculation

For EMA we have used the experimental values of the dielectric constant and effective mass tensors [140]. In addition, we have also used the effective mass values obtained from our theoretical calculations. Electronic structure calculations have been performed within density functional theory (DFT) using all electron full-potential Linearized Augmented Plane Wave (FPLAPW) plus local orbital [141] and Projector Augmented Wave (PAW) [142] methods implemented through WIEN2k [143] and VASP [144–147] packages respectively. In both cases we have used the generalized gradient approximation (GGA) [148] for the exchange and correlation potential. In the FPLAPW calculations the 3d, 4s, 4p electrons of Ga and Se atoms and the 4p, 4d, 5s, 5p electrons of the impurity atoms (Cd, In, Sn) were treated as valence electrons. Convergence was assumed when the energy difference between the self-consistent cycles was less then 0.0001 Ry (1.36 meV). The product between the smallest muffin tin radius and the largest reciprocal lattice vector was chose as $R_{MT}K_{max} = 7.0$. In the case of bulk GaSe, where the atomic radii were chosen as 2.17 a.u. and 2.18 a.u. for Ga and Se respectively, this corresponds to a cutoff energy of 141.7 eV. The accuracy (see next paragraph) in the bulk energy calculation was achieved by using a relatively dense k-mesh of 19x19x4, which gives 120 k-points in the irreducible Brillouin zone (BZ). The defect calculations using FPLAPW methods were performed on 3x3x1 supercells (72 atoms) with one impurity atom (Cd, In, Sn) replacing a Ga atom. The smallest muffin tin radius was chosen to be 2.06 a.u., which gives an energy cutoff of 157.2 eV, and the BZ was sampled by a 6x6x3 mesh (17 k-points in the irreducible BZ). The k-point meshes used are suitable for the modified tetrahedron integration scheme [149].

Since the PAW method is computationally less demanding than the FPLAPW, we use it for calculations involving large supercells (up to 400 atoms). The Ga and Se vacancy calculations were also performed using PAW methods. However, in order to compare the two methods, we have performed calculations on bulk GaSe and on 3x3x1 supercells with Cd and Sn impurity. In the case of PAW method the outermost *s* and *p* electrons of all the atoms were treated as valence electrons but in addition, the 3*d* electrons of Ga and Sn were also included in the valence region. The electronic relaxations were performed until the total energy difference relative to the previous cycle was less than 10^{-4} eV. In the PAW calculations the energy cutoff was set to 300 eV. For the smaller supercells (3x3x1) we have carried out geometric relaxation but for the large ones (containing 400 atoms/supercell), due to limited computing time, we have not been able to do full atomic relaxation and complete band structure calculations.

Since the spin-orbit effects are expected to be small for III-VI compounds [22], we did not include spin-orbit interaction in our calculations.

3.3 Pure GaSe

3.3.1 Crystal structure and geometric relaxation

The crystal structure of GaSe is quite interesting. It consists of Ga-Se layers that can be stacked in different ways leading to different poly-types (β , γ , δ or ϵ). All these poly-types are wide band gap semiconductors with room temperature band gaps of 1.996 eV (for ϵ and γ), 2.026 eV (for δ) and 2.046 eV (for β) [150]. Since all these structures contain Ga-Ga dimers as a common motif, the origin of the ~2.00 eV band gap is most likely related to this geometry.

Several energy band calculations have been done for ε -GaSe [16,23,24,26,151,152] and a few for β -GaSe [16,22]. These prior works show that the differences in the electronic structure between different polytypes are negligible, which means that we have the choice of the polytype to perform our calculations. We only consider the β -type lattice, which has the highest symmetry and contains the smallest number of molecules (eight) in the unit cell and it will make easier the comparison between our results and prior works. β -GaSe crystallizes in layered, hexagonal system, having the space group P6₃/mmc. The GaSe layers consist of two planes of Ga atoms sandwiched between two planes of Se atoms as illustrated in Fig. 3.1. In each plane the Ga or Se atoms are arranged in a two-dimensional hexagonal lattice. The nearest neighbor coordination of the Ga atoms differ from that of Se atoms: each Ga has three Se nearest neighbors (NN) and one Ga NN, while each Se is only coordinated by three Ga atoms and no other Se atoms.

For the structure optimization we first relaxed the volume of the unit cell, keeping


Figure 3.1: Schematic view of the crystal structure of β -GaSe. The unit cell extends over two layers of GaSe and contains four Ga and four Se atoms. In each layer two monoatomic sheets of Ga are sandwiched between two monoatomic sheets of Se. In this figure 9 unit cells are shown

Table 3.1: The theoretical lattice constants of GaSe and the Ga-Ga, Se-Se and Ga-Se bond lengths calculated by FPLAPW and PAW methods. For comparison the experimental values are also given as in Ref. [153]. All distances are given in angetroms.

	a, b	с	d_{Ga-Ga}	d_{Se-Se}	d_{Ga-Se}
FPLAPW	3.83	16.29	2.45	3.83	2.50
PAW	3.80	16.17	2.45	3.80	2.49
Exp.	3.74	15.92	2.32	3.74	2.48

the ratio of the lattice constants a:b:c fixed and then we optimized the internal structural parameters by minimizing the total energy as a function of atomic positions, keeping the volume of the unit cell constant. As a second step, after obtaining the optimized theoretical crystal structure, we performed an additional iteration in the volume relaxation (keeping a:b:c constant) and analyzed the changes in the lattice parameters. Since we have found that these changes are quite small (less than 0.3%) we assumed that the unit cell volume and the internal structural parameters were at their optimal values. We note that we have also tried to optimize the c/a ratio keeping the volume of the unit cell fixed. We observed a large elongation of the unit cell along the z-axis (perpendicular to the GaSe layers): for example, the lattice constants obtained after the c/a optimization using the PAW method, were a = 3.77 Å and c = 16.39 Å. These values are ~0.7% smaller and ~1.4% greater compared to the values obtained after the volume relaxation, respectively. As pointed out in Ref. [23], this result is a consequence of the fact that DFT cannot describe van der Waals interactions adequately. Therefore, in this chapter, we present the results obtained using the theoretical crystal structure resulted after the first volume optimization and relaxation of the atomic positions at the experimental c/a ratio.

The difference between the FPLAPW and PAW lattice parameters and bond lengths are less than 0.5% (listed in Table 3.1). The theoretical lattice constants of bulk GaSe are larger than the experimental ones reported in Ref. [153]. This is due to the well known overestimation of the lattice parameters by GGA. The shortest Se-Se distance is between Se atoms located in the same monoatomic sheet and it is more than 50% longer than the Ga-Ga dimer. On the other hand, the length of the Ga-Se bond is comparable with the Ga-Ga bond length, leading to a strong hybridization between the orbitals of Ga and Se.

3.3.2 The electronic structure of GaSe

Before describing the detailed band structure of the GaSe, we will discuss the bonding scheme in this system qualitatively as shown in Fig. 3.2. This will help us in developing an intuitive picture of the band gap formation in this valence mismatched system. The states mainly responsible for bonding are Ga 4s and Se 4p valence orbitals. If the mixing between Ga s and Se p states is turned off, then for each Ga-Ga dimer we have a bonding s state and an antibonding s state. In the unit cell there are 4 Ga atoms (2 Ga dimers) and 4 Se atoms, so there are 2 bonding s states, 2 antibonding s states and additional 12 p states coming from the 4 Se. In the presence of Ga s and



Figure 3.2: Qualitative scheme showing the bands responsible for bonding in GaSe. The bottom of the valence band has a strong Ga s character, followed by a strong mixture of Ga s and Se *p*-states. Two Se p bands split off the valence band as a result of this hybridization, and form the bottom of the conduction band. The lowest conduction bands also display $Ga-p_z$ character.

Se p hybridization the Ga s bands pick up Se p character and vice-versa. The main effect of this mixing is the splitting off of 2 Se p derived bands near the top, giving rise to an energy gap in the band structure of GaSe. The electron counting is such that 4 Ga-Ga s bands and 10 Se p bands (per unit cell) can accommodate 28 electrons (12 from 4 Ga and 16 from 4 Se). Thus the gap in the DOS discussed above is the true semiconducting gap. Both the valence bands and the lowest conduction band are derived from the Se p orbitals mixed with Ga s states. There is however some additional complexity due to the presence and subsequent mixing of Ga p_z bands, which contribute primarily to the lowest conduction bands with some admixture with states near the top of the valence band.

As pointed out before, the electronic structure of GaSe has been extensively investigated during the last two decades, using empirical tight-binding approach [16,22] as well as *ab initio* methods [23, 24, 26, 151, 152]. We briefly review some of the general features of the band structure for β -GaSe, obtained with the full potential method (Fig. 3.3(a), (b), (c)and (d)), and explore the nature of bonding and atomic characters of the valence and lowest conduction band states to confirm our qualitative picture described above. We further note that the electronic structure of pure β -GaSe was also calculated with the PAW method and it is very slightly different than the one obtained by the FPLAPW scheme as regards the occupied states. The differences in the energy eigenvalues at the Γ point are less than 50 meV (when the energy of the valence band maximum was set to zero in both calculations).

Let us look at Fig. 3.3(a) first. The semiconducting band gap (0.65 eV) is direct, located at the Γ -point and it is significantly smaller than the experimental value of 2.046 eV reported for β -GaSe [150]. This is the well-known limitation of the LDA and GGA, which underestimate the band gap in semiconductors [154]. The valence band is split into three sub-bands: one between -7.4 eV and -6.4 eV (denoted III), originating from the s states of Ga slightly hybridized with p_x and p_y states of Se; sub-band II, between -6.5 eV and -3.5 eV, which is also derived from the Ga s orbitals, but in this case the mixing with Se p is much stronger, resulting in a larger dispersion of this sub-band; finally the much broader band between -4.6 eV and 0 eV (denoted as I) which comes from the p states of Se hybridized with the s and p_z states of Ga. Whereas the states near the middle and the bottom of this band come primarily from the Se p_x and p_y orbitals, the states near the top of this sub-band (which is also the top of the valence band) correspond to the Se p_z orbitals. There are four low lying conduction bands between 0.6 and 3.0 eV which consist of mixtures of Se p, Ga s and Ga p_z orbitals. The lowest bands (IV) in the Fig. 3.3(a) correspond to the Se 3s core states.

To get a better understanding of the chemical bonding in GaSe, we have analyzed the orbital character of different energy bands (in which each eigenvalue is associated





(d)

Figure 3.3: (a) Band structure of β -GaSe. In addition to the scheme presented in Fig. 3.2, the Se *s*-states are also shown here (subband IV). The zero energy is chosen at the top of the valence band. (b) The Ga *s* orbital contribution to the band structure. The Ga *s* antibonding state hybridizes with the Se *p* states, pushing up some Se *p*-states into the conduction band. The lowest conduction bands, therefore also display Ga *s* character. (c) The Se $p_x + p_y$ orbital contribution to the band structure. (d) The Brillouin zone corresponding to the hexagonal unit cell. The Γ -A direction is perpendicular to the GaSe layers.

with a circle, whose radius is proportional to the specific orbital character of that state - the fat band representation). Fig. 3.3(b) shows the contribution of the Ga s orbitals to the band structure. The "fat" bands III and II, with strong Ga scharacter, correspond to Ga-Ga bonding (III) and anti-bonding (II) states. The antibonding state (II) is strongly hybridized with a linear combination of Se p orbitals of appropriate symmetry (Γ_2 at the Γ point) and is broad compared to the bonding band (III). As a result of this strong hybridization two of the Se p bands split off from the rest of the Se p bands leading to the formation of a gap in the DOS of Se derived p-bands. Therefore the lowest conduction bands originate from Se p orbitals, but these bands also display Ga s and Ga p_z character as a result of hybridization. This can be observed from Fig. 3.3(b) and (c), which show the contributions of Ga s and Se $p_x + p_y$ orbitals to the band structure respectively. The relative admixture of Se p and Ga p_z states near the conduction band minimum and valence band maximum determines the effective mass anisotropy (see discussions below). Note that because of small LDA band gap the hybridization between Se p and Ga p states may be overestimated. The Brillouin zone corresponding to the hexagonal unit cell is shown in Fig. 3.3(d). The Γ -A direction is perpendicular to the GaSe layers.

3.4 Defects in GaSe

When Ga is substituted by another atom or there is a vacancy at the Ga site, the local electronic structure of the Ga-Ga dimer can change dramatically depending on the energy mismatch between the energies of Ga 4s and the valence s-state of the defect. This can perturb the valence band and if the perturbation is sufficiently strong it can give rise to different types of defect states. One also expects to see strong local perturbation if there is a Se vacancy in the neighborhood of Ga dimer.

3.4.1 Atomic relaxations in the presence of defects

The calculations in the presence of defects have been performed with two different supercells: 3x3x1 (72 atoms) and 5x5x2 (400 atoms) with one Ga being replaced by an impurity. This corresponds to 1 impurity/36 cations (~3 at.% concentration) and 1 impurity/200 cations (~0.5 at.% concentration) respectively. Supercells of the same size were also used for the electronic structure calculations associated with the vacancies. As suggested in Ref. [155], to reduce the spurious strain induced by the impurity-impurity interactions within neighboring supercells, we performed the calculations using the theoretical lattice constants and allowed for the relaxation of the atomic positions.

In the FPLAPW calculations we only relax the positions of the Ga and Se closest to the impurity (limited relaxation). We find that when a Ga atom is replaced by Cd (or Sn) there is significant outward relaxation (away from the impurity, along the impurity-host bond direction) of the Ga and Se atoms surrounding the defect. The minimum energy corresponds to the situation when the Ga-Cd/Sn bond length expands by 3/7% relative to the Ga-Ga dimer length, while the Se-Cd/Sn bond length expands by approximately 5/7% compared to the original Se-Ga distance.

Since for large systems we use PAW method (because such calculations are not feasible within FPLAPW method), we first want to compare these two methods in terms of atomic relaxation. In the PAW calculations we have performed two types of relaxation of the internal parameters. First we carried out limited relaxation studies as in the case of FPLAPW method. Then we relaxed the positions of all the atoms (full relaxation) in the defect containing 3x3x1 supercell. The results are summarized in Table 3.2. In the first case, the changes in the bond lengths are nearly identical in the two methods indicating that PAW method is as good as FPLAPW. When all the atoms are allowed to relax the outward relaxation of Cd and Sn NNs are

	Cd impurity			In	In impurity			Sn impurity		
	Ga-Cd	Se-Cd	Se-Se	Ga-In	Se-In	Se-Se	Ga-Sn	Ga-Sn	Se-Se	
LAPW ^a	0.07	0.14	0.26	0.10	0.15	0.23	0.18	0.18	0.26	
PAW^{a}	0.07	0.15	0.26				0.17	0.18	0.25	
PAW	0.12	0.16	0.25				0.31	0.19	0.32	

Table 3.2: The changes in the Ga-Ga, Ga-Se and Se-Se bond lengths when Ga is replaced by an impurity (Cd, In or Sn). All distances are given in angstroms. (a limited relaxation where only the defects' nearest neighbor atoms were allowed to relax

more pronounced: comparing the Ga-Cd/Sn distance to the Ga-Ga dimer length we observe an increase by $\sim 5/11\%$ while the Se-Cd/Sn bond length increases by $\sim 6/7\%$ compared to the original Se-Ga distance. The larger outward relaxation in PAW calculation is easy to understand, because all the atomic positions in the supercell were optimized.

In the case of Sn impurity we observe that the increase in the Ga-Sn distance is much larger than the increase of the Se-Sn distance (~11% compared to ~7%), suggesting a stronger Coulomb attraction and therefore a more ionic character of the Se-Sn bond, compared to Ga-Sn bond. In the case of Ga vacancy, the relaxation of the atomic positions leads to a contraction of the three NN Se atoms (by ~14%) toward the vacancy and to an expansion of the NN Ga (by ~4%) away from the vacancy. The GaSe system with Se vacancy, on the other hand, minimizes its energy by contracting of the NN Ga and Se atoms toward the vacancy (Ga ~12% and Se ~3%).

3.4.2 Hydrogenic effective mass approximation

In the effective mass approximation, the energy levels of shallow donors or acceptors in a semiconductor with anisotropic effective mass and dielectric constant, are given by the solutions of a Schrödinger equation with the Hamiltonian [102, 156]:

$$H_{0} = -\frac{\hbar^{2}}{2} \left[\frac{1}{m_{\perp}} \left(\frac{\partial^{2}}{\partial x^{2}} + \frac{\partial^{2}}{\partial y^{2}} \right) + \frac{1}{m_{\parallel}} \frac{\partial^{2}}{\partial z^{2}} \right] + \frac{e^{2}}{\sqrt{\varepsilon_{\perp} \varepsilon_{\parallel}}} \frac{1}{\sqrt{x^{2} + y^{2} + \frac{\varepsilon_{\perp}}{\varepsilon_{\parallel}} z^{2}}} \quad (3.1)$$

In the above equation m_{\perp} and m_{\parallel} are the effective masses, and ε_{\perp} and ε_{\parallel} are the static dielectric constants, while the parallel and perpendicular directions are considered with respect to the c-axis (which is perpendicular to the GaSe layers).

Let us consider the acceptor case first. We have used the experimental values of these parameters (top most valence band effective mass) given in Ref. [140]. These are: $\varepsilon_{\perp} = 10.6$ and $\varepsilon_{||} = 6.18$; $m_{\perp} = 0.8 m_0$ and $m_{||} = 0.2 m_0$ (where m_0 is the free electron mass). Taking the units of length and energy as $a = \hbar^2 \sqrt{\varepsilon_{\perp}^2 \varepsilon_{||}} / m_{\perp} \varepsilon_{\perp} e^2 = 1.64$ Å and $\varepsilon_0 = m_{\perp} \varepsilon_{\perp} e^4 / 2\hbar^2 \varepsilon_{\perp}^2 \varepsilon_{||} = 166$ meV, equation (3.1) becomes dimensionless:

$$-\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \gamma \frac{\partial^2}{\partial z^2} + \frac{2}{r}\right)\Psi(\vec{r}) = E\,\Psi(\vec{r}),\tag{3.2}$$

where the anisotropy factor is: $\gamma = m_{\perp} \varepsilon_{\perp} / m_{||} \varepsilon_{||} = 6.86$. The calculated theoretical values of effective mass parameters obtained from *ab initio* calculations in GaSe are $m_{\perp} = 1.4 m_0, m_{||} = 0.1 m_0$ and give a larger value for this anisotropy factor, $\gamma = 24.01$. It is interesting to point out that even if GaSe appears to be layered the acceptor defect states are more one-dimensional because the anisotropy factor $\gamma >> 1$. This is due to the strong hybridization between the Se p and Ga p_z states near the top of the valence band. The anisotropic Schrödinger equation (Eq. (3.2)) can be solved using a variational perturbation theory where one expands the wave function $\Psi(\vec{r})$ in a basis of anisotropic hydrogen-like orbitals [102, 156]:

$$\Psi(\vec{r}) = \sum_{nlm} \left(\frac{\beta}{\gamma}\right)^{1/4} \psi_{nlm}\left(x, y, \sqrt{\frac{\beta}{\gamma}}z, \alpha\right).$$
(3.3)

In Eq. (3.3) $\psi_{nlm}(x, y, z, \alpha) = R_{nl}(\alpha, r)Y_{lm}(\theta, \varphi)$ are normalized hydrogenic wave functions and α and β are variational parameters, which can be varied to minimize the energy. This approach is known to give accurate energies for the lowest hydrogenic s and p like states: earlier calculations for the effective mass binding-energies were done for donor levels in Si ($\gamma = 0.2079$) and Ge ($\gamma = 0.0513$) [156]. We are not aware of any earlier calculations for which the anisotropy factor is much larger than 1. Equation (3.2) was diagonalized using this method and the ground state energy converged surprisingly well for a 6 by 6 Hamiltonian matrix. The dependence of the energy surface on the variational parameters for the 6×6 case is shown in Fig. 3.4. The lowest energy, calculated using the experimental dielectric constants and effective masses ($\varepsilon_{\perp} = 10.6, \varepsilon_{||} = 6.18; m_{\perp} = 0.8 m_0$ and $m_{||} = 0.2 m_0$), is $E_0 = -77.46$ meV. The corresponding values for the variational parameters are $\alpha = 0.6$ and $\beta = 1.7$. This gives a binding energy (BE) of 77.46 meV. If we use the theoretical value of the γ parameter, the acceptor BE is 41.54 meV (see below)

For the donor case, we only used the experimental values of the effective mass parameters of the lowest conduction band $m_{\perp} = 0.5 m_0$, $m_{||} = 1.6 m_0$ [140]. The values of the length and energy scale parameters are a = 2.63 Å, $\varepsilon_0 = 104$ meV, and the anisotropy factor is $\gamma = 0.54$. Note that in contrast to the acceptor state, which is elongated along the z-axis (cigar shaped), the donor state is more pancake like. The donor BE from the variational perturbation calculation, turns out to be 126 meV and the corresponding values for the variational parameters are $\alpha = 1.1$ and $\beta = 0.9$.

Comparing the theoretical acceptor BE of 77.46 meV to the energy of the acceptor levels obtained from photoluminescence measurement by Sighetomi et al. [41] (130 meV and 180 meV), we conclude that the hydrogenic EMA is not adequate to describe the acceptor levels in GaSe, even if we assume that Cd related defect BE is the smaller of the two, namely 130 meV. The disagreement is worse for the anisotropy factor, $\gamma = 24.01$, obtained from the theoretically calculated effective masses. For this case



Figure 3.4: The dependence of the energy surface on the variational parameters α and β . The minimum is located at -77.5 meV.

we obtained the BE = 41.54 meV (α = 0.4 and β = 2.4). Similarly for the donor state for Sn impurity the experimental BE is 360 meV [34] whereas our theoretical calculation gives 126 meV. Here again the central cell corrections (234 meV) are quite large and the EMA is not adequate. Thus we need to carry out calculations that take proper account of the short distance corrections to the EMA. This has been done using *ab initio* DFT calculations and the results are discussed below.

3.4.3 Ab initio calculations of defects in GaSe

To characterize the substitutional impurity states we first compare the total DOS with and without the impurity (Fig. 3.5), calculated using the 3x3x1 supercells, to see if there are any noticeable changes in the neighborhood of the band gap. For Cd (Fig. 3.5(b)) there is a peak near the valence band maximum and for Sn (Fig. 3.5(c))



Figure 3.5: The total DOS of (a) pure GaSe (b) Cd doped and (c) Sn doped GaSe. (b) Cd_{Ga} introduces a defect state (indicated by the arrows) near the valence band maximum and (c) Sn_{Ga} introduces a state near the conduction band minimum.

there is a peak near the conduction band minimum. We argue that these peaks are the impurity-induced states and they are broad (full width at half maximum ~0.15 eV) due to strong impurity-impurity interaction. For the 3x3x1 supercells the minimum impurity-impurity distance is 11.4 Å. To probe these defect states further we have analyzed their Cd (or Sn) orbital character and orbital characters associated with atoms located at different distances from these defects (see Fig. 3.6).

Substitutional Cd on Ga site (Cd_{Ga}) . As we can see in Fig. 3.6 (a-d), the main contribution to the impurity-induced peaks are coming from Cd s and p states as well as from the states associated with the NN Ga (denoted Ga1), NN and next NN Se atoms of the defect (Se1 and Se2). The next NN Ga (denoted Ga2) has very little



Figure 3.6: Partial density of states associated with the impurity (a) Cd s, p and (e) Sn s, p orbitals and those associated with atoms located at different distances from the defects as indicated in the figure (b-d, f-h). The atoms Ga1 and Se1 are the nearest neighbors (NN) of the defects, while the atoms Ga2 and Se2 are the next NN of the same defects. The contribution of the Sn to the DOS is larger compared to that of Cd, suggesting a more localized nature for the defect state associated with the Sn impurity.

contribution to the states near the peak. However, the contribution of the NN Se p is comparable to that of the next NN Se p. We find that the greatest contribution to the DOS near the peak comes from the p orbitals of the next nearest Se atom (~0.38 states/eV/atom) followed by the nearest Se p orbitals (~0.30 states/eV/atom) as shown in Fig. 3.6 (d). So the defect state associated with Cd impurity is not strictly localized near the defect and its nearest neighbors, but rather extends to the next NN Se atoms.

The origin (parentage) of this defect state can be understood in terms of the Ga

s bonding-antibonding picture described in the case of pure GaSe. Since there is a considerable mismatch between the energies of the atomic Ga s and Cd s orbitals (-11.15 eV and -7.21 eV respectively), they will not form strong bonding and antibonding states anymore, but the Ga s orbital will rather mix with the p_z states of the neighboring Se atoms. As the result of this hybridization, the Se p_z state is perturbed, pushed up in energy and splits off from the top of the valence band. This defect-induced band becomes partially occupied since the Cd atom substituting for a Ga atom, provides one less electron to the Se network. The dispersion of this band looks qualitatively similar to the highest GaSe valence band. One may therefore confuse this band with the perturbed host band. To make sure that this is indeed a defect state band, one has to increase the size of the supercell and take a look at its dispersion. The increase in the supercell size should decrease the width of the defect band. On the other hand if this band is a perturbed host band its band width will not decrease much and it should show the effect of band folding. These points are discussed below.

As pointed out in the literature (see for example references [95, 157]), in supercell calculations the defects change the host band extrema and one has to correct for this defect-induced change in order to properly estimate the energy of the defect state. We note that in the single defect limit (dilute impurity limit) one expects the host bands to approach the bands of pure GaSe. In order to put the band structures of the defect containing and the defect free supercells in a common energy scale we matched the energies of the Se 3d semicore states calculated in both, the defect containing and pure GaSe. This alignment is based on the assumption that unlike the valence states the energies of core and semicore states do not change in the presence of defects. Other energy scale alignments are also possible [26, 55], but in our all-electron calculation matching some core (or semicore) states seems to be natural choice. We then compare the energy of the defect-induced band to the energy of the valence band of the pure



Figure 3.7: The electronic band structure of GaSe(Cd) along the $\Gamma - A$ direction, calculated with the non-relaxed (a) 3x3x1 and (b) 5x5x2 supercells. The width of the topmost VB decreases from 0.55 to 0.11 eV in going from (a) to (b), indicating that this is a defect level. As a guide to the eye, the topmost VB calculated using the two supercells is enclosed in red rectangles. The host bands show folding (e.g. see the lowest CB) and their dispersion does not change considerably

GaSe at the Γ -point to estimate the energy level of the defect. This method was successfully used in literature; e.g. in Ref. [158] the authors have determined the single electron energy levels at Γ -point and aligned them using some core levels, to study the defects in CdTe.

Our calculation for Cd impurity at the Ga site gives the defect state at 120 meV above the VBM. This value is in fairly good agreement with experimental BE of 130 meV obtained by Shigetomi et al. [41]. However this agreement should be critically examined. There are still several important issues that need to be resolved vis-a-vis *ab initio* calculations of defect BEs using supercell model for GaSe. Whether our identification of the "top most valence band" state with the defect band is justified? How does this band change when the distance between the defects is increased? If the impurity band flattens without appreciably affecting the energy at the Γ -point then our current estimates will be unchanged. If, on the other hand, the impurity band flattens with its average remaining the same then the impurity levels will merge into the valence band, making it a resonant state rather than a bound state, in disagreement with experiment. To check these issues we have performed the calculations using PAW methods in combination with a 5x5x2 supercell (containing 400 atoms) containing one Cd atom on Ga-site. For computational reasons, we did not perform atomic relaxations in this large supercell.

We find that the dispersion of the "top most valence band" decreases dramatically as the distance between the impurities increases from 11.4 Å to 19.3 Å in the xy plane and from 16.17 Å to 32.34 Å along the z-direction. Because of large computation time we only looked at the band structure along the Γ -A direction in the BZ (corresponding to the crystal c-axis), where the dispersion was the largest. As shown in Fig. 3.7, the width of the band decreases from ~ 0.55 eV to ~ 0.11 eV as we double the size of the cell in the z-direction and there is no band folding. The band just below this defect band does not narrow, in fact it broadens, and shows zone-folding that is characteristic of a perturbed host band. We therefore confirm that the top most band as indeed the defect band and it is half filled because divalent Cd replaces a trivalent Ga. To confirm this further we have calculated the charge density associated with this band using the 3x3x1 supercell results and show it in Fig. 3.8. As seen in the figure the defect state extends to the next NN of the Cd impurity and is formed predominantly by the nearest Ga s orbital and the next nearest Se p_z orbital. There is also somewhat smaller contribution from the nearest Se p_z states. This finding is consistent with the partial DOS shown in Fig. 3.6(d).

The energy of the defect level (in the dilute limit) was also estimated from the 5x5x2 supercell calculations by measuring its value at the Γ -point from the Ga 3*d* semicore state and comparing with the VBM of the pure GaSe after matching the Ga 3*d* energies in the two cases. We find it to be 143 meV above the VBM. The Ga



Figure 3.8: Electronic charge density associated with the Cd impurity induced defect band. It extends to the impurity's next NN Se atomn (Se p_z orbitas). The Cd impurity is represented by the red sphere in the figure.

3d states are nearly flat (width ~5meV), therefore even in the limit when we match the extrema of the Ga 3d bands, the defect energy level will not be affected by more than 10 meV. The difference between 3x3x1 and 5x5x2 (120 meV vs. 143 meV) can come from many sources, the dominant one being the neglect of atomic relaxation in the case of the latter.

Substitutional Sn on Ga site (Sn_{Ga}). To analyze the nature of the defect level introduced by the Sn impurity, first we look in Fig. 3.6 (e-h). The contribution to the impurity-induced peak (at 0 eV) of the next nearest Ga s orbital (Ga2 s) is almost 90% less then that of the nearest Ga s (Ga1 s). The former gives ~0.058 states/eV/atom compared to ~0.55 state/eV/atom for the latter. This indicates the strongly localized nature of the defect state and is perhaps the reason why EMA fails badly in this case. The main difference between Cd and Sn is that whereas Cd contributes ~0.275 states/eV near the maximum of the impurity state, Sn contributes



Figure 3.9: Electronic charge density associated with the Sn impurity induced defect band. The contribution to this defect state comes from Sn s and its NN Ga s and Se $p_x + p_y$ orbitals

~0.8 states/eV. This suggests that the Sn donor state is much more localized than the Cd acceptor state, which is consistent with the experimental BEs (0.36 eV for Sn [34] and 0.13, 0.18 eV for Cd [41]). In Fig. 3.9 we show the charge density associated with the impurity-induced band. The defect state is indeed much more localized compared to the Cd acceptor case and is predominantly formed by the Sn s orbital mixed with the nearest neighbor Ga s. In contrast to the case of Cd defect however, the Sn s is mixed with the nearest neighbor Se $p_x + p_y$ orbitals rather than p_z orbital.

In the case of the donor BE, the natural choice of the energy reference for the defect induced gap state would be the CBM. However, the band gap is considerably smaller in the LDA/GGA calculations and in the case of Sn impurity in GaSe, the defect energy level is not sufficiently deep and hybridizes with the bottom of the conduction band. As a result it contains a strong admixture of the conduction band states. This is shown in Fig. 3.10 where we plot the band structure of the Sn doped GaSe showing



Figure 3.10: Electronic band structure of GaSe with Sn impurity on the Ga site, showing the Sn s orbital character. The impurity induced band lies in the CB; therefore it is strongly hybridized with the CB states.

the Sn s orbital character. Due to the underestimation of the band gap, the lowest conduction band dips below the defect level along the $A-\Gamma-M$ direction and makes the impurity band a resonant state rather than a bound state in the gap. It is therefore not possible to extract the binding energy of the defect state associated with the Sn impurity, from the LDA/GGA supercell calculations. Any improved calculation that gives a better estimation of the band gap (i.e. nonlocal exchange models [159]) will also affect the donor energy and hence can give an accurate estimation of the donor BE.

Ga vacancy in GaSe (V_{Ga}) . The nature of the defect states introduced by the Ga vacancy in GaSe is similar to that of Cd substitutional impurity and can be related to the Ga *s* bonding-antibonding scheme. While in the Cd case, there is a large mismatch in the energies of Ga *s* and Cd *s* orbitals, in the case of the vacancy, the Ga dimer bonding and antibonding *s* states cannot appear because of the missing Ga atom. As a result the *s* orbital of the Ga atom nearest to the vacancy will be more like that of a Ga atom rather than that of a Ga dimer. Consequently, the existing hybridization between the dimer bonding and antibonding *s* states with the nearest Se *p* orbitals will be drastically affected. This can not only perturb the Se *p* states in the valence band but also give rise to new states in the gap arising from the conduction band which is also derived from the Se *p* states.

Figure 3.11 (a) shows the band structure of GaSe with Ga vacancy as calculated for a 3x3x1 supercell (Ga35Se36). There are two major changes in the band structure compared to the pure GaSe. First, the states near the top of the valence band are strongly perturbed (bands denoted as D_2 and $D_{3,4}$) and second, a new state appears in the gap ~ 0.66 eV above the perturbed valence band maximum, measured at the Γ -point (denoted as D₁). The Fermi energy cuts the valence band (hole doping). Let us first discuss the parentage of the defect band D_1 , lying in the middle of the gap. This band does not split off from the valence band (occupied states in the pure GaSe). We confirmed this by counting the number of occupied states at the Γ -point. Ignoring the Ga 3d and Se 4s as core states, in the pure GaSe there are 36 Ga 4s(18 bonding and 18 antibonding dimer states) and 90 Se 4p states. The rest 18 Se 4p states are split off from the valence band forming the bottom of the conduction band. The occupied 126 states contain 252 electrons (108 from Ga and 144 from Se). In the presence of a Ga vacancy (Ga35Se36) we find that there are 35 Ga 4s(nominally 17 bonding, 17 antibonding and 1 non bonding) and 90 Se p states. These 125 states accommodate 249 electrons (105 from Ga and 144 from Se) resulting in



Figure 3.11: (a) Electronic band structure of GaSe with Ga vacancy. There is a deep defect state located in the band gap (D_1) as well as a defect induced state at the top of the VB $(D_2, D_{3,4})$. (b) The defect levels D_1 , D_2 and $D_{3,4}$ are shown along the band structure of the pure GaSe

a partially filled valence band. The unoccupied defect state in the gap (D_1) does not come from the valence band but from the conduction band formed out of Se porbitals. To further analyze the nature of this gap state we plot the charge density associated with it, in Fig. 3.12. We see that the defect state is quite localized and just like in the case of Cd impurity most of the contribution to the charge density comes from the nearest Ga s and neighboring Se p_z orbitals with some admixture of Se p_x and p_y orbitals. It is actually an antibonding combination of Ga 4s and 4p and p states of neighboring three Se atoms.

We next discuss the vacancy induced changes in the states near the top of the valence band. We have seen a large inward relaxation of Ga and Se atoms surround-





Figure 3.12: Electronic charge density associated with the Ga vacancy-induced defect band D1. The contribution to the charge density comes from the Ga s and Se pz orbitals from the vicinity of the vacancy.

ing the vacancy (see Section 3.4.1) and this should change the local bonding. In Fig. 3.11(a) we see that there are three bands which appear to split off from the rest of the valence band with a small overlap near the A-point. Two of these three bands (D_{3,4}) are relatively flat where as the third one (D₂) has a large dispersion along Γ -A (z-direction). Band D₂ is above the other two at the Γ -point. In fact the two flat bands are dispersionless along Γ -A. Whether these three bands are impurity-induced bands or simply perturbed host bands is an important question. To address this issue we have done a 5x5x2 supercell calculation. Again due to large computation time we have calculated energies at three symmetry points Γ , A, and M. We find that band D₂ flattens out considerably (width ~0.08 eV). The other two also flatten but appear to overlap with folded perturbed host bands and it is not easy to see whether they are split off from the rest of the valence band states or not. We will therefore focus on the defect state D₂, which splits off from the rest of the valence bands.

Following the method described for the Cd impurity and using the energies at the Γ -point obtained in 3x3x1 supercell, we find two defect-induced energy levels in the gap region: one acceptor level at ~0.26 eV (D₂, which splits off from the valence band and is partially occupied) and one at $\sim 0.92 \text{ eV}$ (D₁, which drops down from the conduction band and is unoccupied) above the VBM of the pure GaSe. This is visible in Fig. 3.11 (b) where we plot the bands D₁, D₂, D_{3,4} along with the band structure of pure GaSe. To plot these two band structures in a common energy scale, as discussed before, we matched the energies of the Ga 3*d* semicore levels, calculated in the pure and defect containing supercells. The acceptor level at 0.26 eV seems to compare well with the hole trapping level measured by Micocci et al. [138] in nonintentionally doped p-GaSe at 0.2 eV. Since the parentage of this level is the occupied valence band state DFT calculation may be somewhat more reliable regarding the energy position of the defect level. In addition to this level Micocci et al. [138] also found a trapping level at ~ 0.8 eV above the valence band maximum. These defect levels were tentatively assigned to Ga vacancy and to some extended defect region (stacking fault or dislocation) respectively. Whether the defect level we find at 0.92 eV has something to do with that found at 0.8 eV needs further investigation.

Se vacancy in GaSe (V_{Se}). In contrast to the Ga vacancy, the Se vacancy does not remove the Ga *s* dimer states. So the physics of defect formation in this case is quite different. In the presence of a Se vacancy three *p* states associated with the Se atom which was occupying the vacancy site are removed. The net effect is (i) a reduction in the number of Se *p* states along with the loss of 4 Se valence electrons and (ii) the change in the vacancy's nearest neighbor Ga dimer states and Ga *p* states. Fig. 3.13(a) shows the electronic structure obtained for the 3x3x1 supercell of GaSe containing one Se vacancy (Ga36Se35). There are two major changes in the band structure compared to the pure GaSe. First, two defect levels (D₁, D₂) drop down from the conduction band, one of them (D₂) has a very large dispersion along the Γ -M direction compared to the other. These two defect bands overlap with the bottom of the conduction band at the Γ -point. Second, the top valence band splits



Figure 3.13: (a) Electronic band structure of GaSe with Se vacancy. There are two defect levels (D₁ and D₂) in the band gap (hybridized with the CB) as well as a defect induced state (D₃) at the top of the VB. (b) The three defect levels D₁, D₂ and D₃ are shown along with the band structure of Pure GaSe, after matching the Ga 3d semicore levels of the pure and vacancy containing GaSe. We have also shifted the CB of GaSe upwards until the band gap reached the experimental value (~2.05 eV)

off (but with a small overlap) from the rest of the valence bands. We will denote it as D_3 . Fermi energy is above D_3 but below D_1 and D_2 . To understand the parentage of these vacancy-induced states we again do the band counting as we did for the Ga vacancy. We find that removal of one Se removes 3 Se *p* states, two of which come from the valence band and one from the conduction band. Since the removal of Se takes away 4 electrons the valence band is filled and the Fermi energy lies above the valence band. In order to understand the nature of D_1 , D_2 , and D_3 further we replot these bands along with the band structure of pure GaSe in Fig. 3.13(b) by matching



Figure 3.14: (a) Electronic charge density associated with the defect bands D_1 and D_2 showing the *s* character of the Ga atoms closest to the vacancy. (b) The charge density associated with the band D_3 . This state extends to the vacancy's next NN atoms and shows Ga *s* and Se p_z orbital character.

the Ga 3d semicore energies of pure GaSe and the one with Se vacancy. Also to show the two levels D_1 and D_2 clearly we have shifted the conduction band of GaSe upwards to match the experimental value of the gap (~2.05 eV). In Fig. 3.14(a) we plot the charge densities associated with the bands D_1 and D_2 ; they are hybridized Ga s states associated with the three nearest-neighbor Ga atoms of the Se vacancy. In Fig. 3.14(b) we show the charge density associated with D_3 ; this is not strictly localized, but rather extends to the vacancy's next nearest neighbor Se and Ga atoms. The contribution to the charge density comes from p_z and s orbitals of the next nearest neighbor Se and Ga atoms of the Se vacancy, respectively.

According to the experimental result of Micocci et al. [34], Se vacancies produce electron trapping centers with energy 520 meV below the conduction band minimum. In Fig. 3.13, the deep defect states D_1 and D_2 at Γ -point are degenerate and lie ~1.1 eV above the valence band maximum. If we compare this energy with that of the shifted conduction band minimum we find that these two defect states are ~0.95 eV below the conduction band minimum. It is tempting to identify these two states with the electron trapping centers. But for a quantitative understanding one needs to do a theory (going beyond local DFT) which not only treats the band gap problem correctly but can be extended to the case of defect states. In general, nonlocal exchange and correlation which appear to improve the band gap will also affect the nature and position of the defect state, particularly for those defects which form out of the conduction band states.

3.5 Summary

In summary we have carried out both hydrogenic effective mass (EMA) and ab initio electronic structure calculations within density functional theory using supercell method for Cd and Sn impurities in GaSe. We have also studied the nature of defect states introduced by Ga and Se vacancies For both donor (Sn) and acceptor (Cd) we find that compared to experiment, the EMA results give lower values of BE (ranging from a factor of 4 to 2) suggesting large corrections and the necessity of incorporating short-range interactions to the EMA. This has been done using ab initio DFT calculations using GGA. The general features of the Ga-site defect states (impurities or vacancy) can be understood using the Ga dimer bonding and antibonding s states and how they interact with the Se states. In the presence of substitutional atoms or vacancies at the Ga sites these dimer states are drastically changed and give rise to localized defect states. In the case of the acceptor impurities (Cd on Ga site and Ga vacancy) we have calculated the energy levels of the defect states with respect to the VBM (at the Γ point) of pure GaSe after matching the energies of the electronic core states. These results should be more reliable since LDA/GGA gives a correct description of the VBM. In fact, the acceptor BE values thus obtained are found to be in reasonable agreement with experiment. In contrast, the position of the defect states arising from donors (as in the case of Sn) or those split off from the conduction band in the presence of vacancies (both Ga and Se) cannot be given reliably because of the problems associated with the band gap and excited states calculated with LDA/GGA. However by going to larger supercells one can distinguish between the defect states from the perturbed host states and analyze the nature of these defect states such as their charge densities, bonding, and localization etc. This has been successfully done in the case of a variety of defects in GaSe.

Chapter 4

Electronic structure of isovalent impurities in GaSe

4.1 Introduction

As we discussed in the previous chapter, the layered GaSe crystal is a highly efficient nonlinear optical material, with applications in second harmonic generation, frequency mixing, generation and detection of terahertz radiation [3, 131, 160, 161]. However, the mechanical properties (hardness and cleavability) of GaSe are unsatisfactory: nearly zero hardness by Mohs scale¹ and enhanced cleavability along planes parallel to the atomic layers [162]. Furhermore the nonlinear properties are difficult to reproduce from sample to sample [160]. All these properties hamper the use of large GaSe crystals in practical applications. Improved crystal quality and secondharmonic generation has been reported in GaSe doped with In [162–165]. Further attempts were made to improve the optical, thermal and mechanical properties GaSe,

¹The Mohs scale of mineral hardness characterizes the scratch resistance of various minerals through the ability of a harder material to scratch a softer material. The scale is based on ten minerals that are all readily available. As the hardest known naturally occurring substance when the scale was designed (1812), diamonds are at top of the scale. For comparison, on the Mohs scale, a pencil "lead" (graphite) has a hardness of 1; a fingernail, 2.5; a copper penny, about 3.5; a knife blade, 5.5; window glass, 5.5; and a steel file, 6.5.

by doping it with Ag and mixing it with AgGaSe₂ [165].

Despite the considerable amount of experimental work, there is a lack of theoretical approach to the subject which deals with the electronic, optical and mechanical properties of GaSe doped with isovalent impurities (Te and In). In this chapter we investigate the elastic properties of $GaSe_{1-x}Te_x$ and $Ga_{1-x}In_xSe$ as a function of the composition x, and examined the electronic structure of several point defects and defect complexes associated with Te and In doping in GaSe.

4.2 Computational method

The results presented in this chapter have been obtained using the projector augmented wave (PAW) [142, 166] method, within density functional theory (DFT) as implemented in the Vienna *Ab-initio* Simulation Package (VASP) [144–147]. The exchange-correlation potential was approximated by the Ceperley-Adler local density approximation (LDA) [167]. This exchange-correlation potential was chosen over the gradient corrected version (GGA) because it is known that GGA underestimates the binding energies, which results in an overestimation of the lattice parameters. As we have seen in Chapter 3, since the interaction between the atomic layers of GaSe is week, van der Waals type, the "GGA effect" becomes much more significant in the direction perpendicular to the atomic layers, resulting in at theoretical structure which is overly elongated in the direction of the crystallographic c-axis. This elongated structure would be inappropriate for the theoretical investigation of the elastic properties of GaSe.

In all calculations the outer s, p, d orbitals of the Ga and In atoms as well as the s and p orbitals of the Se and Te were included in the valence states, while the rest were treated as core states. The cut-off energy for the plane wave basis was set to 300 eV and the convergence of self-consistent cycles was assumed when the energy

difference between them was less than 10^{-4} eV.

To explore the effect of the isovalent impurities on the physical properties of GaSe the dopant atoms were placed at several substitutional (Te_{Se} , Te_{Ga} , In_{Ga}) and interstitial (Te_i , In_i) sites inside the host matrix. In addition, we have also examined the electronic structure and defect formation energies associated with substitutional indium - gallium vacancy complex ($In_{Ga}-V_{Ga}$).

Before discussing the details of electronic structure and elastic stiffness calculations, we briefly review the elastic constants of GaSe, which has hexagonal symmetry. A crystal with hexagonal symmetry is characterized by 5 elastic constants: C_{11} , C_{12} , C_{13} , C_{33} and C_{44} . We have determined linear combinations of these quantities from total energy calculations for five different strain configurations [168]. When the lattice is distorted by a small strain, the lattice vectors change according to:

$$\mathbf{a}' = (\mathbf{I} + \boldsymbol{\epsilon}) \, \mathbf{a} \tag{4.1}$$

where **a** and **a'** are matrices that contain the components of the old and new lattice vectors, **I** is the identity matrix and ϵ is the strain matrix, which has the form:

$$\boldsymbol{\epsilon} = \begin{bmatrix} e_1 & \frac{1}{2}e_6 & \frac{1}{2}e_5 \\ \frac{1}{2}e_6 & e_2 & \frac{1}{2}e_4 \\ \frac{1}{2}e_5 & \frac{1}{2}e_4 & e_3 \end{bmatrix}$$
(4.2)

The specific strain configurations along with the corresponding energy densities used to determine the elastic moduli of the hexagonal $GaSe_{1-x}Te_x$ and $Ga_{1-x}In_xSe$ are listed in Table 4.1.

In order to calculate of the elastic constants of $\text{GaSe}_{1-x}\text{Te}_x$ (x = 0, 0.0625, 0.25) and $\text{Ga}_{1-x}\text{In}_x$ Se (x = 0, 0.0625, 0.25, 1) we have computed the theoretical crystal structures by minimizing the total energies with respect to the lattice constants

Table 4.1: Strains and elastic moduli for crystals with hexagonal symmetry. ΔE is the change in energy due to the specific strain and V₀ is the equilibrium unit cell volume.

Strain configuration (unlisted $e_i = 0$)	Energy density $(\Delta E/V_0)$
$e_1 = e_2 = \delta$	$(C_{11}+C_{12})\delta^2$
$\mathbf{e_1} = \mathbf{e_2} = -2\mathbf{e_3} = \delta$	$(C_{11}+C_{12}-4C_{13}+2C_{33})\delta^2$
$e_3 = \delta$	$1/2 imes (\mathrm{C_{33}}) \ \delta^2$
$e_6 = \delta$	$1/4 \times (C_{11} - C_{12}) \delta^2$
$e_4 = e_5 = \delta$	$(C_{44}) \delta^2$

(at each concentration x): first with respect to the volume of the unit cell keeping the c/a ratio fixed and then with respect to c/a keeping the previously obtained equilibrium volume constant. The elastic constants of $GaSe_{1-x}Te_x$ (x = 0, 0.25) and $Ga_{1-x}In_xSe$ (x = 0, 0.25, 1) were obtained using small unit cells (8 atoms/cell) and the Brillouin zone (BZ) was sampled by a Γ -centerd 12x12x3 k-mesh. In the case of x = 0.0625 the calculations were performed on 2x2x1 supercells with the BZ sampled by a 6x6x3 grid of k-points.

The electronic structure and defect formation energies were calculated using 3x3x1 supercells with the theoretical lattice constants of GaSe and the integration of the BZ was carried out on a Γ -centered, 4x4x3 set of k-points. The 3x3x1 supercells containing one impurity correspond to a composition of $x \simeq 0.028$. For all the calculations described in this chapter the internal structural parameters were fully relaxed until the Hellmann-Feynman forces were less than 0.02 eV/Å.

4.3 Theoretical crystal structure

The calculated equilibrium lattice parameters of $GaSe_{1-x}Te_x$ and $Ga_{1-x}In_xSe$ are listed in Table 4.2, along with other available theoretical [25, 26] and experimental [140] data. We observe a monotonic increase in the lattice constants as the concentration of the impurities (x-value) increases. This is not surprising because the

Compound	x		a (Å)	c (Å)	c/a	d_{Ga-Ga}/c	d_{Se-Se}/c
$ ext{GaSe}_{1-x} ext{Te}_x$	0	Pres. calc. Ref. $[25]^a$ Ref. $[26]^a$ Ref. $[140]^b$	3.715 3.724 3.720 3.755	15.77 15.68 15.62 15.94	4.244 4.21 4.199 4.245	0.153 0.150 0.154	0.300 0.350 0.302
	0.0625	Te _{Se} Te _i	3.733 3.654	$\begin{array}{c} 15.85\\ 17.28\end{array}$	4.246 4.730		
	0.25	Te _{Se}	3.801	15.99	4.207		
	0.0625	In _{Ga} In _i	3.730 3.800	$15.81 \\ 15.87$	4.239 4.176		
$Ga_{1-x}In_xSe$	0.25	In _{Ga}	3.773	15.93	4.233		
	1	Pres. Calc. Ref. $[140]^b$	3.972 4.005	16.49 16.64	4.151 4.155		

Table 4.2: Optimized theoretical lattice parameters of $GaSe_{1-x}Te_x$ and $Ga_{1-x}In_xSe$. (*a*theory; *b*experiment)

sizes of the dopant atoms (In and Te) are larger compared to the host atoms. In the case of the end compounds GaSe and InSe the theoretical lattice constants are less than 3% smaller compared to experiment, while the c/a ratios are within 0.7% of the experimental values. The underestimation of the lattice parameters is due to the well-known overbinding effect of LDA. It has been shown that in GaSe_{1-x}Te_x a phase transition takes place from hexagonal (GaSe) to monoclinic (GaTe) structure in the composition range 0.26 < x < 0.60 [169]. Thus in the case of GaSe_{1-x}Te_x we have limited our calculations to the maximum value of x = 0.25, because the comparison between the elastic constants of the monoclinic and hexagonal lattices not quite meaningful.

4.4 Elastic properties of $GaSe_{1-x}Te_x$ and $Ga_{1-x}In_xSe$

To determine the elastic constants, we have calculated the total energies of the strained $GaSe_{1-x}Te_x$ (x = 0, 0.0625, 0.25) and $Ga_{1-x}In_xSe$ (x = 0, 0.0625, 0.25, 1) crystals for δ between -0.03 and 0.03 and fit the results to a second order polynomial. The calculated elastic constants are given in Table 4.3, along with previously calculated theoretical [25, 26] results and experimental [170, 171] data. The earlier theoretical calculations were performed using norm conserving pseudopotential and plane wave (PW) basis set [25] and full-potential augmented plane-wave method with local orbitals (APW+lo) [26]. Our calculated values of the elastic moduli of GaSe and InSe using the PAW method are in overall good agreement with the available experimental values and earlier theoretical calculations.

In the case of the Te doping we do not observe a systematic change in the elastic constants with the dopant concentration. For example C_{11} increases by ~0.3% as concentration goes from x = 0 to x = 0.0625 but when the dopant concentration is further increased (x = 0.25), the elastic modulus C_{11} decreases by more than 6% compared to the original value. Similar changes are observed for all other elastic moduli, except for C_{44} , which behaves in an opposite way: first it decreases and then increases as the dopant concentration grows. The unsystematic changes in the elastic constants of $GaSe_{1-x}Te_x$ might be related to the structural phase transition from hexagonal to monoclinic structure, which takes place in the compositions between 0.26 < x < 0.60 [169]. At the concentration of at x = 0.25, which is close to the lower end of the transition range, the hexagonal phase might be unstable with respect to the monoclinic one, thus the elastic constants obtained at this composition might not be realistic.

In the case of substitutional In impurity on Ga site, we observe a systematic

	x		C ₁₁	C ₁₂	C ₁₃	C ₃₃	C ₄₄	$C_{11} + C_{12}$	$C_{11} - C_{12}$
	0	Pres. calc.	100.9	27.0	9.7	33.9	8.3	127.9	73.8
e_x		Ref. [25] ^a			12.4	35.4		130.2	
$GaSe_{1-x}T$		Ref. [26] ^a			13.4	34.4		127.9	
		Ref. $[170]^{b}$			12.2	35.7		132.5	
		Ref. [171] ^b	105.0	32.4	12.6	35.1	10.4	137.4	72.6
	0.0625	Te _{Se}	101.2	27.3	10.5	34.3	8.2	128.5	73.9
	0.25	$\mathrm{Te}_{\mathrm{Se}}$	94.5	25.3	10.5	32.2	11.5	119.8	69.2
$\operatorname{Ga}_{1-x\operatorname{In}_x\operatorname{Se}}$	0.0625	In _{Ga}	99.2	27.1	10.5	34.7	8.8	126.3	72.1
	0.25	In _{Ga}	91.3	25.6	11.4	36.1	9.7	116.9	65.7
	1	Pres. calc.	70.3	23.5	14.2	38.5	11.5	93.9	46.9
	L	Ref. [171] ^b	73.0	27.0		36.0		100.0	46.0

Table 4.3: Elastic contants of $GaSe_{1-x}Te_x$ and $Ga_{1-x}In_xSe$. All values are given in GPa. (^atheory; ^bexperiment)

change in the elastic constants with defect concentration as shown in Fig. 4.1. The changes in the elastic moduli of $Ga_{1-x}In_xSe$ depend linearly on the concentration of In. On the one hand, we observe a monotonic decrease in C_{11} and C_{12} as the x-value increases, but on the other hand, the elastic constants C_{13} , C_{33} and C_{44} reveal steady enhancements with the increase in dopant concentration. This indicates that when In impurity occupies Ga sites, the crystal becomes softer in the a- and b-directions (parallel to the atomic layers) and stiffer along the c-axis (perpendicular to the atomic layers).

The "Vegard-law type" behaviour [172] of substitutional In impurity on the elastic properties of GaSe can be understood if we examine the connection between structural and electronic properties of the end-compounds: GaSe and InSe. The elasticity of the layered $Ga_{1-x}In_xSe$ in the c-direction is determined predominantly by the interaction between the atomic layers. The electronic structure of the III-VI layered compounds is discussed in detail in several earlier reports (e.g. Ref. [173]); however for an easier comparison between GaSe and InSe we also show the calculated band structures in


Figure 4.1: The elastic constants of $Ga_{1-x}In_xSe$ depend linearly on the composition. The increase in C_{13} , C_{33} and C_{44} suggests the strengthening of GaSe in the direction perpendicular to the atomic layers as the concentration of In increases

Fig. 4.2. First let us analyze the top of the valence band (VB), which is mainly of Se p_z character. Since the Se atoms are facing the interlayer region, we expect that the dispersion of the top VB along the Γ -A direction to be sensitive to the interlayer interaction. Indeed, according to our calculated band structure, the Γ -A dispersion of the top VB increases by ~40 meV (see Fig. 4.2), in going from GaSe to InSe, indicating that the interlayer interaction is stronger in InSe compared to GaSe. This is consistent with the smaller interlayer separation between Se-monoatomic sheets in InSe (2.96 Å) than in GaSe (3.15 Å). Thus, when the concentration of In substitutional impurities increases, the interlayer Se-Se distance becomes smaller, the interaction becomes stronger, and as a consequence, the crystal becomes stiffer in the direction perpendicular to the atomic layers.

The softening of $Ga_{1-x}In_xSe$ in the a- and b-direction with the increase in the



Figure 4.2: The calculated band structures of GaSe and InSe. $A-\Gamma$ and $\Gamma-M$ directions are perpendicular and parallel to the atomic layers respectively.

composition x, can also be easily understood, because the intralayer distances are longer and therefore the intralayer covalent bonds are weaker in InSe than in GaSe [22,24]. Inspecting Fig. 4.2 we observe that indeed, the lower lying valence bands of InSe, with predominantly Se p_x and p_y character, disperse less in the Γ -M direction compared to the corresponding bands of the GaSe. Given that in the a- and bdirections there are no "interlayer regions" which could counteract the weakening of the atomic bonds, the crystal becomes softer as the In concentration increases. Although the substitutional In impurity seems to enhance the elastic properties of GaSe along the c-axis, the effect is rather small (e.g. C₃₃ increases by 7.8% from GaSe to InSe). So, we we have to look for different mechanisms for In induced interlayer rigidity enhancement as seen experimentally [162-165]. This aspect will be discussed later, in Section 4.8. But before this we discuss the formation energies of different defects to find out which defect is more likely to be present in GaSe.

4.5 Formation energies and electronic structure of defects

In order to identify the preferred location of the impurities inside the GaSe matrix, we calculate the formation energies of the Te and In defects located at different substitutional and interstitial sites. The formation energies and charge transition levels are calculated using the formalism described Section 2.4.2.

As pointed out in Section 2.4.4, an important parameter in supercell calculations is the position of VBM, which is usually considered to be the reference for the electron chemical potential. In the present calculations E_{VBM} was determined as the average of the one-electron energy level of the VBM over the k-points where the total energy was calculated. As pointed out S. B. Zhang [128] this approach has the advantage that transition levels calculated this way (from total energy differences) are consistent with the single-particle energy levels. Furthermore, the band gap of GaSe calculated with the "average band-edge" approach ($E_{\text{gap}}^{\text{average}} = 1.68 \text{ eV}$), is closer to the experimental value ($E_{\text{gap}}^{\text{exp}} = 2.13 \text{ eV}$) than the direct gap located at Γ -point ($E_{\text{gap}}^{\Gamma} = 0.85 \text{ eV}$). The transition levels associated with the various defects in GaSe are calculated using Eq. (2.53).

Equation (2.52) shows that the formation energies of the defects depend on the chemical potential (μ) of the constituents as well as on the charge state (q) of the defect. The values achievable by the chemical potentials are limited by several conditions (see Section 2.4.3): (a) to avoid precipitations, μ_i 's must be negative and (b) to maintain a stable host compound, the chemical potential must satisfy $\mu_{\text{Ga}} + \mu_{\text{Se}} = \Delta H(\text{GaSe})$, where $\Delta H(\text{GaSe})$ is the formation enthalpy of GaSe. Our



Figure 4.3: (a) Formation energies of Te impurity in GaSe. For all values of E_F within the band gap, Te prefers to occupy the Ga site. (b) Formation energies of In impurity in GaSe. When E_F is very close to VBM, the In impurity becomes positively charged (+3) and moves to the interstitial site.

theoretical calculation gives $\Delta H(\text{GaSe}) = -1.12$ eV. In order to avoid secondary phase formation between the host elements and impurities, we can impose some further conditions on the chemical potentials of the defects as described in Section 2.4.3. However, the effect of these conditions would be a constant shift in the formation ener-

Defect	$\Delta E(X^0)$	Transition levels (measured from the VBM)					
		$\varepsilon(+3/+2)$	$\varepsilon(+2/+1)$	$\varepsilon(+1/0)$	$\varepsilon(0/-1)$	arepsilon(-1/-2)	ϵ (-2/-3)
Tese	0.65		0.08	0.34	1.45	1.62	
TeGa	2.07		0.13	0.45	0.72	1.11	
Tei	3.58		1.04	0.70	1.01	1.28	
In _{Ga}	0.28	-0.10	-0.02	0.28			
Ini	1.89	0.34	0.41	1.41			
$In_{Ga}-V_{Ga}$	1.76				0.39	1.71	2.10

Table 4.4: Formation energies of neutral defects and the charge transition levels. All values are given in eV.

gies and since we are only interested in the relative formation energies associated with the same dopant located at different lattice sites (i.e. we do not compare In induced defects to Te induced ones), we can consider for all cases $\mu_{def} = \mu_{Te} = \mu_{In} = 0$. The calculated formation energies are represented as a function of E_F in Fig. 4.3 (a) and (b) for Te and In impurities, respectively In these figures both the theoretical $(E_g^{\text{theor}} = 1.68 \text{ eV})$ and experimental $(E_g^{\text{exp}} = 2.13 \text{ eV})$ band gaps are indicated. The calculated defect transition levels $\varepsilon (q/q')$ and formation energies $\Delta E (X^q, q = 0)$ are listed in Table 4.4.

4.6 Te induced defects

For the case of Te doping we have considered the configurations with Te located at Se and Ga sites as well as at the interstitial site. The interstitial configuration with the lowest energy was found when the impurity atom was located midway between the Ga-Se-Se-Ga layers at equal distances from the 6 nearest neighbor (NN) Se atoms.

The formation energies of the Te induced defects, under Se-rich growth conditions $(\mu_{\text{Se}} = 0, \mu_{\text{Ga}} = -1.12 \text{ eV})$ are represented in Fig. 4.3(a). The lowest formation energy occurs when the Te atom is located at Se site (Te_{Se}). In neutral charge state the calculated formation energy of Te_{Se} is $\Delta H_f(\text{Te}_{\text{Se}}^0) = 0.65 \text{ eV}$. When the

Fermi energy (E_F) is closer to the valence band (VB)(p-type sample), Te_{Se} becomes positively charged, and gives rise to two charge transition levels located at $\varepsilon(+2/+1) = 0.08$ eV and $\varepsilon(+1/0) = 0.34$ eV above the VBM. Photoluminescence and Hall effect measurements have shown that the carrier transport in p-GaSe doped with Te, is dominated by two acceptor levels at 0.08 and 0.02 eV above the VB [32,39]. Our calculated $\varepsilon(+2/+1)$ transition level is in excellent agreement one of the experimental values. When the Fermi energy (E_F) is close to the conduction band (CB)(n-type conductivity), Te_{Se} becomes negatively charged, the transition levels being located at $\varepsilon(0/-1) = 1.45$ eV and $\varepsilon(-1/-2) = 1.62$ eV above the VBM.

The formation energies of the substitutional Te atom at the Ga site (Te_{Ga}) is slightly higher compared to Te_{Se}. However, when the defect is -2 charge state (Te_{Ga}⁻²), the difference between the formation energies ΔH_f (Te_{Se}⁻²) and ΔH_f (Te_{Ga}⁻²) becomes small (~ 0.18 eV) suggesting that under Se-rich growth conditions, Te atoms can fill up the Ga vacancies. Under Ga-rich conditions, according to Eq. (2.52), the formation energy of Te_{Ga} defect is shifted up by 1.12 eV, making it less likely for Te to occupy Ga site. This is not surprising because under Ga-rich conditions, there are less Ga vacancies available.

The interstitial Te defect (Te_i) has the highest formation energy therefore it is less likely to occur. As shown in Fig. 4.3(a), the formation energy of the defect in neutral charge state $\Delta H_f(\text{Te}_i^0)$ is almost 3 eV higher compared to $\Delta H_f(\text{Te}_{\text{Se}}^0)$, and the difference becomes somewhat smaller when Te_i is in doubly charged negative (Te_i⁻²) or positive (Te_i⁺²) state. However, according to recent experimental results of Evtodiev et al. [32] at high Te doping concentration, part of the Te atoms localize in the interstitial sites within the interlayer region. Therefore we cannot exclude the possibility that the Te atoms can occupy interstitial sites, which clearly would affect the cleavability of the GaSe crystal. It is also interesting to note that the Te related defects can behave as either donor or acceptor, depending on the position of E_F relative to the band edges.

4.7 In induced defects

We have studied three types of In induced defects, In substituting for Ga (In_{Ga}) , interstitial In (In_i) , and substitutional In - Ga vacancy complex $(In_{Ga} - V_{Ga})$. In Fig. 4.3(b) we show the calculated formation energies as a function of E_F for In induced defects in GaSe, in different charge states. We find that the formation energy of In_{Ga}^0 is 0.28 eV and there is one charge transition level associated with this defect: $\epsilon(+1/0) = 0.28 \text{ eV}$ above the VBM. This value is in fairly good agreement with the acceptor level at 0.21 eV, measured by Cui et al. using deep level transient spectroscopy (DLTS) [31]. This, along with the result for Te_{Se} discussed earlier, gives us confidence in our total energy calculations using DFT and the supercell model to understand the defect physics.

The defect states with lowest formation energies are: \ln_i^{3+} for $E_{\text{VBM}}(=0 \text{ eV}) \leq E_F \leq 0.135 \text{ eV}$, \ln_{Ga}^{1+} for $0.135 \text{ eV} \leq E_F \leq 0.28 \text{ eV}$ and \ln_{Ga}^0 for $0.28 \text{ eV} \leq E_F$. \ln_{Ga}^0 is the most stable defect for a wide range of E_F . However when the Fermi energy is tuned towards the VBM energy, \ln_i^{3+} defect becomes most stable. We will discuss the underlying physics of this change by examining the single particle density of states, in the next paragraph. As regards the effect of \ln_{Ga}^0 defect on the electronic structure, we find that the band structures near VBM and CBM are affected very little. One therefore does not expect much change in the transport properties in In doped GaSe if the impurity goes to a Ga site in the neutral charge state. One can understand this lack of significant change by looking at the In 5s-Ga4s dimer antibonding state (which hybridizes with the Se p bands to give rise to states in the neighborhood of the band gap) and observe that it is not significantly different from the Ga4s-Ga4s dimer antibonding state (see Section 3.3.2).



Figure 4.4: The total DOS of GaSe with In_i and the projected DOS of the In s-orbital showing the positions of the HDDS (-5.5 eV) and DDS (just above E_F) introduced by the charged In_i defect.

To understand why \ln_i^{3+} has the lowest formation energy when $E_F \leq 0.135 \text{ eV}$, we look at the electronic structure, the single particle density of states (DOS) and the nature of defect state introduced by In_i. Figure 4.4 gives the total and partial (associated with In s) DOS for this case. We see that In_i introduces a hyper deep defect state (HDDS) near the bottom of the Se p bands (at ~ -5.5 eV). It is a bonding state formed out of In 5s and neighboring Se p states. The corresponding antibonding state splits off from the Se p valence band states and is denoted as the deep defect state (DDS). The charge density distribution associated with the DDS is represented in Fig. 4.5 showing this state is indeed an antibonding combination of the In s and the surrounding Se p orbitals. This picture is very close to what happens when In is a substitutional defect in PbTe [97]. The strong mixing between In 5s and the neighboring Se p states leads to the removal of one state (per spin) from the Se p band which becomes the DDS. In terms of electron counting, two of the three



Figure 4.5: Charge density distribution associated with the localized band introduced by In_i in the band gap of GaSe. The dominant contribution comes from the In sorbital, hybridized with the NN Se p_z orbitals.

electrons from In occupy the HDDS and the three electrons (two from the electrons occupying the valence band in pure GaSe and one from In) fill the DDS and partially occupy the conduction band. Thus In_i acts like a donor. Since the three electrons occupy states with energies larger than E_{VBM} , clearly the formation energy of In_i in charge state q = 0, 1, and 2 are higher than In_{Ga} for which neither the band structure nor the electron count change. By removing three electrons from In_i to obtain q = 3 charge state we can lower its formation energy².

Figure 4.3(b) also shows the calculated defect formation energy associated with the substitutional In-Ga vacancy complex ($In_{Ga} - V_{Ga}$). In the neutral charge state, the formation energy of this defect complex is relatively high. However, as the position of the E_F moves up in energy across the band gap, $In_{Ga} - V_{Ga}$ becomes negatively charged and its formation energy decreases considerably. Within the theoretical band gap we find one transition level associated with this defect complex, located at $\varepsilon(0/-1) = 0.40$ eV. This is in fact in good agreement with the acceptor level at 0.44 eV,

 $^{^2 \}rm The$ formation energy of neutral In interstitial defect is underestimated in our calculation since on electron/defect occupies the bottom of the conduction band and the LDA gap is 0.85 eV compared to the average band gap of 1.68 eV and the experimental value of 2.13 eV.



Figure 4.6: The total density of states associated with $\ln_{Ga} - V_{Ga}$ defect complex, for different charge states. When the defect complex is triply negatively charged, the defect state is located in the gap (lower panel).

measured using DLTS and assigned to $In_{Ga} - V_{Ga}$, by Y. Cui et al. [31]. As shown in Fig. 4.3(b) the other two calculated transition levels of $In_{Ga} - V_{Ga}$ are located above the theoretical CBM, but within the experimental gap. The values are also listed in Table 4.4.

To obtain a better understanding of the nature of the defect states introduced by $In_{Ga} - V_{Ga}$, we calculated the total DOS associated with this defect complex in different charge states. As shown in Fig. 4.6, the DOS reveals an interesting feature which is only present for the -3 charge state: a localized level appears in the gap (indicated by the arrow). The origin of this defect state can be understood from a careful analysis of the relationship between the ionic relaxation and the bonding of In and its NN Se atoms. From the charge density distribution shown in Fig. 4.7 we see that the defect state in fact corresponds to the antibonding combination of In s and its NN Se p_z orbital, the dominant contribution coming from the In s orbital. To locate



Figure 4.7: Charge density distribution associated with the localized band introduced by $\ln_{G_a} - V_{G_a}$ in the band gap of GaSe. The dominant contribution comes from the In *s* orbital, hybridized with the NNS ep ₂ orbitals.

the corresponding bonding combination, we have calculated at the partial density of states associated with the In s orbital. This is represented in Fig. 4.8 where we have plotted the In s partial DOS corresponding to the neutral and -3 charge states of $In_{Ga} - V_{Ga}$. The origin of the energy scale was chosen at the highest occupied energy state. We notice that the splitting between the bonding and antibonding levels decrease by ~ 1.5 eV as the defect complex becomes triply negatively charged. To pin down the cause of this energy shift, we have examined the differences between the ionic relaxations of neutral and triply charged systems. We found that independently of the charge state, the In atom prefers to occupy the position located at the center of the Ga-Se-Se-Ga atomic layer, at equal distances from the 6 NN Se atoms (see Fig. 4.7). However, the distances between In and its NN Se atoms increase as more negative charge is localized at the defect center. This is due to the increasingly stronger Coulomb repulsion between the In ion and the neighboring Se anions. We find that the average In–Se distance increases by ~ 0.34 Å as the state of the defect center changes from neutral to the triply negatively charged. The splitting between the In s – Se p_z bonding and antibonding states becomes smaller as the separation



Figure 4.8: The DOS projected on the In s orbital for the neutral and -3 charge state of the $In_{Ga} - V_{Ga}$ defect complex. The splitting between the bonding and antibonding states decreases mainly because the distance between the In and Se atoms increases.

between the atoms becomes larger. Consequently, at -3 charge state (when the In–Se distance is the largest), the energy of the antibonding state becomes small enough such that it appears to be located in the band gap of GaSe. For all the other charge states the In s – Se p_z antibonding combination is resonant in the CB. One of the important predictions of our calculation is the presence of a deep defect state just above the valence band maximum when In is present as an interstitial defect (see Fig 4.4). Deep level spectroscopy should be able to see this defect.

4.8 Rigidity enhancement of GaSe by In doping

As we have seen in Section 4.4 the elastic constants do not change appreciably in In doped GaSe when In goes as a substitutional impurity. This is also seen in the calculations of energy barrier associated with relative shearing of two atomic blocks



Figure 4.9: The energy barrier which must be overcome in order to cleave the GaSe crystal increases dramatically when In occupies the interstitial site compared to the case when In occupies substitutional site. For comparison the case of pure GaSe is also shown. The asymmetry of the energy barrier associated with In_{Ga} is due to the geometry of the 2x2x1 supercells considered in the calculations: while in the case of the pure GaSe and In_i the atomic configurations are symmetrical with respect to the relative displacement of the atomic layers by d/a = 0.5, in the case of In_{Ga} the atomic configuration is only symmetrical with respect to the displacement of d/a = 1.0.

(each block being made up from 4-atomic planes) in a unit cell. Fig. 4.9 compares the energy barriers involved in this relative shearing. The energy barriers for both pure GaSe and $Ga_{1-x}In_xSe$ are very small and comparable. Thus substitutional In does not enhance the shear rigidity of GaSe. In the same figure we show the energy barrier associated with similar shearing in the presence of an interstitial charged In defect (In_i^{3+}) . The energy barrier and the initial slope increase dramatically (by factors of ~10 and ~7 respectively) in the presence of In_i^{3+} . Clearly GaSe is very soft and inserting interlayer charged In defects can make the crystal rigid against shear distortion. We note that for certain shear configurations the interstitial In could not be accommodated by atomic relaxation within the 2x2x1 supercell. Thus for consistency, we have given and compared the results obtained for rigid shear only (without relaxation) for all three cases: In_i , In_{Ga} and pure GaSe. In order to perform the atomic relaxations, one should either increase the size of the supercell or allow for volume optimization.

The mechanism responsible for rigidity enhancement discussed here is quite general and applicable to a large class of layered materials with weak interlayer bonding.

4.9 Impurity clustering

We have also investigated the possibility of In and Te cluster formation inside the GaSe host. This was done by performing supercell (3x3x1, 72 atoms) calculations with impurities located close and far away from each other and comparing the corresponding total energies. These calculations were performed using the theoretical lattice constants of GaSe and relaxing all the internal atomic positions. In the case of Te doping we find that the total energy is 40 meV/supercell lower when the impurities are located far from each other, suggesting that Te clustering does not take place. In the case of In doping, the situation is similar, but the energy difference is smaller: 9 meV/supercell. Considering that the accuracy of our total energy calculations is less than 10 meV, we cannot exclude the possibility of In clustering in GaSe.

4.10 Summary

We have investigated the dependence of elastic properties of $GaSe_{1-x}Te_x$ and $Ga_{1-x}In_xSe$ as a function of defect concentration, using first-principles methods, within DFT. In the case of Te doping we did not observe a systematic change in the elastic constants with the dopant concentration. This is most likely related to the structural phase transition which occurs in the range of 0.26 < x < 0.60. In the case of substitutional In doping (In_{Ga}) we find a monotonic increase in the C_{13} , C_{33} and C_{44} elastic constants which indicate a strengthening of the crystal in along the direction perpendicular to the atomic layers.

The defect formation energy calculations show that Te and In prefer the substitutional Se and Ga sites, respectively. Nevertheless, in the case p-type GaSe (when E_F is close to VBM) indium impurity can acquire +3 charge state and can occupy interstitial sites between the GaSe layers. This strongly influences the cleavability of the crystal along planes parallel to the atomic layers and it is the main source of the observed improvement of the structural properties of In doped GaSe [162–165].

We find that in the case of $In_{Ga} - V_{Ga}$ defect complex the atomic relaxation plays a major role in the stabilization of the charge states. The variations in the distance between the host Se atoms and the In impurity as a function of the charge states, are responsible for the position of the defect level relative to the band edges of GaSe. One should be able to probe this defect using experimental methods.

Chapter 5

Electronic structure of defects in GaTe

5.1 Introduction

One of the main characteristics of the III-VI systems is the presence of cation-cation dimers oriented perpendicular to the layers. GaTe occupies a special place among the members the III-VI family, since its crystal structure is more complex compared to the other members [174]. In this compound there are Te-Ga-Ga-Te layers and Ga-Ga dimers, similar to the rest of the family, but only two-thirds of these dimers are oriented perpendicular to the atomic layers while the rest one-third the Ga-Ga bonds lie almost in the layer plane (see Fig. 5.1). GaTe belongs to the B2/m space group and crystallizes in the monoclinic system [175]. Although the overall crystal structure of GaTe appears to be more complicated, the local coordination of the atoms is similar to that of the other III-VI compounds: each Ga atom is fourfold coordinated by three Te and one Ga atom, while each Te atom is threefold coordinated by three Ga atoms. The bonds within the layers have a strong covalent character while the layers are bound mainly by weak van der Waals type interaction. Unlike GaS, GaSe and InSe,



Figure 5.1: The crystal structure of GaTe. Dark spheres are the Ga atoms and the light spheres are Te atoms. In each layer one can see the Ga-Ga dimers two oriented normal to the layer and one oriented along the layer.

no polytypism has been observed in GaTe [28, 176]. Whether this has to do with the presence and orientation of Ga-Ga (In-In) dimers in the layer is not known at the present time.

Experimental investigations in GaTe have focused on the structural, optical, and photo emission properties associated with its layered structure [27,177–181]. Schwartz et al. [182] have observed that GaTe undergoes a structural phase transition at 10 GPa into a metallic NaCl-type structure. Pellicer-Porres et al. [183] used x-ray absorption spectroscopy (XAS) to study the evolution of the bond lengths in GaTe under pressure. The same authors [184] observed a nonlinear pressure dependence of the direct band gap in their optical absorption measurements. Extensive transport measurements have been carried out in p-type GaTe by Efeoğlu et al. [185]. Experiments dealing specifically with defect energy levels will be discussed along with our theoretical calculations.

Because of its more complex structure, there is a lack of detailed theoretical in-

vestigation of the electronic properties of GaTe. Yamamoto et al. [28] calculated the electronic structure of GaTe using *ab initio* tight binding linear muffin-tin orbitals (TB-LMTO) method within the atomic sphere approximation (ASA). For the exchange and correlation potential they have used the *von Barth-Hedin* local density approximation (LDA). From a comparison of their theoretical band structure to optical absorption spectra they concluded that the dominant excitations were associated with j-j coupled, optically allowed exciton states.

A more detailed analysis of the GaTe band structure was done by Sánchez-Royo et al. [27], using numerical atomic orbitals and density functional theory (NAO-DFT), in the local density approximation. The dispersion of the valence bands along different directions in the Brillouin zone (BZ) was compared with angle-resolved photoemission spectroscopy (APRES) measurement. Although there were qualitative agreements between theory and experiment as regards band dispersion, there were also major differences. To explain this difference Sánchez-Royo et al. [27] suggested that spinorbit interaction (SOI) might increase the mixing between the Te p_z states from the top of the valence band (VB) and the deeper Te p_x , p_y states, leading to an upward shift and flattening of the topmost VB near the Γ -point. We have carried out electronic structure calculations incorporating spin-orbit interaction to test their suggestion and the results are discussed later in this chapter.

In general, electronic transport and dominant optical properties of a semiconductor are determined mainly by the electronic states near band gap region. These states are easily influenced by the defects present in the system. The defects therefore play an important role in the performance of a semiconductor. In this chapter we investigate the nature of the defect states in GaTe associated with native point defects (Ga and Te vacancies) and substitutional impurities (Ge and Sn) on Ga-site. As in other systems, all calculations have been done within *ab initio* density functional theory (DFT) using generalized gradient approximation (GGA). The defects are placed in large super cells to minimize defect-defect interactions. It is well known that due to the underestimation of the band gap by LDA or GGA and due to the limitations of the supercell model [139], accurate calculation of the defect energy levels represents a serious theoretical challenge, particularly when they are formed out of conduction band states (donor states) or they overlap with conduction band (deep defect states overlapping the conduction band). However, in the case of acceptor states, derived mostly from the valence band, their position relative to the valence band maximum (VBM) can be obtained with reasonable accuracy using supercell models provided proper corrections are made to take care of the effect of the defects on the host valence band structure. In this work we have estimated the energy of the defect levels when these are derived mainly from the valence band or when they are deep defect states lying in the band gap. We have also calculated the formation energies of defects in different charge states and discuss the dependence of the formation energies on the chemical potentials of the constituent elements under equilibrium growth conditions.

5.2 Computational details

We have performed structural optimizations and electronic structure calculations using Projector Augmented Wave (PAW) [149] methods implemented through VASP [144– 147] package. The exchange and correlation potential was approximated by generalized gradient approximation (GGA) [148]. The 3d, 4s and 4p states of Ga and 5s and 5p states of Te were treated as valence states and the rest as cores. The energy cutoff was set to 300 eV and convergence was assumed, when the energy difference between consecutive cycles was less than 10^{-4} eV. The internal structural parameters of pure and defect containing GaTe were optimized using the conjugate gradient algorithm and the convergence criterion for atomic relaxation was set to 10^{-3} eV energy difference between two consecutive ionic relaxation steps. For structure optimization and total energy calculation of pure GaTe, we have used the conventional unit cell containing 12 Ga and 12 Te atoms. The Brillouin zone (BZ) was sampled by a Γ -centered Monkhorst-Pack [186] grid of 2x4x10 kpoints (36 k points in the irreducible (IBZ)). To model Sn and Ge substitutional defects in GaTe, we have constructed 1x2x4 supercells (192 atoms) starting from the conventional unit cell and replaced one Ga atom by either Sn or Ge. Supercells of the same size were used to simulate the intrinsic defects (such as Ga and Te vacancies) in GaTe. These calculations were performed using 3x3x3 Γ -centered Monkhorst-Pack k-meshes. In order to reduce the spurious defect-defect elastic interactions within neighboring supercells, the calculations were performed using the theoretical (relaxed) lattice constants of the bulk GaTe, as suggested in reference [155].

To check the accuracy of our calculations obtained with the PAW method we have compared the band structures of pure GaTe with that obtained using full potential linearized augmented plane wave (FP-LAPW) [141] method, implemented through Wien2k [143] package. For the full potential calculation we used the following setup: the 3d, 4s, 4p electrons of Ga and 4d, 5s, 5p electrons of Te were treated as valence electrons, the product between the smallest muffin tin radius (R_{MT}) and the largest reciprocal lattice vector (K_{max}) were chosen such that $R_{MT}K_{max} = 7.0$. The atomic radii were 2.17 a.u. for Ga and 2.35 a.u. for Te and convergence was assumed when the energy difference between the self-consistent cycles was less then 0.0001 Ry (1.36 meV). The FP-LAPW calculations were performed using the experimental crystal structure [175]. The small differences in the results obtained by the two methods are related primarily to the volume relaxation and structure optimization. The electronic band structures and the density of states, however, are nearly identical, as expected. Thus, all the results presented in this chapter are obtained with PAW method except for the band structure of pure GaTe (which was calculated using both PAW and FPLAPW methods). To verify whether the large effect of SOI on the band structure suggested in reference [27] is reasonable, we have calculated and compared the electronic structures of bulk GaTe with and without SOI using FPLAPW. We find SOI effects on the band structure to be quite small and have not therefore included it in our defect containing supercell calculations.

5.3 Crystal and electronic structures of pure GaTe

To relax the structure of bulk GaTe, using PAW method, first we performed volume optimization keeping the ratio of the lattice parameters a:b:c constant and then minimized the internal structural parameters at constant volume allowing for the shape of the cell to change. The initial a:b:c ratio was chosen based on the values of the experimental lattice constans [140] and it was allowed to change when the internal parameters were varied. The obtained lattice parameters a, b, and c are larger than the experimental ones by 6.4%, 4.7% and 1.5% respectively. The large overestimation of the lattice constants a and b are attributed to the underbinding effect of GGA, which is enhanced by the weak Van der Waals interlayer interaction along the aand b-axis. Since the crystal c-axis lies in the plane of the GaTe layers (and the intralayer interaction is strong, covalent type), the effect of overestimation of the lattice constants by GGA is less evident on the c-axis. After this two-step relaxation process we have performed one more volume optimization to check if the calculated lattice constants are close to their optimal values. Since the lattice parameters after the additional volume optimization increased by only ~ 0.01 Å, we considered that the crystal structure obtained after the initial two-step process is close enough to the fully relaxed structure. The theoretical lattice constants and the relaxed Ga-Ga dimer lengths are given in Table 5.1.

In Fig. 5.2 we show the total density of states (DOS) of GaTe calculated with the PAW method along with the partial DOS of Ga and Te, with SOI included. The

Table 5.1: The experimental and theoretical lattice parameters of bulk GaTe. The distances are given in angstroms and the monoclinic angle γ in degrees. d_{Ga-Ga}^{\perp} and d_{Ga-Ga}^{\parallel} refer to the Ga-Ga dimer lengths that are perpendicular and parallel to the layer planes, respectively.

	a	b	с	γ	$\mathrm{d}_{Ga-Ga}^{\perp}$	$\mathrm{d}_{Ga-Ga}^{\parallel}$
Exp. [140]	17.44	10.46	4.08	104.4	2.43	2.44
Theor.	18.56	10.96	4.14	107.6	2.46	2.49

origin of the energy was chosen at the highest occupied level. The valence band of GaTe can be divided into three main groups. The first group of peaks located between -12.5 eV and -10.5 eV originates mainly from Te 5s states with a very small Ga 4s and 4p contribution. The second group of bands, from -7.2 eV to -4.0 eV displays a pronounced Ga 4s character with significant contribution from the Te 5p states. The highest group of bands from -4.0 eV to 0 eV (energy of the highest occupied state) is formed primarily by a strong hybridization of Te 5p and Ga 4p states. The bottom of the conduction band is a mixture of almost equal contributions from Te 5p and Ga 4s, with a smaller Ga p character.

For a better understanding of the electronic structure of GaTe, we analyze the band structure of bulk GaTe, obtained by the FPLAPW method in the primitive unit cell (6 Ga and 6 Te atoms), with SOI included (Fig. 5.3). We can identify the three main group of valence bands mentioned in the previous paragraph: (i) the lowest group of 6 bands (Te 5s) is split off from the upper part of the valence band by approximately 3.0 eV; (ii) the next 6 bands, with strong Ga 4s character, correspond to Ga-Ga bonding and antibonding states associated with the Ga-Ga dimers; (iii) the upper 15 bands originate from Te 5p states (15 out of 18 Te p states associated with 6 Te atoms/unit cell) hybridized with Ga 4p states. The electron counting is such that the 6 Ga s and the 6 Te s bands together with the 15 hybridized Te-Ga p bands can accommodate the total number of 54 valence electrons (18 from Ga and



Figure 5.2: (a) Total density of states (DOS) of the Gate crystal calculated using PAW method; (b) and (c) Projected DOS of s and p orbitals respectively of the Ga and Te.

36 from Te). Therefore 3 Te 5p states (out of 18) remain empty and are pushed up in energy giving rise to a semiconducting gap in the band structure of GaTe. If we look at the dispersion of the Ga s bands we see one bonding band is quite flat compared to the other two. It is also present to some extent for the antibonding s bands. This asymmetry is a result of the structure where two of the three Ga dimers are oriented differently compared to the third one.

The overall structure of the electronic DOS and band structure calculated by PAW and FPLAPW methods are similar, and also agree to those obtained previously by tight-binding (TB-LMTO) [28] and pseudo-potential (NAO-DFT) [27] approaches. Small differences in the orbital contributions to the DOS, however, exist throughout



Figure 5.3: Band structure of GaTe crystal along high symmetry directions, calculated using FP-LAPW method. The Brillouin zone used in this calculation is identical to the one described in Ref.[27]

the valence band. According to our PAW calculations the Ga s contribution to the low-energy valence bands (-12.5 eV to -10.5 eV) is stronger than the Ga p contribution, in contrast with the results reported by Sánchez-Royo et al. [27], where the Ga p character was found to be stronger than the Ga s. Also the contribution of Te s and Te p to the DOS in the region -7.2 eV to -6.0 eV is about the same order in our calculations, whereas in reference [28] the Te p character is much more pronounced. The quasi-gap in the valence band at about $\sim 4 \text{ eV}$ was also present in the TB-LMTO calculation of Yamamoto et al. [28] and it is in agreement with the



Figure 5.4: Band structure of GaTe (a) without and (b) with spin-orbit interaction. The bands with $p_x - p_y$ character, which lie below the topmost VB, split under spin-orbit interaction and those with j = 3/2 shift up in energy by ~0.1 eV.

ultraviolet photoelectron spectroscopy (UPS) measurement [187].

In order to understand the effect of SOI in GaTe in more detail, we plot in Fig. 5.4 the calculated band structures along Γ -Z direction (a) without SOI and (b) with SOI. As seen in the figure, the most significant effect is the energy shift-up of the top valence bands at the Γ -point when SOI is included in the calculation. This effect has been explained by Sánchez-Royo et al. [27]; the bands with p_x - p_y character, which lie below the topmost VB, split under spin-orbit interaction and those with j = 3/2 shift up in energy. However, the magnitude of the energy shift calculated with FPLAPW method (~0.1 eV) is much less than the energy shift estimated in reference [27] (0.7-0.9 eV) inferred from the atomic data. Thus in solids where the Te orbitals are much more diffused, SOI effects are quite small. The effect of SOI on the energy position of the Te bands has been calculated in PbTe [188], and a similar value of ~0.1 eV was obtained. The above analysis clearly suggests that the SOI in GaTe is rather small, just like in the other members of the III-VI family [22].

From our band structure calculations we see that GaTe is a direct-gap semiconductor with the gap located at the Z-point, at the edge of the BZ, in agreement with the previous theoretical results [27,28]. Our band gap of 0.98 eV (and 1.098 eV obtained in reference [27]) is underestimated by a factor of almost two compared to the experimental value of 1.799 eV [140], due to the well-known limitation of LDA (GGA), which underestimates the band gap in semiconductors [154].

5.4 Defects in GaTe

5.4.1 Substitutional impurities: Sn_{Ga} and Ge_{Ga}

In the case of simple extrinsic impurities, one should be able to predict whether the impurity will give rise to a donor state or acceptor state by simply counting the number of valence electrons of the dopant and the host atoms. The addition of group IV elements, such as Si, Ge, Sn or Pb, to the Ga site, introduces more electrons in to the system, giving rise to donor states. Figure 5.5(a) shows the calculated band structure for the Ge impurity. Since Sn behaves very similar to Ge, we only present the results for the latter and point out the noticeable differences between the two.

Let's first discuss the local atomic relaxation in the neighborhood of the impurity. Since one of the major differences between Ge and Sn atoms is in their atomic sizes, we observe noticeable differences in the relaxation of the atomic positions around the Ge and Sn defects. In both cases the atoms surrounding the Ge or Sn relax outward, but in the case of the Sn, the relaxation is much more pronounced. The optimized impurity-host bond lengths are listed in Table 5.2.

Next we look at the position of the defect states. The defect level lies deep in the gap region, closer to the CBM and it is partially filled. Due to the well known problem of the underestimation of the band gap by LDA/GGA, the position of this



Figure 5.5: (a)The band structure of GaTe doped with Ge (or Sn) on the Ga site. (b) The charge density associated with the impurity induced defect band.

Table 5.2: Optimized impurity-host bond lengths. The last row contains the percent increase in the bond lengths relative to the ones obtained for the bulk GaTe.The notations Tel and Te2 refer to the NN and next NN Te atoms of the defect

	d _{Ge-Ga}	dGe-Te1	d _{Ge-Te2}	d _{Sn-Ga}	d _{Sn-Te1}	$d_{\mathrm{Sn-Te2}}$
	2.56	2.75	2.74	2.73	2.92	2.90
Increased by:	4.5%	2.6%	1.1%	9.8%	8.9%	7.4%

level with respect to the CBM can not be obtained reliably. However, if we measure their position from the respective VBM, we find that they are about ~ 1 eV above the VBM and compared to Sn, the Ge level is closer to the VBM by ~ 50 meV. Figure 5.5(b) shows that the charge density associated with the impurity state is localized around the impurity and it originates primarily from Ge and Ga s and the surrounding Te p orbitals.

5.4.2 Vacancies V_{Ga} and V_{Te}

For the vacancy calculations we minimize the energy of the 1x2x4 supercell containing one Ga vacancy (V_{Ga}) or one Te vacancy (V_{Te}). For V_{Ga}, the supercell contains 96 Te, 95 Ga, and a vacant Ga site. The shortest distance between two vacancies is 16.56 Å. After the optimization of the atomic positions we observe a large inward relaxation of the atoms that are nearest neighbors (NN) of the vacancy. There are significant changes in the bond lengths and bond angles. To quantify this inward atomic relaxation we give, in Table 5.3, the distances between the vacancy and the Ga and Te atoms surrounding the vacancy. For comparison we also give the corresponding bond lengths for pure GaTe inside parenthesis. The vacancies are considered to be at the ideal atomic positions.

To understand the nature of the defect states introduced by the vacancies in GaTe, we have calculated the electronic band structure of the defect containing supercells and the charge densities associated with the defect induced bands. Introducing a Ga vacancy means that there is one less Ga s state in the VB and three less electrons in the system. Thus, for one Ga atom removed, we expect partially filled bands near the top of the VB. From the band structure plot in Fig. 5.6(a) we see that there is indeed one partially filled band crossing the E_F along Γ -P and A- Γ directions. Besides this, a Ga vacancy introduces a narrow defect band lying deep in the gap region. The energy of this deep defect state with respect to the VBM of the vacancy containing supercell (which occurs at the Γ -point) is ~0.78 eV. This value is consistent with the hole trapping level measured by deep-level transient spectroscopy at 0.8 eV above the VB by Sighetomi et al. [43]. Manfredotti et al. [189] also report an acceptor level at 0.74 eV above VB in melt grown samples of GaTe. It is tempting to presume that this defect level originates from the Ga vacancy. One should however note that in experiments the defect concentrations are much smaller than what we have in our supercell calculations. Consequently one must correct for the changes in the VBM energy. To estimate these corrections we match the energies of the Ga 3d semicore states of the pure and vacancy containing GaTe, at Γ -point. We find that the energy of the defect level with respect to the VBM of the pure GaTe shifts to ~ 0.82 eV. This

Table 5.3: The distances between the vacancies and their nearest neighbors. The notations of Ga1 and Ga2 refer to the Ga atoms from the dimers oriented perpendicular and parallel to the atomic layers respectively. The bond lengths of the pure GaTe are given in parenthesis. The distances are given in angstroms.

	Gallium vacancy	Tellurium vacancy		
Vacancy – Gal	1.87 (2.46)	2.27 (2.73)		
Vacancy – Ga2		2.59(2.71)		
Vacancy – Te	2.23(2.71)	4.07 (4.19)		
Te – Te	3.64 (4.19)			

value is still in good agreement with the experiment, suggesting that the defect level might indeed come from Ga vacancy. Figure 5.6(b) shows the electronic charge density associated with this deep defect band. The charge density originates mainly from Ga s states and Te p states from the vicinity of the vacancy and it is quite localized.

For V_{Te} we find that the band structure also changes drastically (see Fig. 5.7(a)) compared to pure GaTe. The changes in the band structure introduced by a Te vacancy can be qualitatively understood in terms of the bonding model described in the case of GaSe in Chapter 3, since the local bonding between Ga and Te is similar to that between Ga and Se. As discussed earlier, the Ga-Ga dimers form bonding and antibonding states (the six Ga s bands indicated in Fig. 5.3). Due to the hybridization between the Ga s states and Te p states, some of the Te bands are pushed up in energy, giving rise to the semiconducting gap. In the case of pure GaTe there are 6 Ga and 6 Te atoms in the unit cell. Three Te p states (out of 18) are pushed up to the CB. Removing one Te atom from the unit cell (Ga6Te5) gives rise to one less Te s state and two less Te p states in the VB and one less Te p state in the CB. Since the number of electrons is reduced by 6 due to the Te vacancy we expect that all the valence bands will be fully occupied (no partial occupation). To check this point we counted the number of valence bands obtained in the pure and in the vacancy containing supercells. The number of valence bands indeed decreases by three (disregarding spin degeneracy) when one Te atom is removed from the 192-atom



Figure 5.6: (a) The band structure of GaTe with Ga vacancy. (b) The charge density associated with the vacancy induced deep defect band (lying in the gap near energy 0.8 eV).

system. In Fig. 5.7(a) we see that Te vacancy introduces two gap states right below the CB and one nearly non-dispersive resonant state near the top of the VB. From the charge density plots associated with the two gap states below the conduction band shown in Fig. 5.7(b) we see that these bands originate mainly from the *s* states of Ga atoms surrounding the Te vacancy. A Te vacancy acts like an attractive potential and lowers the energies of the neighboring Ga states. An interesting prediction is that doping these two states can give rise to magnetism.

5.4.3 Defect formation energies

In this Section we discuss the formation energies of different types of defects in GaTe and see how they depend on the atomic chemical potentials. We adopt the formalism presented earlier in Sections 2.4.2 and 2.4.3. As an example, we will describe the details of calculations for the case of substitutional Ge impurity on Ga site (Ge_{Ga}). The formation energies and the charge transition levels for the other defects under



Figure 5.7: (a) The band structure of GaTe with Te vacancy. (b) The charge density associated with the two, vacancy induced deep defect bands which lie below the CB.

consideration can be obtained in a similar way, using the values given in the footnote¹. The calculated enthalpy of formation for GaTe compound is ΔH (GaTe) = -0.72 eV, therefore the μ 's must satisfy: $\mu_{\text{Ga}} + \mu_{\text{Te}} = -0.72 \text{ eV}$ and $\mu_i \leq 0$ (i = Ga, Te, Ge). Since Ge can form secondary phase with Te, with calculated ΔH (GeTe) = -0.14 eV, the maximum achievable value of the chemical potentials are further limited by the condition: $\mu_{\text{Ge}} + \mu_{\text{Te}} = -0.14 \text{ eV}$. Under Ga-rich growth conditions ($\mu_{\text{Ga}} = 0$, $\mu_{\text{Te}} = -0.72 \text{ eV}$) this gives $\mu_{\text{Ge}} = -0.14 + 0.72 = 0.58 \text{ eV}$. However, in order to avoid precipitations of Ge, we have to impose $\mu_{\text{Ge}} = 0$. Under Te-rich conditions ($\mu_{\text{Ga}} = -0.72 \text{ eV}$, $\mu_{\text{Te}} = 0$) on the other hand, μ_{Ge} is reduced to -0.14 eV. Using Eq. (2.52), the formation energy of Ge_{Ga} in neutral charge state is $\Delta H_f(\text{Ge}_{\text{Ga}}^0) = 1.18 \text{ eV} + \mu_{\text{Ga}} - \mu_{\text{Ge}}$. Under Ga-rich conditions ($\mu_{\text{Ga}} = 0, \mu_{\text{Te}} = -0.72 \text{ eV}$ and $\mu_{\text{Ge}} = 0$) this gives $\Delta H_f(\text{Ge}_{\text{Ga}}^0) = 1.26 \text{ eV}$, whereas under Te-rich conditions $\Delta H_f(\text{Ge}_{\text{Ga}}^0) = 1.26 \text{ eV}$.

¹The calculated formation energies $\Delta E(X^q)$ using Eq. (2.52) are: $\Delta E(V_{Te}^q) = 2.17$ eV, $\Delta E(V_{Te}^{+1}) = 2.15$ eV, $\Delta E(V_{Te}^{+1}) = 2.12$ eV, $\Delta E(Ge_{Ga}^{0}) = 1.18$ eV, $\Delta E(Ge_{Ga}^{+1}) = 0.43$ eV, $\Delta E(Ge_{Ga}^{+2}) = 0.42$ eV, $\Delta E(Sn_{Ga}^0) = 1.02$ eV, $\Delta E(Sn_{Ga}^{-1}) = 0.24$ eV, $\Delta E(Sn_{Ga}^{-1}) = 0.24$ eV, $\Delta E(Sn_{Ga}^{-1}) = 0.24$ eV, $\Delta E(Sn_{Ga}^{-1}) = 0.12$ eV, $\Delta E(Sn_{Ga}^{-1}) = 0.14$ eV and $\Delta H(SnTe) = -0.61$ eV.

decreases to 0.60 eV. This is because under Te-rich (Ga-poor) conditions, Ga vacancies are more likely to appear making it easy for Ge atoms to occupy these vacancies. In the case of the charged defects, the formation energy depends also on the Fermi level, because in order to ionize the defect, electrons must be taken from or added to the electron reservoir with energy E_F . The donor transition levels for Ge_{Ga} are calculated using Eq. (2.53): $\varepsilon(+/0) = 0.01$ eV and $\varepsilon(+2/+) = 0.75$ eV.

Figure 5.8 shows the calculated formation energies as a function of E_F for different defects. For V_{Ga} we find two acceptor levels $\varepsilon(0/-1)$ and $\varepsilon(-1/-2)$ in the band gap at 0.13 eV and 0.83 eV above the VBM, respectively. The latter is in very good agreement with the experimental results reported in Refs. [43,189]. V_{Te} appears to be in neutral charge state for almost all values of E_F across the band gap. Nevertheless, it introduces a deep donor level at 0.03 eV above VBM. Furthermore, our calculations (not shown in the figure) show that the donor level $\varepsilon(+2/+1)$ is slightly higher in energy than $\varepsilon(+1/0)$, meaning that V_{Te} is a negative-U center [190], with unstable +1 charge state. A defect has negative-U properties if it can trap two electrons (or holes) with the second bound more strongly than the first. The subsitutional defect Sn_{Ga} behaves similarly to Ge_{Ga}. The deep donor levels $\varepsilon(+2/+1)$ and $\varepsilon(+1/0)$ associated with Sn_{Ga} are located at 0.06 eV and 0.78 eV above the VBM.

From Fig. 5.8 we observe that the defect formation energies are quite sensitive to the growth conditions. First let us look at the intrinsic defects V_{Ga} and V_{Te} . At the Te-rich limit (Fig. 5.8(b)), the formation energy of V_{Ga} is always less compared to V_{Te} , indicating that Ga vacancies are more likely to appear during the Te-rich growth process. However, at the Ga-rich limit (Fig. 5.8(a)), we find that the formation energy of V_{Ga} relative to V_{Te} depends on the position of the Fermi level. If E_F is closer to VBM (p-type material) the Te-vacancy will be the dominant intrinsic defect, whereas if E_F is above the midgap (n-type material), the acceptor V_{Ga} will dominate over the donor V_{Te} .



Figure 5.8: Calculated defect formation energies in GaTe as a function of Fermi energy, under (a) Ga-rich and (b) Te-rich conditions. The slope of the energy lines indicates the charge state of the defect and the value of E_F where the slope changes, represents the charge transition level.

We observe that the growth conditions also influence the solubility of Sn relative to the solubility of Ge. Under Ga-rich conditions it is easier to incorporate Sn in GaTe, whereas at the Te-rich limit Ge becomes more soluble than Sn. This is because the Sn-Te bond being stronger than the Ge-Te bond ($\Delta H(\text{SnTe}) = -0.61$ eV and $\Delta H(\text{GeTe}) = -0.14 \text{ eV}$), it will be more likely for Sn to form secondary phases with the Te atoms, during the Te-rich growth process. In order to avoid this, one has to decrease the atomic chemical potential of the Sn, which in turn, increases the defect formation energy. This prediction has to be checked by experiment.

5.5 Summary

In summary, we have performed electronic structure calculations in pure and defect containing GaTe to understand the nature of local bondings and how they effect the overall band structure of pure GaTe and the defect states. The results obtained for the pure system indicate that it is a direct gap semiconductor. As in other III-VI semiconductors containing Ga-Ga dimers, the presence of these dimers and the interaction of the dimer states with Te p states lead to the formation of the band gap. Our results obtained without SOI agree with previous works [27,28]. In contrast to the suggestion made by Sánchez-Royo et al. [27] we do not find the SOI to be important in GaTe; the shifts in the energy levels near VBM and CBM are ~ 0.1 eV rather than ~ 0.8 eV. To investigate the nature of various defects in GaTe, we constructed large supercell models (192 atoms). We find that Ga vacancy introduces a deep defect state in band gap region at ~ 0.78 (~ 0.82 eV) above the VBM of the defect containing (defect free) system, at the Γ -point. The charge density associated with this defect level is strongly localized around the vacancy's NN Ga atom. The energy of the Ga vacancy induced defect band is in quite good agreement with the experimental observation [43,189]. Te vacancy introduces two localized states near the CBM and a resonant state just below E_F . Charge densities associated with the gap states reveal the nearly localized character for these bands. Ge and Sn substitutional impurities behave almost identically in the GaTe host, introducing a deep donor state in the band gap region.

Our calculations show that the defect formation energies depend not only on the charge state of the defect but also on the growth conditions (Ge-rich or Terich). In the case of n-type samples, however, V_{Ga} is always the dominant intrinsic acceptor, which can compensate the intentional donors. The calculated acceptor level $\varepsilon(-1/-2) = 0.83$ eV above VBM is in good agreement with the experiment [43,189]. We find that V_{Te} is a negative-U center [190] with a deep $\varepsilon(+2/0)$ donor transition level located at 0.03 eV above VBM. Our results also indicate that as the growth conditions change from Ga-rich to Te-rich, the solubilities of Sn and Ge interchange with respect to each other. Both, Ge_{Ga} and Sn_{Ga} , are deep donors with the $\varepsilon(+2/+1)$ level located at 0.01 eV and 0.06 eV above VBM and $\varepsilon(+1/0)$ level located at 0.75 eV and 0.78 eV above VBM.

Chapter 6

Hydrogen in CdTe

6.1 Introduction

Cadmium telluride (CdTe) is a semiconducting material which, under normal, conditions crystallizes in the zincblende structure. It is a direct gap semiconductor, with the smallest gap at Γ -point, in the center of the BZ. The experimentally determined gap at room temperature is 1.475 eV [140]. CdTe has been extensively studied experimentally and theoretically during the last several decades due to the possible applications in room-temperature X-ray and γ -ray detector [46,47]. As we have mentioned in the introduction (Section 1.2), the performance of the CdTe based radiation detectors and solar cells is often limited by the presence of the defect states in the band gap of the CdTe, which act as recombination centers for the charge carriers. Furthermore, the excess holes and electrons originating from the native defects reduce the required high resistivity for a detector grade semiconductor (>108 Ω cm). One way to improve the efficiency of CdTe in detector devices and solar cells is to achieve the passivation of electrically active defects by hydrogen. The best known property of atomic hydrogen in many semiconductors is the increase of resistivity by passivation of donors and acceptors [191].
In CdTe, hydrogen is usually introduced in order to purify the material from oxygen impurities (mainly cadmium and tellurium oxide compounds incorporated in CdTe). During the hydrogenation process, hydrogen can be trapped inside the crystalline lattice and can significantly influence the electrical and optical properties of the semiconductor. Extensive studies have been carried out to investigate the infrared (IR) vibrational spectra of CdTe using samples exposed to different levels of hydrogenation in an effort to understand the distribution of H in CdTe [192–195]. Using *ab initio* modeling for hydrogen-group V complexes in CdTe and calculating the local vibrational mode (LVM) frequencies, it has been found that the ground state location of H is near the bond center, closer to the acceptor (group V) atom [196].

From theoretical point of view it is attractive to study H, the most elementary atom, as an impurity in semiconductors. It is known that H does not behave as a "hydrogenic" effective-mass-type impurity, but rather introduces deep levels in the semiconducting band gaps. In most semiconductors, atomic hydrogen acts as amphoteric impurity, being either in positively charged state (H⁺, donor) or negatively charged state (H⁻, acceptor), depending on the value of the electron chemical potential (position of the fermi level within the band gap). The neutral charge state is usually unstable, indicating that H introduces a negative-U center in most materials [58, 59, 59–61, 191].

The interaction of H with defects in semiconductors is still an area of active research. State-of-the-art calculations have helped reveal many of the fascinating properties of H in semiconductors and made H a model system for defect studies [103,197]. Recently, Du et al. [54] reported that complex of $O_{Te}H$ may play an important role in the carrier compensation in CdTe. Hydrogen easily forms complexes impurities and native defects in semiconductors. Takenaka et al. [198] briefly reported the existence of hydrogen-cation vacancy complex in CdTe. The stability and the electronic properties H defects in CdTe and the mechanism of hydrogenation have not been reported systematically as yet, to our knowledge. To this end, we performed the total energy calculations based on density functional theory to investigate the stability and electronic properties of the hydrogen related defects in CdTe.

6.2 Method of calculation

We have performed electronic structure calculations based on density functional theory (DFT), using both the generalized gradient approximation (GGA) [148] and the local density approximation (LDA) [167] with projector augmented wave (PAW) [167] pseudopotentials as implemented in VASP [144-147] code. The 4d and 5s states of Cd and the 5s and 5p states of Te were treated as valence electrons. The cutoff energy for the plane wave basis was set to 300 eV and convergence was assumed when the total energy difference between consecutive cycles was less than 10^{-4} eV. The defect calculations were performed on 2x2x2 supercells using the theoretical lattice constants with the defect located near the center of the cell. To see if the 2x2x2 supercell (64 atoms) is adequate for the calculations of defect formation energies and transition levels, we have also performed several calculations using 3x3x3 supercells (216 atoms). The atomic positions in the defect containing supercells were relaxed until the quantum mechanical forces were smaller than 0.02 eV/Å The BZs of the 64-atom and the 216-atom supercells were sampled by 4x4x4 and 2x2x2 Γ -centered Monkhorst-Pack grids, respectively. In the case of charged defect calculations, a uniform background charge was added to preserve the charge neutrality of the supercell.

The formation energies and charge transition levels were calculated using the formalism from Sections 2.4.2 and 2.4.3. The chemical potential of the hydrogen $\mu_{\rm H}$ (= -3.38 eV) was taken as half of the calculated ground state energy of the H₂ molecule. The enthalpy of formation of pure CdTe calculated using GGA (ΔH (CdTe) = -0.93 eV) is in good agreement with the experimental value of -0.96 eV [199].



Figure 6.1: Locations of H impurity inside the CdTe lattice

6.3 Location of hydrogen in CdTe

In order to study the behavior of H in CdTe, we have performed total energy and electronic structure calculations for several different positions and configurations of the impurity, as shown in Fig. 6.1. CdTe crystallizes in zinc-blend structure. Inside the zinc-blend structure there are two tetrahedrally coordinated interstitial sites: one surrounded by anions and the other surrounded by cations. In Fig. 6.1, if we consider that the red spheres represent the Cd atoms, then the hydrogen (small blue sphere) located at the center of the cell is tetrahedrally coordinated by anions (Te atoms), whereas the one located at the lower right area of the cell is tetrahedrally coordinated by cations (Cd atoms). We denote these two sites as T_{Te} and T_{Cd} , respectively. We have also investigated the configurations in which H is placed at the Cd-Te bond center (BC) and when it substitutes one Cd atom (H_{Cd}) or one Te atom (H_{Te}). For each location of the H atom, the host lattice was fully relaxed. This is essential in order to obtain the low energy position of the H impurity in the CdTe host. For example, the BC site in Si turned out to be the lowest energy position for H only after the relaxation of Si atoms were allowed [59]. Hydrogen in semiconductors can occur in different charge states: H^+ , H^0 and H^- . In order to produce a certain charge state, electrons have to be exchanged with a reservoir of energy equal to the Fermi level (E_F) , therefore the preferred charge state of the impurity depends on the position of the E_F . Van de Walle et al. [58] found that the location of the H impurity in a Si lattice depends strongly on the charge state of H. For H^+ and H^0 the high-electron-density region located at the BC site is more stable, while H^- prefers the low-electron-density interstitial regions in the Si lattice located at the tetrahedral site. We anticipate that H behaves similarly in CdTe. However, in the case of the BC site since the two neighbor atoms are not identical, H will prefer to move closer to the anion or cation depending on its charge state.

In the following sections we will discuss the results of electronic structure calculations (obtained with the GGA) for a H impurity occupying the above mentioned lattice sites in CdTe.

6.3.1 Substitutional hydrogen in CdTe

The electronic structure of substitutional H in CdTe can be understood in term of simple molecular orbital theory. When a vacancy is created in the zinc blend lattice, four anion-cation bonds are broken, thus four dangling bonds are created on the atoms surrounding the vacancy. As shown in Fig. 6.2, these four dangling bonds will give rise to a singlet state a_1 (s-like) and a threefold-degenerate state t_2 (p-like) (not including spin degeneracy). In the case of a Te-vacancy, the a_1 -combination is occupied by two electrons and lies below the VBM, while the empty t_2 states are located above the conduction band minimum (CBM) [55]. The s orbital of the H atom placed at the vacancy site interacts with the singlet state a_1 and creates a bonding state deep in the VB and an antibonding state located in the band gap, closer to CBM (see Fig. 6.2(a)). There are three electrons associated with a H_{Te} defect center:



Figure 6.2: Simple bonding scheme for substitutional hydrogen on the (a) Te site and (b) Cd site

two electrons coming from the Cd s dangling bonds and one from the H s orbital. Two of these three electrons will stabilize the defect center by occupying the bonding state and one electron will be promoted to the high-lying antibonding state, located below the CBM.

The electronic structure of H_{Cd} is slightly different (Fig. 6.2(b)). The a_1 and t_2 combinations are now created from the Te dangling bonds surrounding the vacancy. They have significant p character. The singlet state a_1 lies deeper in the VB while the threefold-degenerate t_2 state is located in the band gap, close to VBM [55]. Two out of the six electrons coming from the four Te dangling bonds are accommodated by the a_1 state while the remaining four electrons are accommodated by the t_2 state. When a hydrogen atom is placed at the Cd-vacancy site, the H s orbital and the a_1 state will interact and give rise to a bonding combination located at the bottom of the VB and occupied by two electrons and an antibonding state located just below

the CBM. The electron, which would have occupied the antibonding state, lowers the energy of the system by transferring to the t_2 level, located at the top of VB (see Fig. 6.2(b)).



Figure 6.3: The density of states (DOS) of CdTe with substitutional H located at (a) Te site and (b) Cd site. In both cases The H s partial DOS is shown along with the nearest neighbor (a) Cd s and (b) Te p partial DOS

We will now analyze the electronic structure of substitutional H in CdTe based on the results of *ab initio* DFT calculations, and see whether the arguments presented above are indeed true. Figure 6.3 shows the total density of states (DOS) of CdTe with H substitutional impurity on the Cd and Te sites as well as the partial DOS associated with the H *s* orbital and the nearest-neighbor (NN) Cd *s* and Te *p* orbitals. In Fig. 6.3(a) and (b), we can identify the states discussed in the previous paragraphs. Common to both H_{Te} and H_{Cd} is the peak located at the bottom of the VB corresponding to the H *s* – a_1 bonding combination. From the partial DOS plots it is evident that this bonding state is a superposition of H *s* and the nearest neighbor Cd *s* and Te *p* orbitals (see Fig. 6.3(a) and 6.3(b), respectively).

In the case of H_{Te} (Fig. 6.3(a)), the H $s - a_1$ antibonding state is located in the band gap, close to the CBM, and it is half-filled. Thus, H_{Te} acts like a donor. The partial DOS plots in Fig. 6.3(a) show that both H s and Cd s orbitals contribute to this antibonding state. The three-fold degenerate t_2 state, with a strong Cd scharacter (and no H contribution), is resonant in the CB, in agreement with the electronic structure of Te vacancy described by Wei et al. [55].

For H_{Cd} , the peak located at the bottom of the CB corresponds to the hydrogen $s - a_1$ antibonding state. The electron which would have occupied this state is transferred to the threefold-degenerate t_2 level located at the top of the VBM (see Fig. 6.3(b)). As a result of this electron transfer, two t_2 states will be doubly occupied and one state will remain half-filled. Consequently, H_{Cd} is an acceptor. We also have to mention that due to partial occupation of the t_2 level, H_{Cd} should undergo Jahn-Teller distortion. This would result in the splitting of the t_2 level into an occupied e level (p_{xy} -like) and a half occupied upper a_1 level (p_z -like) [200], along with a symmetry lowering atomic relaxation. We will address the issue associated with the Jahn-Teller effect in Section 6.4.

To further analyze the nature of the defect states introduced by substitutional H





Figure 6.4: The charge density distributions associated with the (a) bonding and (b) antibonding combinations between H s orbital and a_1 singlet state. The main contribution comes from the H s and the nearest-neighbor Te p orbitals. (c) The charge density of the three-fold degenerate t_2 state showing the Te p contribution (and no H s contribution)

in CdTe, we illustrate in Fig. 6.4 the three-dimensional visualization of the charge densities associated with the bonding, antibonding and t_2 states for the case of H_{Cd}. Figure 6.4 (a) and (b) show the charge density distributions of the low-lying bonding state located at the bottom of the VB and the high-lying antibonding state at the bottom of the CB, respectively. The dominant contribution to these states comes from the H s orbital and the NN Te p orbitals, as described in the previous paragraphs. The charge density associated with the state t_2 , located at the top of the VB, is shown in Fig. 6.4(c). We observe that the only contribution to this state comes from the Te p orbitals (no H s contribution), showing that the H s orbital interacts mostly with the a_1 combination of the Te dangling bonds, as required by symmetry.

From the charge density distributions shown in Fig. 6.4 (a) and (b), we see that H is equally bonded to all nearest neighbors. This suggests the possibility that substitutional H in CdTe can develop multi-coordinated bonds, similar to the case of substitutional H in ZnO and MgO [201]. This is specially true for the case of H_{Te}, where no Jahn-Teller distortion is expected, since this configurations has a partially occupied *s*-like state (a_1 level) in the band gap (and no partially unoccupied, degenerate *p*-like states). In contrast to ZnO and MgO, in CdTe, however, the Cd-Te bondlength (~2.87 Å) is much larger than the Cd-H or Te-H bondlengths (~1.7 Å) and so we cannot exclude the possibility that two or more H atoms will occupy the vacancy site to saturate the dangling bonds.

For the substitutional H impurity at the Cd site we have also carried out calculations using 3x3x3 supercell (216 atoms) to check the energy convergence and the atomic relaxation with respect to the size of the supercell. We have calculated the formation energy of H defect in neutral charge state and we find that the values produced by the 64- and 216-atom supercells differ by less than 4% (3.47 and 3.33 eV respectively). Further, we have found that the atomic relaxations around the defect are not very sensitive to the size of the supercell. In the case of the 216-atoms system the defect's NN and next NN atoms move 0.7% and 0.5% closer to the H atom compared to the 64-atoms system. Since the formation energy calculations are based on total energies differences, we expect the errors associated with the supercell size and k-point sampling to mostly cancel out [155].



Figure 6.5: Simple scheme for level splitting due to H impurity at tetrahedral interstitial site.

6.3.2 Interstitial hydrogen at the tetrahedral sites: T_{Cd} and $$T_{Te}$$

In the case of a H interstitial impurity in CdTe, the defect levels appear to be mainly due to the interaction between the H orbitals and the hybrid orbitals of the NN host atoms. The splitting of the energy levels is shown schematically in Fig. 6.5. Two pairs of a_1 - t_2 levels are created. The first pair, originating mainly from the hybrid orbitals of the impurity's NN host atoms, is situated deep inside the VB. The second pair, derived mostly from the H orbitals, lies above the VBM [200]. The electron of the H atom is accommodated by the a_1 state in the band gap. The position of this state depends on the potential of the defect center. For example, it has been found that in the case of Cd and Te interstitial impurities at the tetrahedral site in CdTe, the a_1 state is located closer to the CBM and below the VBM respectively [55].



Figure 6.6: The density of states of CdTe with interstitial hydrogen on (a) tetrahedral site with Cd NNs and (b) tetrahedral site with Te NNs. In both cases the H s partial DOS is show along with the nearest-neighbor (a) Cd s and (b) Te p partial DOS.

Figure 6.6 shows the calculated DOS associated with the H impurity located at the two tetrahedral interstitial sites (T_{Cd} and T_{Te} in Fig. 6.6 (a) and (b) respectively). In both cases we observe that the sharp peaks located at E_F originate primarily from the contribution of H s orbital to the DOS. The contributions of Cd s and Te p orbitals to this state (a_1) are insignificant, suggesting that the interaction between H at the tetrahedral site and the surrounding host atoms is rather weak. This is also indicated by the very little relaxation of the Cd and Te atoms in the vicinity of H: when H is at the T_{Te} site, the Te atoms relax towards the H by ~0.07 Å, whereas for H at T_{Cd} site, the Cd atoms move towards the H by ~0.18 Å.

Hydrogen at T_{Cd} (Fig. 6.6(a)) introduces a defect state (a_1) near the top of VB. As discussed earlier in this section, this state is half filled and we therefore expect H at T_{Cd} to act as an acceptor impurity. On the other hand, H at T_{Te} introduces a deep defect state near the middle of the band gap closer to CBM, which could act as a donor state.

6.3.3 Interstitial hydrogen in CdTe: the bond center (BC) site

The electronic states introduced by H located at the center of the Cd-Te bond (BCsite) can be understood (to a first approximation) by considering only the states of the H atom and the nearest Te and Cd atoms. If the impurity is not present, the Cd s and Te p orbitals form bonding and antibonding states located in the VB and CB respectively, as illustrated schematically in Fig. 6.7. If H is placed at the BC site, the H s orbital couples to the bonding state, lowering its energy and giving rise to a new (antibonding) state near the CBM.

To check the validity of this idea, we plot in Fig. 6.8(a) the partial DOS associated with Cd s and Te p orbitals located in the vicinity of the H impurity. We also



Figure 6.7: Bonding scheme for H in CdTe located at the bond center (BC) site.

show the partial DOS of the H s orbital. The peak at the bottom of the VB in Fig. 6.8(a) corresponds to the Cd-Te bonding state, which is lowered in energy due to the interaction with the H s orbital. We can also identify the peak near the bottom of the CB as the new (antibonding) state created by the antibonding coupling of the H s and the original Cd-Te bonding states. This can be further verified by looking at Fig. 6.8(b) where we show the three-dimensional charge density distribution associated with the defect state located near the bottom of the CB. The dominant contribution comes from the Te p and H s orbitals.

We observe a significant relaxation of the atoms around the H impurity placed at the BC site. Initially, the H atom was placed midway between the Cd and Te atoms.



Figure 6.8: (a) The partial DOS associated with the s and p orbitals of the Cd and Te atoms located in the vicinity of the H impurity. The lower panel shows the H s partial DOS. (b) The charge density distribution associated with the defect state located near the bottom of CB. The dominant contribution comes from the Te p and H s orbitals. The H impurity is located at the bond center site.

After relaxation, Cd-Te distance increases by 1.07 Å, while the H atom (in neutral charge state) moves closer to the Te atom (H-Te distance is 1.72 Å and the H-Cd distance is 2.21 Å).

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6.4 Jahn-Teller effect

We have mentioned in Section 6.3.1 that in the case of the substitutional H on Cd site (H_{Cd}), due to the partial occupation of the t_2 level located at the top of the VB (Fig. 6.2(b)) the system is susceptible to Jahn-Teller distortion. The electronic structure and atomic relaxation calculations, performed with H at the ideal Cd site as starting configuration, showed neither the splitting of the t_2 nor the expected symmetry lowering atomic distortion [155]. This is similar to the case of Cd-vacancy (V_{Cd}) in CdTe, described by Lany et al. [202], where the experimentally observed Jahn-Teller effect could not be confirmed theoretically by DFT calculations.

In order to investigate the Jahn-Teller effect theoretically we have performed calculations starting from a configuration with lower symmetry: we have displaced the H atom from the ideal Cd vacancy position and then let the system relax. During the relaxation process we observed that the H atom moved closer to one of the Te atoms, lowering the tetragonal symmetry of he system. As a result of the relaxation, the shortest H-Te distance becomes 1.69 Å and the total energy of the system is lowered by 1.22 eV/(64 atom-supercell) compared to the case when H is located at the high symmetry site (Cd-site).

To further analyse the Jahn-Teller effect, we compare the band structures of the distorted and undistorted H_{Cd} configurations. In Fig. 6.9 we observe several diffrences between the two band structures, but what is relevant to the present discussion is the splitting of the top VB, when H is moved out of the high symmetry configuration. As a result of the relaxation, the t_2 level located at the top of the VB splits into a doubly-degenerate level and a single band (see Fig. 6.9. The removal of the 3-fold degeneracy of the t_2 level, associated with the lowering of the spatial symmetry of the defect center, followed by the lowering of the total energy can be attributed to the Jahn-Teller effect. At the Γ - point, the Jahn-Teller splitting (see Fig. 6.9

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Figure 6.9: The band structures of CdTe with (a) H at the ideal Cd site and (b) H removed from the quasi-equilibrium site. When H occupies the ideal Cd vacancy position (panel (a)), the t_2 level is 3-fold degenerate at Γ -point. The degeneracy is removed by the Jahn-Teller distortion (panel (b)). The Jahn-Teller splitting is \sim 74 meV at Γ -point.

(b)) is approximately 74 meV. We have also analyzed the charge density distribution associated with t_2 bands. We found that in the Jahn-Teller distorted system, the t_2 levels are localized on only three Te atoms from around the defect center. The Te atom which captures the H, is not involved in the re-hybridization of the dangling bonds around the Cd vacancy.

6.5 Defect formation energies

In the previous sections we have discussed the properties of a neutral H impurity located at several different sites in CdTe. However, since the formation energy of a defect configuration depends on its charge state (see Eq. (2.52)), in order to establish the preferred location of the H, one has to calculate the formation energies of the defect in different charge states. Depending on the position of the Fermi level (E_F) ,



Figure 6.10: The formation energies of the H defect located at different sites in CdTe, as a function of Fermi energy. The lowest energy locations are at the BC site for H^+ and H^0 and at the T_{Cd} site for H^- .

a hydrogen impurity can generally occur in three different charge states: H^+ , H^0 or H^- . The dependence on the Fermi energy is due to the fact that, in order to produce a certain charge state, electrons must be exchanged with the electron reservoir with energy equal to E_F .

Figure 6.10 shows the calculated formation energies of the H defect located at different sites in CdTe as a function of Fermi energy, using Eq. (2.52). We observe that for H^0 and H^+ the lowest formation energies occur when H is located at the bond center (BC) site. This indicates that the energy gained due to the formation of the strong H-Te bond compensates the energy lost due to the significant strain induced in the lattice due to the presence of H at the BC site. H^- on the other hand, prefers to occupy the tetrahedral interstitial site with Cd nearest neighbors (T_{Cd}). This is because the defect level induced by H at T_{Cd} is located near the VBM (see Fig 6.6(a)) and it therefore requires less energy to create H^- by placing a second electron on this level, compared to the case when H is at T_{Te} or BC sites, where the

	CdTe			Formation energies	
	E_{gap} (at Γ)	$E_{gap} (average)^1$	$\Delta H({ m CdTe})$	H ⁺ at BC site	H ⁻ at T _{Cd} site
LDA	0.63	1.92	-0.74	$0.29 + E_F$	$2.42 - E_F$
GGA	0.56	1.74	-0.93	$0.22 + E_F$	$2.63-\bar{E_F}$

Table 6.1: The CdTe band gap, formation enthalpy and the formation energies of the lowest energy defects and charge states. All values are given in eV.

defect levels are closer to CBM (Fig. 6.6(b) and Fig. 6.8(a)).

Our calculations suggest that H^0 is not stable in CdTe. As shown in Fig. 6.10, the formation energies of H^+ and H^- are less compared to H^0 for all values of E_F throughout the band gap. When E_F is closer to VBM (p-type samples), H gives up its electron and therefore acts as a donor, compensating the holes in the VB. If E_F is raised above the midgap (n-type samples), H acquires an electron, acting as an acceptor. This suggests that H acts as an amphoteric impurity, always compensating the intentional donors or acceptors in CdTe.

6.6 Comparison between the LDA and GGA results

It is known that the results of the DFT electronic structure calculations on a given system can be slightly different, depending on the approximation used for the exchangecorrelation functional. The LDA and the GGA usually produce different values for the lattice parameters, band gaps, cohesive energies, formation enthalpies. Due to the overbinding character of the LDA, it provides smaller lattice constants, compared to the experimental values. The GGA on the other hand, tends to overestimate the structural parameters. In the case of CdTe we find that the theoretical lattice constant calculated with the LDA and the GGA are ~0.6% smaller and ~3% larger than the experimental value of 6.46 Å [140], respectively.



Figure 6.11: Comparison between the LDA and GGA results for the formation energies of the lowest energy hydrogen defects in CdTe. Despite the small quantitative variations, there is good qualitative agreement between the LDA and GGA results.

In order to see how the defect formation energies depend on the choice of the exchange-correlation functional, we performed both LDA and GGA calculations on the systems with the lowest defect formation energies (i.e. hydrogen at BC and T_{Cd} sites). The comparison between the LDA and GGA results is shown in Fig. 6.11 and the calculated numerical values are listed in Table 6.6. We observe that the LDA provides higher formation energy for H⁺ at BC site compared to the GGA. On the other hand, the formation energy of H⁻ at T_{Cd} site as calculated with the LDA, is lower than the GGA result. As pointed out in Ref. [203], these variations in the defect formation energies, formation enthalpies and band gaps. For example we find that in the case of pure CdTe, the heat of formation is -0.74 eV in the LDA and -0.93 eV in the GGA, the latter being in better agreement with the experimental value of -0.96

¹the VBM and CBM are taken as average over all special k-points where the total energy was calculated (see Ref. [128])

eV [199]. Also the chemical potential of hydrogen is 0.04 eV smaller in the GGA [204]. Since the energy position of the defect levels relative to the band edges is influenced by the size of the gap, the differences between the LDA/GGA band gaps could also influence the formation energies. However, despite the quantitative differences, there is good qualitative agreement between the LDA and GGA results.

6.7 Summary

The formation energy calculations indicate that the ground state position of the H inside the CdTe lattice depends on its charge state. The lowest energy position for H^0 and H^+ is at the BC site while H^- prefers the T_{Cd} site. We find that H in CdTe acts as an amphoteric impurity: in p-type materials, H is in a positive charge state acting as a donor to neutralize the free holes in the VB and in n-type materials, H acquires an electron, compensating the donors in the sample. We find that despite some small quantitative variations, the LDA and the GGA provides qualitatively similar results. The configuration in which H occupies the Cd vacancy site undergoes Jahn-Teller distortion due to the presence of the partially filled t_2 (p-like) level at the top of the VB. As a result, the H atom moves closer to one Te atom, lowering the symmetry of the defect center. The degeneracy of the t_2 level is removed and the total energy of the supercell is lowered by 1.22 eV, which is an extremely large effect. The Jahn-Teller splitting of the t_2 level at the Γ -point is 74 meV.

Chapter 7

Ytterbium containing systems

7.1 Introduction: the LDA+U method

We have mentioned in Sections 1.3 and 2.3.3 that the LDA, as an approximation, cannot be successful for all systems, although in principle, the exact DFT should be capable of obtaining the ground-state properties. The deficiency of LDA is most clearly seen in the case of strongly correlated materials, such transition metal (TM) or rare-earth (RE) metal containing systems, with partially filled d (or f) shells. When a one-electron method with an orbital-independent potential (like the LDA) is applied to TM (or RE) compounds, the result is a partially filled d (or f) band with metallic-type electronic structure and itinerant d (or f) electrons. This result is incorrect for the late-transition-metal oxides and rare-earth metal compounds where d (and f) electrons are well localized and usually there is a large energy separation between occupied and unoccupied subbands.

There were several attempts to improve the LDA in order to take into account strong electronelectron correlations. One of the most popular approaches is the selfinteraction correction (SIC) method [205]. It reproduces quite well the localized nature of the d (or f) electrons in transition metal (rare earth metal) compounds, but the SIC one-electron energies are usually in strong disagreement with spectroscopy data.

The Hartree-Fock (HF) method [206] is appropriate for describing Mott insulators because it explicitly contains a term which cancels the self-interaction. The fact that the self-interaction is treated in an averaged way in the LDA is the main reason for which the LDA gives the qualitative disagreement with experimental data. However, a serious problem of the Hartree-Fock approximation is the unscreened nature of the Coulomb interaction used in this method. The "bare" value of Coulomb interaction parameter U is rather large (15-20 eV) while screening in a solid leads to much smaller values: 7-8 eV or less [207, 208]. Due to the neglect of screening, the HF energy gap values are a factor of 2-3 larger than the experimental values [206].

The problem of screening is addressed in the GW approximation [110,209], which may be regarded as a HartreeFock theory with an orbital-dependent screened Coulomb interaction. The GW has been applied with success to real systems ranging from simple metals to transition metals but applications to more complex systems have not been feasible up to now due to the large computational task.

In Section 2.3.3 we indicated that a successful way to overcome the LDA deficiency in describing strongly correlated systems is the so-called LDA+U method [84-86]. In this method the orbital dependent Coulomb interaction is taken into account for the localized states, while the delocalised states are treated by the standard LDA potential. This idea is reflected in Eq. (2.48), in which the on-site Coulomb interaction is considered by the addition of the Hubbard like term to the LDA energy functional. Naturally, in order to avoid double counting, the corresponding average d-d (or f-f) Coulomb interaction energy must be subtracted. This Coulomb interaction energy given by LDA is a good approximation, however, the orbital energies (eigenvalues) are wrong.

If we rewrite Eq. (2.48), in which (for simplicity) the exchange interaction and the

anisotropy of the Coulomb interaction within the locaized shell are neglected:

$$E = E_{LDA} - UN(N-1)/2 + \frac{1}{2}U\sum_{i\neq j}n_in_j,$$
(7.1)

where $N = \sum_{i} n_{i}$, we can calculate the orbital energies ϵ_{i} as derivatives of (7.1) with respect to the orbital occupancies n_{i} :

$$\epsilon_{i} = \frac{\partial E}{\partial n_{i}} = \frac{\partial E_{LDA}}{\partial n_{i}} + U\left(\frac{1}{2} - n_{i}\right) = \epsilon_{LDA,i} + U\left(\frac{1}{2} - n_{i}\right)$$
(7.2)

This above equation shows that the energy of the occupied orbitals $(n_i = 1)$ is shifted by -U/2 and the energy of the unoccupied orbitals $(n_i = 0)$ is shifted by +U/2. The orbital dependent potential can be calculated in a similar way starting from (7.1), but the variation is taken not on the total charge (occupation) associated with the orbital *i*, but the charge density of the *i*th orbital:

$$V_i(\vec{r}) = \frac{\delta E}{\delta n_i(\vec{r})} = V_{LDA,i} + U\left(\frac{1}{2} - n_i\right)$$
(7.3)

The additional contribution to the LDA potential is independent of \vec{r} . The oneelectron potential given by the above expression has a discontinuous behavior as a function of the occupation number. From Eq. (7.3) we see that the one-electron, orbital-dependent potential is attractive for orbitals occupied by more than 1/2 electrons and it is repulsive for orbitals occupied by less than 1/2 electrons.

If the exchange interaction is taken into account, then the interaction energy for electrons with the same spin projection σ will be (U - J). Furthermore, the non-sphericity of the Coulomb and exchange interactions (dependence on which particular orbital m and m' are occupied or empty) can also be considered by introducing the matrices $U_{mm'}$ and $J_{mm'}$. The energy functional in this case takes the form:

$$E = E_{LDA} - [UN(N-1)/2 - JN(N-2)/4] + \frac{1}{2} \sum_{m,m',\sigma} U_{mm'} n_{m\sigma} n_{m',-\sigma} + \frac{1}{2} \sum_{m \neq m',m',\sigma} (U_{mm'} - J_{mm'}) n_{m\sigma} n_{m'\sigma}$$
(7.4)

The above scheme was developed by Anisimov et al. [85]. The double-counting term (the second term in Eq. (7.1) and (7.4)) has been chosen to ensure an atomiclike limit of the LDA, which approximately removes the electron self-interaction, hence it is usually referred to as the "self-interaction corrected" (SIC) LDA+U method. A slightly different version of the LDA+U method was formulated by Czyżyk and Sawatzky [86], in the literature, referred to as an "around mean field" (AMF) correction. The former scheme (SIC) is usually more appropriate for highly localized electrons while the latter (AMF) might be better for weakly correlated systems. The detailed description of the two methods can be found in the literature [85,86], but we can easily illustrate the difference between AMF and SIC models by considering only the diagonal elements of the density matrix and neglecting the exchange interaction. The orbital-dependent corrections to the LDA potential have then the following form:

$$V^{AMF} = V^{L(S)DA} + U\left(n^0_\sigma - n_{m\sigma}\right)$$
(7.5)

$$V^{SIC} = V^{L(S)DA} + U\left(\frac{1}{2} - n_{m\sigma}\right)$$
(7.6)

where $n_{\sigma}^{0} = \frac{1}{2l+1} \sum_{m} n_{m\sigma}$ is the average occupation and $n_{m\sigma}$ is the occupation number of orbital m with spin σ . The difference between the two methods is clear: assuming positive U, the AMF correction to the potential is attractive for orbitals occupied with more than the average and repulsive for states occupied with less than the average occupancy. The SIC potential (as we have already mentioned) does the same for states occupied by more or less than one-half.

Despite its considerable success, the L(S)DA+U approach has several shortcomings. First, strictly speaking, it is not a fully *ab initio* method, since it contains two parameters which determine the orbital potential felt by the localized d or f states: the Hubbard and exchange parameters U and J. The values of these parameters can be determined by comparing the positions of the d (or f) levels obtained from xray photoemission spectroscopy (XPS) measurements to the theoretical value. It has been found that the physically reasonable values of the Coulomb term U for the fstates are in the range of 5-9 eV and the values of the exchange term J are ${\sim}10\%$ of U [210]. There are also theoretical methods to find the value of U and J based on electronic structure calculations using supercell methods [208]. The second problem with L(S)DA+U comes from the fact that in the case of partially filled d or f states, the electrons can be arranged in many different ways over the different orbitals, and it is possible that in each case a converged solution is obtained. In other words, the self-consistent cycle can easily be trapped in a local energy minimum, which may not necessarily be the true ground state. In order to overcome this problem of L(S)DA+U, one can perform "constrained density matrix" (CDM) calculations [66,211]. The main idea in the CDM method is that one can do a series of calculations keeping the density matrices unchanged (the diagonal elements of the density matrix represent the orbital occupation number) and then, based on the fact that L(S)DA+U (for fixed U) is a variational method [212], one can use the total energy criterion to obtain the ground state configuration. In Ref. [66] the method was applied successfully to CeSb and it was found that the lowest-energy Ce f^1 configuration corresponds to the case when m = -3 spin-up state was occupied (in agreement with Hund's rules). This result is relevant to our case, since Yb is often considered as "one f-hole" analogue the Ce f^1 configuration. A more recent example of CDM calculation can be found in Ref. [211], where the properties of RE-ion impurities in Fe host lattice have been investigated.



Figure 7.1: The crystal structure of YbNiFeAl₈ viewed down on the z-axis. In this figure the M1 and M2 sites are occupied by Ni and Fe respectively

In the next sections we apply the LDA+U method combined with the CDM approach to several Yb-containing intermetallics to investigate the role played by the Yb ion in the electronic and magnetic properties of these materials.

7.2 Electronic structure of YbNiFeAl₈

 $YbNi_{2-x}Fe_xAl_8$ crystallizes in the CaCo₂Al₈ structure type in the space group Pbam. The existence of a large number of isotypical ternary phases [213–216] indicates that this is a rather stable structural arrangement. $YbNi_{2-x}Fe_xAl_8$ seems to be the first quaternary analog of this structure type. In the structure of $YbNi_{2-x}Fe_xAl_8$, a total of 12 atomic sites including one Yb, two transition metal sites (M(1) and M(2) occupied by Ni/Fe) and nine Al sites were identified. Figure 7.1 depicts the structure of $YbNi_{2-x}Fe_xAl_8$, viewed down the z-axis. The M(1)- and M(2)-centered polyhedra, composed of Al atoms, form a three-dimensional framework with Yb ions sitting in small channels. In order to understand the nature of bonding between different atoms and the orbital distributions of Yb f electrons and Ni and Fe d electrons, we have performed electronic structure calculations in a series of compounds. According to the singlecrystal structure refinement, the transition metal sites M(1) and M(2) are occupied by a mixture of Ni/Fe: 42%/58% on M(1) and 62%/38% on M(2) [217]. To model this mixed occupancy we constructed a 1x1x2 supercell, which corresponds to placing two unit cells next to each other along the [001] direction. In one unit cell the M(1) and M(2) sites were assigned as Ni and Fe respectively, while in the second unit cell the assignments were switched, i.e. Fe on M(1) and Ni on M(2). This supercell model corresponds to 50%/50% occupancy of Ni/Fe on both M(1) and M(2) sites in a quasiperiodic structure, which is close to the experimental observation. The total number of atoms in the supercell is 88 (8 Yb, 8 Ni, 8 Fe and 64 Al atoms).

Before discussing the results of our calculations we make a few general remarks about the ability of LSDA+U calculations to describe the physics of Yb (f^{14} and f^{13}) systems, particularly the mixed valence ground state. There are many calculations which give the Yb³⁺ (f^{13}) state properly (e.g. Refs. [218,219]). In these calculations 13 f states lie below the Fermi level (E_F) and 1 f state lies above E_F , the splitting between the occupied and unoccupied levels being $\sim U$. The calculations by Antonov et al. [219] on YbInCu4 system, using the LMTO method indicate that the above single f level is pinned to the Fermi energy thereby giving a mixed-valent ground state for this compound, which is in agreement with experiment. This pinning was found to be not very sensitive to the exact value of U as long as U was greater than 5 eV, but it depended sensitively on the density of states associated with non-f states. We have redone the calculation in this compound using all-electron FPLAPW method and found the same result. Thus we conclude that LSDA+U calculation is capable of giving a mixed-valent ground state.

The total density of spin-up and spin-down states for $YbNiFeAl_8$ are shown in



Figure 7.2: Results from the electronic band calculations for YbNiFeAl₈.(a) and (b): Total spin-up and spin-down DOS of YbNiFeAl₈. (c) Yb 4f spin-up DOS, with 6 occupied states and one hole located at 2 eV. (d) Yb 4f spin-down DOS, with all 7 states occupied. (e) Ni(1) 3d and Ni(2) 3d DOS. (f) Fe(1) 3d and Fe(2) 3d DOS. (g) and (h) p states of Al atoms located around M(1) (Al10 and Al9) and located around M(2) (Al11 and Al5)

Fig. 7.2 (a) and (b) respectively. The main features of these two DOS figures are the sharp peaks located between -5 eV and -7 eV below E_F , which is set to be at 0 eV. They are split because of the spin-orbit (SO) interaction and the anisotropy of the Coulomb interaction within the 4*f* shell of the Yb ions. The peak (width ~0.2eV) located nearly 2 eV above the E_F , which is only present in Fig. 7.2 (a), represents the main difference between the spin-up and spin-down DOS. This band originates from the hole in the 4*f* spin-up state of Yb with $m_I = +2$ character. Convergent solutions

were also obtained for unoccupied $|3,\uparrow\rangle$, $|1,\uparrow\rangle$ and $|0,\uparrow\rangle$ states, but it was found that the lowest energy configuration corresponded to the unoccupied $|2,\uparrow\rangle$ state.

The splitting within the f shell can be seen more clearly in Fig. 7.2 (c) and (d), which show the projected DOS of Yb 4f states. The left panel (Fig. 7.2 (c)) displays the spin-up DOS, with six out of seven states fully occupied, while the seventh spinup state, located at 2 eV above E_F , is empty. In Fig. 7.2 (d), all seven 4f spin-down states are situated below E_F . From this picture we can conclude that the valence state of Yb is 3+. Another character shown in both total spin-up and spin-down DOS Fig. 7.2 (a) and (b) is the uniform background due to Al, Ni, and Fe states, as well as a finite DOS at the Fermi level, indicating the metallic nature of the system. This is consistent with very small value of thermopower observed in this system (~-1 μ V/K at room temperature) [217]. The broad hump in the DOS located between E_F and -4 eV comes from the d states of Ni and Fe. The Ni 3d bands (Fig. 7.2 (e)) are located well below E_F , suggesting a filled $3d^{10}$ configuration. Therefore, the Ni is essentially reduced to a diamagnetic state $(d^8s^2 \rightarrow d^{10})$. This is also evident from the spin-up and spin-down DOS, which are almost identical for both Ni atoms (only the spin-up DOS is shown). This type of behavior in late transition metals has been observed in several intermetallic systems containing more electropositive elements [220]. The Fe 3d spin-up states, shown in Fig. 7.2 (f), have a significant contribution to the DOS near the Fermi level, indicating that these states are not fully occupied. However, the spin-up and spin-down DOS of the Fe d levels are identical, just as they were in the case of Ni. Thus Ni and Fe do not show a local magnetic moment. They, however, contribute to Pauli paramagnetic susceptibility.

An interesting feature, shared by both Ni and Fe d states, can be observed from Fig. 7.2 (e) and (f): they become energetically more stable when the atom occupies the M(2) site. The difference in the DOS of the d levels of the Fe occupying different sites in the supercell is in agreement with the result of the Mössbauer spectroscopy [217] which shows different local charge densities at two different Fe sites in the structure. The coordination environments of M(1) and M(2) sites are similar in that both are surrounded by 9 Al atoms, but there are fundamental differences. The transition metal atoms located at the M(1) sites form dimers. It seems that the dimer geometry reduces the degree of mixing between some Al p and Ni/Fe d orbitals. This can be verified by analyzing the contribution to the DOS of the p orbitals of several different Al atoms. Figure 7.2 (g) and (h) show the p states of Al(10) and Al(9) from the tricapped trigonal prism surrounding M(2) as well as the p states of Al(11) and Al(5) surrounding M(1). It is evident that the Al p states hybridize more with the d states of Ni(2) and Fe(2), than with the d states of Ni(1) and Fe(1). Because of the higher degree of p - d hybridization between Al and Ni/Fe located on M(2), these states are energetically better stabilized.

Next we discuss the magnetic properties of the system coming primarily from the unfilled Yb f shell. The calculated spin and orbital magnetic moments for the two Yb ions are: $\mu_{spin} = 1.0059\mu_B$; $\mu_{orb} = 1.9811\mu_B$ for Yb1 and $\mu_{spin} = 1.0044\mu_B$; $\mu_{orb} = 1.9810\mu_B$ for Yb2. This adds up to approximately 2.99 μ_B per Yb ion suggesting a strong atomic character and trivalent configuration. The fact that the 13 occupied and the 1 empty f states are far removed from the Fermi energy argues against a mixed-valence picture. A similar result showing a hole in the 4f shell of Yb was recently obtained on YbRh₂Si₂ [218]. This kind of electronic structure, where the empty and occupied f states are well separated and located far from E_F , together with the absence of long range magnetic order, suggest the possibility of Kondo-lattice scenario. We have to emphasize, however, that DFT with LSDA+U approximation is an effective single particle theory and therefore cannot describe the complex correlated many-body ground state of a Kondo lattice system. Finally, the results presented here point to the need to investigate in more detail the parent compound YbCo₂Al₈ with respect to magnetism, the role of Co atoms and the electronic state of Yb.



Figure 7.3: (a) the top view and the (b) side view of $Yb_3Au_3In_3$ hexagonal crystal structure. $Yb_3AuGe_2In_3$ is obtained by replacing the two Au atoms/cell indicated by the arrows

7.3 The valence state of Yb in Yb₃Au₃In₃ and Yb₃AuGe₂In₃

Yb₃Au₃In₃ crystallizes in a hexagonal system in the space group $P\bar{6}2m$ [221]. The crystal structure, shown in Fig. 7.3, can be regarded as three Au-In dimensional framework, in which one dimensional channels run along the crystallographic c-axis. These channels are occupied by 1D chains of Yb atoms. The figure also indicates that Yb₃AuGe₂In₃ is obtained by replacing two Au atoms in a unit cell by two Ge atoms. The crystallographic analysis of Yb₃Au₃In₃ and Yb₃AuGe₂In₃ reveals a peculiar feature: on the one hand the a- and b-axis of the Yb₃Au₃In₃ are larger than those of Yb₃AuGe₂In₃. This, of course, can be related to the fact that Au atoms are larger than Ge atoms. On the other hand, the c-axis of Yb₃Au₃In₃ is 10% shorter than that of Yb₃AuGe₂In₃, which cannot be understod by the size difference between Au and Ge. We will try to explain this feature, using electronic structure calculations on Yb₃Au₃In₃ and Yb₃AuGe₂In₃ focusing on the role played by the Yb *f* electrons in the electronic and structural properties of the two systems.



Figure 7.4: (a) Band structure of Yb₃Au₃In₃ with the In 3*p* orbital character emphasized. The unoccupied 4*f* level lies at 1 eV above E_F . (b) Band structure of Yb₃AuGe₂In₃ showing the Ge 3*p* orbital character. The band structures were calculated for U = 6.75 eV.

The band structure obtained for Yb₃Au₃In₃ is shown in Fig. 7.4(a). The states near the Fermi level are associated with In p, Au p and Yb d orbitals. Yb 5d bands are mostly unoccupied, but they hybridize with In p states therefore we find Yb 5d character even below E_F . The flat band located at 1 eV above E_F represents an unoccupied level in the 4f shell of the Yb atom. The occupied Yb 4f bands lie between -5 eV and -7 eV below E_F , they are split into $4f_{5/2}$ and $4f_{7/2}$ manifolds under spin orbit (SO) interaction of approximately 1.3 eV. The two spin-orbit complexes are further split due to the anisotropy of the Coulomb interaction within the 4fshell [212] and possibly due to crystal field effect. All the bands originating from Yb f orbitals are quite flat, and hybridize weakly with the other electronic states. Unlike in YbInCu₄ and YbNiFeAl₈ we find that the splitting between the empty and occupied 4f levels is very sensitive to the value of the Coulomb repulsion U. This is shown in Fig. 7.5(a) where we plot the spin-up DOS associated with the Yb f states in Yb₃Au₃In₃ for different values of U. We observe that the empty f level is the one, which shifts up or down on the energy scale as the value of U increases or decreases, while the occupied bands remain mainly at the same position. However, at bandtheory level, for physically acceptable values of U [210], the occupied and empty 4fstates are well separated (the separation between them being approximately equal to the U value) and located sufficiently far from E_F , indicating a trivalent configuration for the Yb ion. In order to calculate the f occupation number we have integrated the DOS associated with the Yb 4f bands from -15 eV to E_F . The results obtained for different U's are listed in Table 7.1 indicating that in Yb₃Au₃In₃, 13 electrons occupy the Yb 4f bands.

In contrast, the electronic structure calculations performed on Yb₃AuGe₂In₃ suggest quite a different picture for the Yb valency. The band structure of $Yb_3AuGe_2In_3$, shown in Fig. 7.4(b), displays an interesting feature: one flat band, originating from Yb f levels is located right at E_F . An important aspect of this observation is that the position of the Yb f level, which is pinned at E_F , does not depend on the U value. This can be observed in Fig. 7.5(b), which shows the DOS associated with the Yb f levels in Yb₃AuGe₂In₃, calculated for different U's. The upper f state is pinned to E_F , while the other f levels are slightly shifted up or down in energy, depending on the value of the Coulomb repulsion U. Since Yb₃Au₃In₃ and Yb₃AuGe₂In₃ are isostructural systems and the latter is obtained by replacing two Au atoms in Yb₃Au₃In₃ by two Ge atoms, the Fermi level pinning must be related to the presence of Ge. When Au $(5d^{10}6s^1)$ is replaced by Ge $(3d^{10}4s^24p^2)$ the number of valence electrons in the system increases, therefore the Fermi level is shifted up. The Ge pband is not completely filled, so that, the bands near E_F have mostly Ge p character. Since the upper Yb f level, which was initially located above E_F , now lies below the top of Ge p band, becomes partially occupied and pinned to E_F . Therefore the position of the upper Yb f level with respect to the Ge p states becomes essential in



Figure 7.5: Spin polarized density of states associated with the spin-up Yb f electrons for (a) Yb₃Au₃In₃ and (b) Yb₃AuGe₂In₃. In the case of Yb₃Au₃In₃ the unoccupied f level is shifted up in energy as the U value increases. For Yb₃AuGe₂In₃ the Fermi level (zero on the energy scale) is pinned to the upper f level.

understanding the Fermi level pinning in Yb₃AuGe₂In₃.

To find the f occupation number and the degree of Yb valency, we have integrated the DOS of associated with Yb 4f. The results for different U's are listed in Table 7.1. We observe that the 4f shell is partially occupied, with an occupa-
U value (eV/Ry)	f occupation number	
	Yb3Au3In3	Yb3AuGe2In3
5.44/0.4	13.01	13.50
6.75/0.5	12.92	13.31
8.16/0.6		13.42
9.52/0.7	12.92	

Table 7.1: The calculated f occupation for different values of the Coulomb correlation U.

tion number of between 13.3-13.5. Therefore, according to our electronic structure calculation, which includes magnetic and relativistic effects as well as intra-atomic correlation (in L(S)DA+U approximation), there is an essential difference between the two systems: in the Yb₃Au₃In₃ the Yb ion is in trivalent configuration (Yb³⁺), with one hole in the 4f shell, while in Yb₃AuGe₂In₃, Yb is calculated to be intermediate valent (Yb^{2+/3+}), with a valency of approximately ~2.6. As a restult, a series of physical properties, closely related to the Yb valency, will be different in the two systems.

The interesting behavior of the lattice parameters, mentioned at the beginning of this section, can also be associated with the valence configuration of the Yb atoms. Since Ge is smaller than Au, one would expect an overall decrease in the lattice parameters of Yb₃AuGe₂In₃ compared to those of Yb₃Au₃In₃. However, in the presence of Ge, the valency of Yb becomes Yb^{2+/3+}. Since Yb^{2+/3+} is larger than Yb³⁺, the overall decrease in the lattice constants will be balanced by the increase in the size of Yb. If we consider the crystal structure of Yb₃Au₃In₃ as being formed by alternating monoatomic sheets of In-Au and Yb-Au stacked along the c-axis we have the following situation: on the one hand the In-Au sheet shrinks when Au is replaced by Ge, but on the other hand, the Yb-Au sheet expands due to the increase in size of the Yb. The net effect is a decrease in the a- and b- and an increase in the c-parameter. To verify this point we have performed structural relaxation calculations

on two hypothetical systems La₃Au₃In₃ and Lu₃Au₃In₃. The two systems were chosen to simulate the change in the size of the Yb atom and to avoid complications arising from the presence of the partially filled f levels, at the same time. The obtained theoretical lattice parameters for La₃Au₃In₃ were a = 7.89 Å; c = 4.36 Å and for Lu₃Au₃In₃ a = 7.85 Å; c = 3.76 Å. We observe that when La is replaced by Lu the decrease in the lattice constant a is ~0.5%, while the decrease in the c parameter is ~14%. From this theoretical study we conclude that the size of the Yb atom primarily influences the length of the crystallographic c-axis.

7.4 Summary

In summary, YbNi_{2-x}Fe_xAl₈, is the first quaternary analog of the YbCo₂Al₈ structure type and can crystallize from excess liquid Al. A mixed Ni/Fe occupancy appears to be present on the two transition metal sites (M1 and M2) in the structure. The studies of the magnetization behavior shows that the ab plane is the easy plane on which the magnetic moments are confined. Both resistivity and thermopower measurements on YbNi_{2-x}Fe_xAl₈ point to a strongly metallic character. Temperature dependent magnetic susceptibility measurements and electronic structure calculations (at T=0K) using the LSDA+U formalism suggest that in these systems the Yb atoms are most likely in the f^{13} configuration. All magnetism in the compound derives from Yb³⁺ species and not from the Ni or Fe atoms. ⁵⁷Fe Mössbauer spectroscopy confirms that the Fe atoms do not have a local magnetic moment, consistent with the theoretical calculations.

Using *ab initio* electronic structure calculations, we found that the differences between the physical properties of two isostructural, Yb-containing systems are strongly related to the valence configuration of the Yb atom. Yb₃Au₃In₃ is an integer valent system, with one hole in the Yb 4f shell. We can also mention that the calculated electronic structure of Yb₃Au₃In₃, with the occupied and unoccupied f levels well separated, and located far from E_F suggests Kondo behavior for the system. Yb₃AuGe₂In₃, on the other hand, was calculated to be an intermediate-valent compound, with approximately Yb^{2.6+} configuration. Fermi level pinning was observed in this system, indicating that Yb₃AuGe₂In₃ is possibly a heavy fermion system [69].

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Chapter 8

Summary and future directions

The III-VI semiconductors (GaS, GaSe, GaTe, InSe) have been subject of extensive research because their potential for use in optical applications. GaSe crystals show great promise in nonlinear optics (frequency mixing, second harmonic generation), and has been proposed as a far-infared conversion material. There is research interest in the structure and electronic properties of GaTe because of the possibility that it, or related compounds, may have applications in the electronics industry. InSe has the potential for use in photovoltaic devices and it has been the subject of extensive investigations. The crystal structure of these semiconductors are similar. They are all layered systems: the strong covalent interactions within the layers and the weak, van der Waals-type coupling between them provide an interesting, quasi-two-dimensional character to the physical properties of these materials.

Throughout the first part of this thesis, the importance of doping and its impact on the properties of semiconductors have been emphasized and explored. In the case of the III-VI family, a vast body of experimental knowledge is available on the subject of defects and impurities, especially in GaSe and InSe. The electrical and optical properties in the presence of numerous impurities (such as Cu, Cd, Zn, Sn, Mn, Cl, In, As, Bi, Sb, Te, Si, Ge) have been investigated and many impurity induced defect levels and binding energies have been detected and measured [8,29–41]. Comparatively little theoretical work has been devoted to the this class of materials and until now, there was a complete lack of theoretical approach to the problem of defects and impurities in III-VI family of semiconductors.

The detailed microscopic understanding of the nature of defect states in semiconductors, in general, is a difficult problem and it is specially challenging in the case of the III-VI family of valence mismatched systems. In this thesis the defect problem has been addressed by carrying out electronic structure calculations (hydrogenic effective mass approximation and self-consistent DFT) in pure and defect containing GaSe and GaTe. The failure of the effective mass approximation to predict the binding energies of Cd and Sn substitutional impurities in GaSe, indicated the necessity of incorporating the short range interaction into the theory [173]. The formation mechanism of the semiconducting band gap in these systems has been explained based on the interaction between the Ga s dimers states (bonding-antibonding states) and the surrounding Se (or Te in case of GaTe) p orbitals. Using this simple molecular orbital model, the general features of the Ga-site defects can be understood: when Ga is replaced by an impurity or it is removed from the system to form a vacancy, the dimer states are perturbed giving rise to localized states in the band gap. The position of the defect state in the band gap, of course, depends on the energy mismatch between the impurity orbitals and the Ga s orbitals. In the case of acceptors impurities, such as substitutional Cd on Ga site (Cd_{Ga}) , the position in the bandgap of the single particle eigenstates associated with the defects are in reasonable agreement with the experimental binding energies |41|. In contrast, the binding energies of the donor states (Sn_{Ga}) and of those split off from the conduction band in the presence of vacancies, can not be estimated reliably, because of the problems associated with the band gap and excited states calculated with LDA/GGA [154]. It is also possible that the energy mismatch between a Ga-site defect orbitals and the Ga s orbitals is

not large enough to produce defect levels in the gap. This is the case of In_{Ga} where the difference between the Ga s (-11.55 eV) and In s (-10.14 eV) orbitals is too small to perturb the dimer states and to give rise to defect states in GaSe.

Formation energy calculations associated with defects in GaTe show that the dominant intrinsic defect is the gallium vacancy (V_{Ga}). It introduces a deep (acceptor) defect state in the gap, located at 0.78 eV above the VBM, as measured at the Γ point. This value is in good agreement with the calculated charge transition level $\varepsilon(-1/-2) = 0.83$ eV and experimental results [43, 189]. The formation energies of Ge and Sn impurities reveal the under Ga-rich growth conditions it is easier to incorporate Sn in GaTe, whereas at the Te-rich limit Ge becomes more soluble than Sn. This information about the solubility is important because Ge and Sn can be used to reduce the large leakage current in GaSe and GaTe by carrier compensation [136].

The electronic structure and mechanical properties of GaSe doped with isovalent impurities (In and Te) has also been investigated in this thesis. According to the formation energy calculations, Te and In prefer to occupy the substitutional Se and Ga sites in GaSe, respectively. The calculated charge transition levels associated with different Te and In defect configurations have been compared to available experimental data [31, 32, 39]. The good agreement between the theoretical and experimental findings indicates that the *ab initio* electronic structure method is quite robust and can be used as a predictive tool for certain defect properties in semiconductors. In order to understand the mechanism of rigidity enhancement observed experimentally in doped GaSe [163, 164], the elastic properties of GaSe_{1-x}Te_x and Ga_{1-x}In_xSe have been studied as a function of composition x. The calculated elastic constants of Ga_{1-x}In_xSe show a very small increase in the elastic stiffness in the direction perpendicular to the atomic layers. The detailed microscopic description of mechanism responsible for the rigidity enhancement can be explained by the In interstitial defect configuration. In p-type GaSe, In impurity can acquire +3 charge state and can occupy an interstitial site between the atomic layers. The calculations show that the energy barrier which must be overcome in order to shear the GaSe crystal increases dramatically when In occupies the interstitial site. Therefore thi is most likely the main source of the observed improvement of the structural properties of In doped GaSe [163, 164]. Further careful measurements of GaSe doped with controlled amount of In under different carrier doping concentrations (n-type od p-type) are suggested.

Understanding the nature of H defects in semiconductors has been a long standing physics problem. There have been extensive studies of H defects in group IV and III-V semiconductors. Similar studies in II-VI semiconductors are limited. In this thesis we look at the problem of H defect in CdTe. The location and the electronic structure of H in CdTe has been investigated using first-principles theoretical methods. The mechanism of defect formation of H in CdTe is explained using simple molecular orbital models. The electronic structure of the different defect configurations were analyzed using ab initio DFT calculations. The location of the H inside the CdTe lattice was obtained by calculating total energy values with H located at many different sites and with the defect in different charge state configurations (-1, 0, +1). It has been found that H⁰ and H⁺ prefers to occupy the bond-center site (BC) located between the Cd and Te atoms, while H^- prefers the low charge density site tetrahedrally coordinated by Cd atoms (T_{Cd}) . The configuration in which H is located at the substitutional Cd site is susceptible to Jahn-Teller distortion, due to the presence of the partially occupied t_2 -level (p-like state) at the top of the VB. Electronic structure calculations show that by lowering the symmetry of the system, the degeneracy of the t_2 -level is removed and the total energy of the supercell is decreased by 1.22 eV. The calculated Jahn-Teller splitting of the t_2 -level at the Γ -point is 74 meV. H in CdTe acts as amphoteric impurity; it always takes the charge state which counteracts the prevailing type of conductivity in the system.

The electronic structure and the valence state of Yb in novel ternary and quaternary Yb-based systems have been investigated within the LDA+U formalism. It has been found that electronic, magnetic and structural properties of these systems strongly depend on the valence configuration of Yb. The LDA+U approach suggests that the Yb atoms in YbNIFeAl₈ are in the trivalent state and all magnetism derives from the Yb³⁺ species. The Ni and Fe atoms do not have local magnetic moments. The differences in the crystal structures of Yb₃Au₃In₃ and Yb₃AuGe₂In₃ have been explained based on the size difference between Yb³⁺ and Yb^{2+/3+} ions. Even though LDA+U is an effective single particle method, it can be useful in predicting complicated many-body effects in strongly correlated systems. For example, the integer valent system Yb₃Au₃In₃, with well separated occupied and unoccupied f levels, located far from the Fermi level is susceptible to Kondo effect. On the other hand, the intermediate valent system Yb₃AuGe₂In₃ with the Fermi level pinned to the partially occupied f level is likely to be a heavy fermion compound.

Finally I would like to make some comments on the use of DFT/LDA and supercell methods to understand the defect physics. Density-functional theory [122, 123] has proven to be a very successful tool for the study of a wide variety of problems in solid state physics. However, in many cases, achieving the required accuracy in total energy calculations (especially when one has to deal with charged defects) is not an easy task and requires careful analysis of several sources of errors. In the Kohn-Sham formalism of DFT (which is most commonly used) the electron-electron interactions are described with an exchange correlation potential, which is a functional of the charge density. Since the exact form of this functional is not known, for practical purposes it has to be approximated, which implicitly introduces sources of errors in the theory. In the local density approximation (LDA) the exchange and correlation potential at a particular point is only a function of the charge density at the same point. A slightly improved version is the generalized gradient approximation (GGA) which takes into account not only the density alone, but also its local spatial variations. Such an approximation fails when the charge density varies rapidly in space. The LDA and GGA have been extensively tested and found to provide a reliable description of a wide variety of solid-state properties, for wide band systems. However, even for such systems, the LDA and GGA have several shortcomings. The classic failure of LDA and GGA is the underestimation of the band gap in semiconductor and insulators, which makes it very difficult to calculate the binding energies of various defects (especially when the defect states are derived from the CB). Another source of error in DFT calculations is related to the choice of numerical cutoff parameters, intergration schemes, sampling of the Brillouin zone, construction of basis sets and pseudopotentials. However, since all these parameters are tractable by explicit convergence tests, the DFT calculations can provide quite accurate estimates of total energies ($\sim 0.01 \text{ eV}/\text{atom}$).

In the case of defect calculations using supercell models, one has to deal with other technical problems such as the spurious interaction between defects in neighboring supercells, which leads to the dispersion of the defect related electronic states. This *finite size* effect can be reduced by a proper scaling analysis as a function of the cell size. However, for computational reasons, one can not consider very large supercells, therefore the host bandstructure, which is the natural reference for the defect states, will always be affected by the presence of defects. Consequently, one has to choose a reference energy-level and align the bandstructures of the defect containing and defect free systems in order to get a proper estimate of the defect ionization levels defects. All these issues make it challenging to obtain quantitatively accurate results for defects in semiconductors, using supercell calculations. The power of DFT however, relies in bringing out systematic trends in the properties of defects in semiconductors, such as the nature of the deep levels, their spin structure point symmetry, energetics, local vibrational modes, potential energy surfaces for defects moving in the lattice. The results of DFT calculation provide a good starting point for more advanced calculations where many-electron effects are treated beyond the mean-field approximation, such as the GW method [110].

Many recent theoretical studies, such as those presented in this thesis, establish the combination of DFT with the supercell technique as a powerful tool for investigating the properties of defects in semiconductors. One area in which theory is not yet able to make accurate predictions is the position of defect levels in the band structure. Methods that go beyond the one-particle description are available (for example the GW method [110]), but presently too computationally demanding. Increasing computer power and/or the development of simplified schemes will allow the firstprinciples prediction of the defect spectra in the future. The dynamics of impurities in semiconductors (especially that of H) also requires more scrutiny: investigations of quantum diffusion, incorporating tunneling effects, and also finite temperature studies will provide a better understanding of how H defects affect the physical properties of semiconductors. While many qualitative results presented in this thesis are doubtlessly of general validity, it is necessary to obtain quantitative answers and broaden our insights, especially where technological applications are very promising, such as the study of other defects in III-VI semiconductors, or the behavior of H in III-V and other II-VI compound semiconductors.

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