Improving Cu(In,Ga)Se2 solar cell absorbers based on atomic-level modeling

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Abstract

Cu(In, Ga)Se₂ (CIGS)-based solar cells are among the most promising candidates to replace crystalline silicon solar cells, thanks to their high efficiencies and low costs. The defect microstructure of the CIGS light absorber layer influences the optical and electronic properties of CIGS solar cells. The recent progress in their efficiency (up to 23.35 %) is mainly due to the incorporation of different alkali metal atoms into the absorber layer. As efficiency increases towards the Shockley-Queisser limit (31 % for a cell with a band gap of 1.3 eV), it becomes more difficult to improve. Thus, knowledge about native point defects and impurities, as well as about the formation of secondary phases in the CIGS absorber layer, is among essential information for optimizing CIGS solar cell performance.

In this thesis, the choice of computational methods and their details strongly affects even the qualitative features of the obtained results. Therefore, the effects of the most important computational parameters are studied carefully in the thesis. Native point defects, native point defect complexes, and alkali metal impurities in the CIGS absorber layer are investigated using first-principles calculations within density functional theory (DFT) in order to understand their effect on the electronic structure. Moreover, based on DFT calculations, a mechanism for secondary phase (e.g. alkali indium selenide) formation is suggested.

Calculating defects in CIGS is not straightforward. It is impossible to model defects directly in CIGS because In and Ga randomly occupy the same sites. Therefore all the calculations presented in this thesis are performed for CuInSe₂ and CuGaSe₂. In this thesis, calculations of native point defect formation energies in CuInSe₂ provide information about the abundances of acceptors and donors for materials of different Cu concentrations. Moreover, it is shown that light alkali metal atoms prefer to accumulate on the Cu sublattice as impurities, and incorporation of heavy alkali metal atoms contributes mostly by phase separation. The formation of alkali indium/gallium selenide secondary phases during the post-deposition treatment is predicted by considering possible reactions between CuInSe₂/CuGaSe₂ and different alkali metal compounds by calculating their formation enthalpies. Interfaces between the secondary phases and the CuInSe₂ absorber layer are studied in terms of band offsets. Finally, comparisons between the hard X-ray photoelectron spectroscopy (HAXPES) data and the density of states calculations with potassium post-deposition treatment (PDT) as a case study reveal the formation of the KInSe₂ phase on the CIGS absorber surface after heavy potassium post-deposition treatment.

In summary, the results in this thesis give information about the energetic characteristics of native point defects, native point defect complexes, alkali metal impurities, and alkali metal secondary phases. The results help to analyse already existing experimental observations of the abundances of point defects, migration mechanisms, and the formation of secondary phases.

Keywords solar cells, DFT, Cu(In,Ga)Se₂, alkali post-deposition treatment.
Preface

The work presented in this thesis has been carried out in the framework of the Sharc25 project with the support of the Horizon 2020 program. I also acknowledge CSC - IT Center of Science and the Aalto Science - IT project for the computational resources. I would like to thank my supervisor Prof. Martti Puska, for giving me the opportunity to be the part of the Electronic Properties of Materials (EPM) group. I truly appreciate his expert guidance and support throughout my research. I have learned so much from Martti, and I’m so appreciative of all the time he has taken to teach me new things.

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Preface

because of you. Thank you for give me a million reasons to be happy everyday.

Espoo, June 11, 2019,

Maria Malitckaya
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This thesis consists of an overview and of the following publications which are referred to in the text by their Roman numerals.


Author’s Contribution

Publication I: “First-principles modeling of point defects and complexes in thin-film solar-cell absorber CuInSe$_2$”

The author carried out calculations of point defects and their complexes, performed detailed benchmarking of the computational parameters, analysed the results, and wrote the first draft of manuscript. All authors contributed to the final manuscript.

Publication II: “Effect of alkali metal atom doping on the CuInSe$_2$-based solar cell absorber”

The author carried out calculations of alkali metal impurities and alkali metal secondary phases, analysed the results, and wrote the first draft of manuscript. All authors contributed to the final manuscript.

Publication III: “Alkali post-deposition treatment-induced changes of the chemical and electronic structure of Cu(In,Ga)Se$_2$ thin-film solar cell absorbers: A first-principle perspective”

The author carried out calculations of density of states of all phases, compared theoretical results with experimental HAXPES spectra, and wrote the first draft of manuscript. All authors contributed to the final manuscript.
1. Introduction

1.1 Cu(In,Ga)Se$_2$ solar cells

In the early stages of solar cell development during the 1950s, polycrystalline Si, Cu$_2$S, CdTe, and CuInSe$_2$ (CIS) materials were chosen as light absorber layers [1, 2, 3, 4]. During the next two decades, solar cells developed slowly, mainly in scientific laboratories. In 1970s when the limit of fossil energy sources became obvious, the solar cell industry attracted more attention.

The light absorber is central for the energy conversion process; it should have a high absorption coefficient, a high carrier mobility, and a low recombination rate for efficient charge collection. The silicon wafers met all of these requirements, except the high absorption coefficient. Thereby, the crystalline silicon solar cell became, supported by its growing efficiency, the leader in the solar cell technology. However, the low absorption coefficient leads to a thick absorber layer, which limits the use of silicon absorbers in thin film solar cells. In contrast, CIS has a high absorption coefficient. Moreover, Cu, In, and Se can be sprayed onto a flexible foil, plastic or glass, or integrated into cement and other building materials. However, CIS solar cells cannot compete with silicon solar cells before various problems are addressed, such as the low CIS efficiency; the scarcity of In; and the toxicity of Cd.

Since 1980s, Cu(In,Ga)Se$_2$ (CIGS) has been used instead of CIS for the absorber layer. Ga on the In site in the CIS chalcopyrite structure contributes by increasing the band gap from 1.04 (for CIS) to 1.7 eV (for CuGaSe$_2$ (CGS)) and helps to increase light absorption over the solar spectrum [5]. A double graded absorber layer with a varying concentration of Ga is used in high-efficiency solar cells (Figure 1.1) [6, 7, 8]. Ga grading is associated with the bandgap decreasing within the absorber layer from the surface towards a notch in the middle, and then increasing towards the back contact. In this way, double grading creates an electric field, which enhances the collection of photogenerated electrons from the absorber layer. Double grading increases the open-circuit voltage by reducing the impact of regions of high recombination, and increases the short-circuit
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In order to get a high conversion efficiency, the absorber layer should have a high \((0.88 < \text{Cu/(In+Cu)} < 0.92)\) concentration of Cu vacancies (Cu-poor CIGS) in the surface layer [9]. Cu vacancies contribute to the CIGS solar cell efficiency by formation of ordered defect compounds in the surface layer and close to grain boundaries, and thereby reduce recombinations at the surface (CIGS/CdS interface in solar cell structure) [10] and at grain boundaries. The high Cu vacancy concentration also increases the hole concentration in the bulk absorber and, thereby, the open-circuit voltage and the short-circuit current.

High-efficiency CIGS solar cells are made by depositing elements on substrates (Figure 1.1), which are nowadays typically soda-lime glass (SLG) [9], stainless steel [11] or plastic materials [8]. Usually, a thick Mo layer is used as the back contact. The Mo back contact acts as an optical reflector, which reflects light back to the absorber layer. The most successful process in the manufacture of CIGS solar cells is the so-called three-stage process in which \((\text{In/Ga})_2\text{Se}_3\) is first deposited on the Mo layer, then Cu and Se are evaporated to make the solar cell Cu-rich, and finally In, Ga, and Se are again deposited to ensure an In-rich and slightly Cu-poor composition. The final CIGS absorber layer is \(p\)-doped by native defects. The next step is coevaporation of alkali metal (AM) fluorides (LiF, NaF, KF, RbF, and CsF). However, there are also approaches where Na and K diffuse from SLG into the absorber layers. The present record efficiency of the thin-film CIGS solar cell of 23.35% [12] has been achieved thanks to incorporation of AM atoms (Li, Na, K, Rb, and Cs) into the absorber layer during the post-deposition treatment (PDT). Such a treatment improves all photovoltaic parameters of CIGS solar cells \(i.e\), the open-circuit voltage, short-circuit current, fill factor, and conversion efficiency. The electrical characteristics of the CIGS solar cells depend on which alkali metal fluoride has been used during PDT. Solar cells treated with heavy AM atoms (K, Rb, and Cs) demonstrate better electrical characteristics and, as a consequence, better conversion efficiencies than solar cells after light AM (Na and Li) PDT [9]. A CdS buffer layer or combination of CdS and ZnO completes the \(p-n\) heterojunction. In order to avoid front surface recombination, a window layer of large band gap is used. CIGS solar cells are finished with antireflection coatings and metallic grids as electrodes.

The thickness of the CdS buffer layer, the qualities of the different interfaces, properties of the window layer above the absorber, the Ga grading, the material of the back reflector, and defects in the CIGS absorber layer affect the efficiency of CIGS solar cells. In this thesis, the defect microstructure evolution in the CIGS absorber layer is considered. \(i.e\)., how the structure of the material, full of defects, changes due to PDT or solar cell operation.
Introduction

coating
ZnO
CdS
CIGS
Mo
substrate

ZnO
CIGS
CdS
Ga grading

Thickness

Figure 1.1. a) Material layers in the CIGS thin-film solar cell. b) Band gap diagram with marked valence band maximum (VBM) and conduction band minimum (CBM) and Ga profile in the CIGS layer.

1.2 Native point defects in Cu(In, Ga)Se$_2$

Knowledge about native point defects in the CIGS alloy helps to understand the electrical and optical properties of the absorber. Moreover, it gives a clue how to change the defect structure of the absorber layer to obtain desired solar cell characteristics.

Different experimental approaches, such as composition-dependent photoluminescence (PL), Hall measurements [13, 14], positron-annihilation spectroscopy (PAS) [15, 16, 17], X-ray photoelectron spectroscopy (XPS) [18], secondary-ion mass spectrometry (SIMS) [19], and atom probe tomography (APT) [20], allow one to investigate only the combined effect of several types of point defects in a material on different device characteristics, but they cannot reveal the effect of an individual defect. Knowing this would help one to control the quality and device operation of solar cells by reducing the number of detrimental defects.

Some defect quantities, such as the diffusion activation energy, or the types and concentrations of defects, are difficult to obtain directly from measurements and the analysis of the results is often based on comparison with well-known materials. For instance, the diffusion profile of Na was measured by SIMS [19] and APT [20]. Based on the comparison between the Na diffusion profile and the diffusion profiles of Cd and Fe (which diffuse via an interstitial mechanism) [21, 22], the interstitial diffusion mechanism was assigned for Na. Experimental information about the abundance of point defects in semiconductors can be obtained from PL and Hall measurements. PL and Hall measurements have been performed on chalcopyrite CIS samples with various Cu concentrations [13, 14]. For the near-stoichiometric (Cu-rich) CIS, experiment gives three acceptor levels and one donor level. In contrast, Cu-poor CIS has only one abundant donor and one acceptor. However, identification of defects which are responsible for the donor and acceptor levels observed can not be obtained from the PL measurements.

Density functional theory (DFT) calculations help to solve these problems. Material properties can be directly obtained from the total energy and atomic
forces of a system. Moreover, it is possible to calculate the properties of only one type of point defect or impurity in various chemical conditions. Thus, DFT calculations can be used to provide a link between the experimentally obtained material properties and the point defects responsible for these properties. For instance, previous DFT results for point defects in CIS [23, 24, 25, 26, 27, 28, 29] obtained with the Heyd–Scuseria–Ernzerhof (HSE06) functional [30, 31] gave information about abundant point defects in stoichiometric CIS. Previous results are consistent with each other with respect to general trends in formation energies for the most important defects, such as a copper vacancy (V$_{\text{Cu}}$), an indium antisite on the copper place (In$_{\text{Cu}}$), and copper interstitial atom (Cu$_{\text{int}}$). However, the results differ in some important cases. For instance, there are different values for the ionization levels within the band gap for the copper antisite on the indium place (Cu$_{\text{In}}$) and for the indium vacancy (V$_{\text{In}}$). In this thesis we investigate possible sources of error, such as the choice of the exchange-correlation functional, the choice of the chemical potential set, and the supercell size.

1.3 Impurities in Cu(In,Ga)Se$_2$

The defect structure of the CIGS absorber layer becomes even more complicated after the incorporation of AM atoms during PDT. The positive effect of light AM atoms (Li, Na) is associated with the increase of the $p$-type conductivity, open-circuit voltage, and fill factor [19]. Heavy AM atoms (K, Rb, and Cs) also improve surface morphology through the formation of secondary phases with Se and/or In. A smooth surface layer allows the deposition of a thinner CdS layer with smaller optical losses. Moreover, the formation of a secondary phase can reduce recombination at the interface and close to grain boundaries [32]. AM atoms accumulate at grain boundaries and modify electronic properties of grain boundaries. Incorporation of Na, K, and Rb results in a diminished downward or increased upward band bending [33, 34].

According to APT measurements [35, 36, 37, 38, 39], Na and K are mainly segregated at grain boundaries and near the absorber surface. However, they are also detected in grain interiors with low concentrations. In contrast, Rb accumulates at the grain boundaries and close to the surface with a high concentration [38]. In the grain interiors, the Rb concentration is under the detection limit [38]. Several experimental studies show that regions close to the absorber surface and near the grain boundaries are Cu-depleted [19, 40, 41]. Cu vacancies are acceptors and they can be responsible for the $p$-type doping of CIGS [14]. Several theoretical works confirm that Li, Na, and K occupy preferably Cu vacancies in Cu-depleted regions and can also replace Cu in stoichiometric CIS [42, 43, 44]. However, AM impurities on Cu sites are neutral in CIS and thus the recent theoretical calculations did not reveal a direct way in which Li, Na, or K can increase $p$-type conductivity [43, 44]. Moreover, impurity formation
energies strongly depend on whether the elemental AM phase or the secondary phase has been chosen to determine the chemical potential of the AM atom.

Information about the diffusion of AM atoms can be obtained from XPS [18], SIMS [19], or a combination of SIMS and APT measurements [20]. The diffusion activation energy for Na inside grain interiors was measured to be about 0.32–0.37 eV [18, 20]. The activation energy can be estimated from theoretical calculations as the sum of the formation energy and the migration barrier for the impurity. The vacancy migration mechanism has been suggested to dominate with migration barriers of 0.61 eV [42], 0.2–0.35 eV [42, 43], and 0.25 eV [42] for Li, Na, and K, respectively. Before the present work, formation energies and migration barriers for other AM atoms had not been studied in detail.

The positive effect of heavy-AM PDT has been associated with the formation of secondary phases in the surface layer and close to grain boundaries [45, 46, 47]. The formation of the Na2Se phase after Na deposition on the CIGS surface has been observed using XPS by Klein et al. [48]. Several research groups have investigated the effect of KF PDT on the CIGS solar cell characteristics and reported on possible formation of the K-In-Se secondary phase [49, 47, 45, 46, 50]. One piece of indirect evidence of the K-In-Se phase formation is that the measured surface band gap of 2.53 eV is higher than the band gap for the Cu-depleted surface layer [47]. The existence of Na2Se, K2Se, and NaInSe2 has been predicted theoretically [51, 42]. A recent experimental study by Ishizuka et al. [52] has shown the formation of a Rb-containing layered phase after RbF PDT.

1.4 Objectives of the dissertation

Since much of the progress in the CIGS solar cell conversion efficiency is a result of changes in the defect structure of the absorber layer, the aim of this thesis is to understand the effect of native point defects and impurities on the electronic structure of the CIGS absorber layer.

Due to discrepancies in recent theoretical studies concerning native point defects in CIS [29, 28, 27, 23], the first step is to revisit point defect formation energies in CIS. Highly accurate DFT calculations require detailed benchmarking for the most important calculation parameters. Thus, Publication I provides information on possible sources of error in formation energy calculations. Based on the calculations of point defect formation energies, abundant acceptors and donors in CIS of different Cu concentrations are distinguished.

The highest recorded efficiency of Cd-free Cu(In,Ga)(S,Se)2 solar cells has recently surpassed 23.35 % [12] thanks to heavy-AM PDT. Despite the fact that AM PDT has been used to produce flexible CIGS solar cells over the last 10 years, the effect of AM atoms on the electronic structure of the absorber layer is not fully understood. In Publication II, the effect of AM PDT on the CIGS absorber layer is investigated theoretically. In the first part of the paper,
AM atoms are considered as impurities in CIS. Calculations of AM formation energies and migration barriers provide information about the AM distribution in the absorber layer. In the second part of the paper, a mechanism for the AM secondary phase formation is suggested.

It is well known that DFT is a powerful tool for the interpretation of experimental results. Thus, in Publication I, composition-dependent PL and Hall measurements are compared with the formation energies of native point defects in CIS. The comparison helps to identify the abundant acceptors and donors in CIS for different stoichiometries. In Publication II, concentrations of AM atoms in different chemical conditions are estimated and compared with measured values. Moreover, direct comparisons between activation energies obtained using different experiments and theoretical calculations reveal the preferable diffusion mechanisms for AM atoms. The surface band gap measured after KF PDT [47, 53] is in a good agreement with the calculated band gap for KInSe₂. Thus, formation of a secondary phase after AM PDT is expected. In order to reveal the stoichiometry of the CIGS surface after AM PDT, data from hard X-ray photoelectron spectroscopy (HAXPES) and calculated densities of states (DOS) for combination of different phases have been compared in Publication III. The results help in understanding changes in the electronic structure of the CIGS absorber layer after KF PDT. One of the most important characteristics of the interface is band offset. Band offsets for the interfaces between the absorber layer and the secondary phases can be obtained from the comparison between experiment and DFT calculations or only from the DFT calculations as in Chapter 4.3.

1.5 Outline of the dissertation

The content of this thesis summary is organized as follows. The origin of the efficiency improvement is discussed based on recent theoretical and experimental studies in Chapter 1. Chapter 2 introduces the basics of the DFT method. More practical aspects related to the present calculations are given in Chapter 3. In Chapter 4, results reported in Publications I–III are reviewed and compared with previous theoretical studies. Moreover, the interfaces between the absorber layer and secondary phases are investigated in terms of their band offsets in Chapter 4. In Chapter 5, the accuracy of the DFT calculations is critically assessed and the roles of the native point defects and AM impurities are discussed. Chapter 6 summarizes the discussed topics and gives perspectives on future work.
2. Theoretical background

2.1 Density-functional theory

Density functional theory for electronic structure is a powerful computational quantum mechanical modeling method successfully used in computational physics, biology, chemistry, and material science [54]. This basically means that one can investigate most of the electronic properties of a variety of materials using DFT. It helps in interpreting existing experimental results as well as in predicting the properties of new materials before synthesizing them. This prospect is quite impressive, but how it is done in practice? To answer this question we should start from the basics of quantum mechanics.

Any existing material can be described as a system with a certain number of electrons and nuclei. The electron and nucleus motions can be decoupled due to the fact that nuclei are heavier than an electron, so we can assume that electrons respond instantaneously to the movements of nuclei. In other words, we can treat the heavy nuclei as fixed point charges, and solve the ground-state quantum mechanical problem for electrons only. This is called the Born–Oppenheimer approximation. The static properties of a system can be predicted by solving the many-body Schrödinger equation

\[ \hat{H} \psi(r_1, r_2, \ldots, r_N) = E \psi(r_1, r_2, \ldots, r_N), \] (2.1)

where \( r_1, r_2, \ldots, r_N \) are the electron vector positions and \( N \) is the number of electrons in the system. \( \Psi \) is the wave function of the quantum system, \( E \) its total energy, and \( \hat{H} \) is the Hamiltonian operator. An analytic solution of the Schrödinger equation is possible only for simple systems such as a hydrogen atom. Moreover, for an \( N \)-body system with \( N \) exceeding already around ten, a solution based on the many-body wave function becomes practically unsolvable because of the large number of interacting particles. In 1964 Kohn and Hohenberg formulated the postulates of DFT [55]. Instead of solving the Schrödinger equation explicitly, \( i.e. \) by using the traditional wave function approach, DFT treats the electron density as the central variable. This reduces
Theoretical background

the computational cost by reducing the number of dimensions and it allows to calculate systems of thousands of atoms and for some systems even more, up to around millions atoms [56]. The total energy of the system in this reformulation is a functional of the electron density $n(r)$, i.e.,

$$E[n(r)] = T[n(r)] + E_{\text{int}}[n(r)] + \int d r v_{\text{ext}}(r) n(r),$$  \hspace{1cm} (2.2)

where $T$ and $E_{\text{int}}$ are the kinetic and interaction energies of the system. $v_{\text{ext}}$ is an external potential. The minimum of the total energy with respect to the electron density gives the ground state of the system. Later, Kohn and Sham [57] proposed the solution of the Schrödinger equation, where the original many-electron system is replaced by single-particle systems, the electron states of which are obtained from the single-particle Schrödinger equation

$$\left[-\frac{\hbar^2}{2m_e} \nabla^2 + V_{\text{eff}}(r)\right] \psi_k(r) = \epsilon_k \psi_k(r).$$ \hspace{1cm} (2.3)

Above, $\psi_k(r)$ is the Kohn–Sham wave function of the single-particle state $k$, the particle mass is $m_e$, $\hbar$ is the Plank constant divided by $2\pi$, and $\epsilon_k$ is the Kohn–Sham energy eigenvalue. The effective potential $V_{\text{eff}}$ depends on the electron density and it is calculated as

$$V_{\text{eff}}(r) = V_{\text{ext}}(r) + V_H(r) + V_{\text{xc}}(r),$$ \hspace{1cm} (2.4)

where $V_{\text{ext}}$ is the external potential created by nuclei and any external field; $V_H$ is the electrostatic potential originating from the interactions between electrons and calculated from the electron density (the Hartree potential); $V_{\text{xc}}$ is the so-called exchange-correlation potential taking care of many-body interactions beyond the mean field approximation. The electron density of the system can be obtained as

$$n(r) = \sum_k f_k |\psi_k(r)|^2,$$ \hspace{1cm} (2.5)

where the summation runs over occupied states and $f_k$ is occupation number. The total energy functional reads as

$$E[n(r)] = T_s[n(r)] + E_H[n(r)] + E_{\text{xc}}[n(r)] + \int d r v_{\text{ext}}(r) n(r),$$ \hspace{1cm} (2.6)

where $T_s$ is the kinetic energy of noninteracting electrons; $E_H$ is the Hartree energy of the electron density; $E_{\text{xc}}$ is the exchange-correlation energy functional; the last term is the interaction of the electron density with the external field.

The above Kohn–Sham equations (Equations 2.3–2.6) can be solved by an iterative procedure. It should start from an initial charge density, and, after the Hamiltonian and the ensuing wave functions are determined, a new charge density is calculated. This loop should continue until the density and the effective potential are self-consistent. Thus, DFT can provide exact information about the ground state of the system. Nevertheless, the exchange-correlation functional still requires approximations in practice.
2.2 Exchange-correlation energy functional

The exchange-correlation energy consists of two separate contributions. The exchange term comes from the antisymmetry of the wave function and the Pauli exclusion principle, which says that two electrons with the same spin cannot occupy the same state. The exchange energy is defined in the Hartree–Fock approximation which uses the Slater determinant of single-particle states as the many-body wave function. In DFT it is approximated as a part of the exchange-correlation functional. The correction to the exact total energy beyond the Hartree–Fock exchange approximation is called as the correlation energy. It can be calculated for a homogeneous electron gas by using the quantum Monte Carlo (QMC) method [58]. In order to approximate the exchange-correlation energy of a system, different exchange-correlation functionals use the results of these QMC calculations, together with several exact constraints that the functional, or its so-called exchange-correlation hole, should fulfill [59].

The oldest and, until recently, the most widely used approximation is the local-density approximation (LDA). It is based on the suggestion that the electron density in the solid is locally nearly uniform, i.e., it behaves as a homogeneous electron gas. The correlation part has been determined accurately by Monte–Carlo simulations and the exchange component is given by the Dirac formula [60, 61]. LDA usually gives good results for a large variety of systems, even if their electron densities are far from that of a homogeneous electron gas. For instance, LDA gives more accurate results for vacancy formation energies in metals than various generalized gradient approximation (GGA) functionals [62, 63]. However, it is not a good choice for semiconductors, because LDA significantly underestimates their band gaps, ionization energies, and lattice constants [30].

A homogeneous electron gas is generally not a starting point from which to describe solids, because in real materials the electron density varies rapidly. This approximation was improved in the generalized gradient approximation method (GGA). This functional gives an estimation of the total energy based on the charge density and its gradient. The GGA method shows significant improvements in many calculated material parameters in comparison with LDA. For instance, the Perdew–Burke–Ernzerhof (PBE) GGA method [64] gives better estimations of total energies and atomization energies, and it gives slightly larger band gaps for semiconductors than different LDA functionals [65]. The underestimation of the band gap leads to large uncertainties in the calculated defect transition levels and formation energies, especially for wide bandgap semiconductors [66].

The main error in the LDA and GGA approximations is caused by the presence of the electron self-interaction. It results from the fact that, in these functionals, an electron interacts not only with other electrons but also with itself through the effective potential. This error is avoided in the Hartree–Fock method, where the self-exchange and self-Hartree energies cancel exactly each other. However,
Theoretical background

The Hartree–Fock method results in overlocalization of states and overestimation of the band gap. Thus, a possible solution is the combination of Kohn–Sham and Hartree–Fock approaches, known as the hybrid exchange-correlation functional.

The Heyd–Scuseria–Ernzerhof (HSE06) [31] hybrid functional combines a screened Hartree–Fock exchange contribution with a part from the GGA PBE [64] semi-local functional. The HSE06 functional uses the electronic density and individual electronic wave functions to compute the exchange-correlation energy. The standard mixing (α) is 25% of screened Hartree–Fock exchange. The standard parameter controlling the short-range interaction (ω) is 0.2 Å⁻¹. However, sometimes, in order to fit the band gap of a given material to the experimental band gap, other mixing values can be used [29]. The use of the HSE06 functional leads to significant improvements over the GGA method for many electronic properties of materials. Thus, properties which depend strongly on the total energy of the system (like defect energy levels in the band gap of a semiconductor) are usually more accurate when predicted with hybrid functionals. Besides, band gaps, dielectric constants, and exciton binding energies for semiconductors give better agreement with experiment when calculated with the HSE06 functional than when calculated with the PBE and LDA functionals [67].
3. Methodology

3.1 Practical implementation of density functional theory

There are many computational DFT codes which show a high efficiency in solving the Kohn–Sham equations. In the present thesis, Vienna Ab Initio Simulation Package (VASP) [68, 69] and Fritz Haber Institute ab-initio molecular simulation package (FHI-aims) [70] are used.

3.1.1 Vienna Ab Initio Simulation package code

To solve the Kohn–Sham equations numerically, electronic wave functions can be represented as values on a real space grid or as a set of functions such as atomic orbitals or plane waves. VASP uses plane waves as basis functions. The advantages of this basis set are that it is good in description of interstitial regions, and that the convergence of the calculations is easy to test.

One of the challenges in the calculations with the plane wave basis set is the rapid oscillations of the wave functions close to the nuclei. This makes calculations numerically difficult because a large number of plane waves is required. In the VASP program, this problem is solved by using the projector-augmented-wave (PAW) method [71]. In this method, pseudo wave functions are used to replace rapidly oscillating atomic all-electron wave functions in the core region by wave functions with significantly fewer nodes. This makes the plane wave basis set practically usable.

In general, the representation of Kohn–Sham orbitals requires an infinite basis set. The supercell method is used to study solid-state systems with periodic boundary conditions. Therefore the effective potential is also periodic and can be described as

\[ V_{\text{eff}}(\mathbf{r} + \mathbf{R}) = V_{\text{eff}}(\mathbf{r}), \]  

where \( \mathbf{R} \) is a Bravais lattice vector. Then the single-electron wave functions obey the Bloch theorem:

\[ \psi_k(\mathbf{r} + \mathbf{R}) = e^{i\mathbf{k} \cdot \mathbf{R}} \psi_k(\mathbf{r}) \]  

(3.2)
where \( \mathbf{k} \) is the wave vector. In the projector-augmented wave (PAW) method employed in this work, the wave functions are, within a chosen cut off radius, smooth pseudo wave functions (Figure 3.1). The cut off radius reduces the number of plane waves needed for a sufficiently accurate description.

![Figure 3.1. Schematic comparison between an all-electron and a pseudo wave function. The pseudo wave function is smoother than its true counterpart for \( r < r_c \) and match it exactly for \( r \geq r_c \). \( r_c \) is the cut off radius for the pseudo wave function.](image)

In the plane wave DFT calculation, the Kohn–Sham eigenstates are given as

\[
\psi_k(r) = \sum_G c_k(G) e^{i(k+G) \cdot r}
\]  
(3.3)

where the sum is over the reciprocal lattice vectors \( G \), and \( c_k \) are the coefficients for plane wave Fourier expansion. \( c_k \) is larger for waves with smaller kinetic energies. For this reason, a cut off energy is defined:

\[
E_{\text{cut}} = \frac{\hbar^2}{2m_e} |G_{\text{cut}}|^2
\]

and

\[
|k + G| < G_{\text{cut}}
\]

\( G \) vectors with energies smaller than \( E_{\text{cut}} \) are used in calculations.

### 3.1.2 Fritz Haber Institute \textit{ab-initio} molecular simulation package

Fritz Haber Institute \textit{ab-initio} molecular simulation (FHI-aims) code uses numerically tabulated orbitals for capturing all the important material properties. This basis set comprises numerical atom-centred basis functions. However, the number of basis functions is usually very small in comparison to the number of plane waves used, for example, in the VASP code. Thus, the FHI-aims code often makes it possible to obtain the same accuracy as the VASP code with lower computational cost. This code can be also used for very large systems (the maximum size in the present work is 432 atoms in the unit cell).

The FHI-aims code can be used for finite and extended systems, so that, respectively, cluster and periodic boundary conditions are used. Instead of a cut
off energy, the accuracy in FHI-aims calculations is controlled by adjusting a
numerically tabulated radial shape for each atomic orbital, by the number of
basis functions, and by the accuracy of the integration grid for the Hamiltonian
matrix. The code allows the optimization of computational parameters for every
element in the system, which is useful in the calculation of partial DOSs. In
this thesis, all the DOS calculations in Publication III and the calculation of the
formation energy of the CuIn antisite in Publication I are carried out using the
FHI-aims package.

3.2 Simulation of point defect properties

Different structural defects can occur in semiconductors during the manufac-
turing process. The importance of their effect on the semiconductor devices can
not be overstated. Structural defects can be divided into three categories: zero-
dimensional, two-dimensional, and three-dimensional. Zero-dimensional defects
include both intrinsic (native) point defects, which involve only atoms of the pure
crystal, and extrinsic defects, which are usually different types of impurities.
In the thesis, zero-dimensional defects have been investigated in terms of their
energetic characteristics, such as formation energies and migration barriers.

3.2.1 Defect formation energy

Defect formation energy is a key parameter in the characterization of native
point defects and impurities in semiconductors. For a given defect, it is the
energy difference between the system containing the defect and the perfect
periodic bulk system without any defects. In order to simulate defect in an
infinite system, a practical method is to use also in this case periodic boundary
conditions. This means the use of the supercell approximation: a finite cell
(which may include several unit cells) repeats periodically containing the defect
and matrix host atoms. It enables fast DFT calculation methods for defects and
their complexes. The defect formation energy can be obtained from the equation
[72]

\[ E_f = E_{\text{tot}}^{\text{defect}} - E_{\text{tot}}^{\text{bulk}} - \sum_i \Delta n_i \mu_i + qE_F + E_{\text{corr}}, \quad (3.6) \]

where \( E_{\text{tot}}^{\text{defect}} \) and \( E_{\text{tot}}^{\text{bulk}} \) are the total energies for the system with and without
the defect, respectively. The calculation for a charged defect should take into
account the charge state \( q \) of the defect. \( \mu_i \) is the chemical potential of an atom
of type \( i \), and \( \Delta n_i \) is the number of atoms added (\( \Delta n_i > 0 \)) or removed (\( \Delta n_i < 0 \))
when creating the defect in the supercell. \( E_F \) is the Fermi level. \( E_{\text{corr}} \) is an
energy correction term. Every term of Equation 3.6 will be explained in more
detail below.

The formation energies of point defects in a material depend strongly on the
chemical potentials of the individual components in the material. If the material
system consists of only one element, the chemical potential is equal to the energy per atom in the stable elemental phase ($\mu^0_0$). However, if the system contains two or more elements, the chemical potential of an individual element cannot be defined uniquely; it depends on the experimental growth conditions. The chemical potential can be written in the form

$$\mu_i = \mu^0_i + \Delta\mu_i, \quad (3.7)$$

where $\Delta\mu_i$ is the deviation from the chemical potential in the stable elemental phase. The deviations of the chemical potentials are the ranges within which the chemical potentials must lie. In the case of a thermodynamically stable system without precipitation of elemental or secondary phases, it is required that

$$\Delta\mu_i \leq 0 \quad (3.8)$$

and

$$n\Delta\mu_A + k\Delta\mu_B = \Delta H_f(A_nB_k), \quad (3.9)$$

where $\Delta H_f(A_nB_k)$ is the formation enthalpy of the $A_nB_k$ compound [73]. However, if the system also consists of secondary phases, the deviations of the chemical potentials should be extended to the stability areas of the secondary phases.

Some point defects may exist in different charge states. The stable charge state for defects at a given Fermi level position is the one that has the lowest energy. The Fermi level position, at which the charge state for the point defect changes, is called the charge transition level [72]

$$c(q_1/q_2) = \frac{E^{q_1}_f(E_F = 0) - E^{q_2}_f(E_F = 0)}{q_2 - q_1} \quad (3.10)$$

where $E^{q_1}_f(E_F = 0)$ and $E^{q_2}_f(E_F = 0)$ are defect formation energies in charge states $q_1$ and $q_2$, respectively, when the Fermi level is at the VBM position. This level corresponds to that measured in a quasi-equilibrium experiment, such as deep-level transient spectroscopy [74] or Hall measurements [14].

Accurate prediction of defect transition levels is impossible without the correct band gap. It is a well-known problem that LDA and GGA functionals always underestimate band gaps for semiconductors (Section 2.2) [75]. Some of the functionals, such as DFT+U [76, 77], and HSE06 [30, 31] have tunable parameters, which are often chosen to match the experimental band gap [78, 79]. Non-local exchange-correlation functionals such as HSE06 solve the problem partly [80]. In the case of tuned HSE06, the accuracy of defect transition level positions is of the order of 0.1 eV [97]. In order to have an unbiased comparison with previously published results for point defects in CIS, the HSE06 exchange-correlation functional with default parameters ($\omega = 0.2$ Å$^{-1}$, $\alpha = 0.25$) has been used in the present thesis.
The last term in Equation 3.6 is the energy correction term. As explained above, for formation energy calculations the supercell approximation and periodic boundary conditions are used. However, supercell calculations with periodic boundary conditions may cause artificial elastic and electrostatic interactions between the defect and its periodic images. They can be partially mitigated by increasing the size of the supercell, but, in practical calculations, additional correction schemes are needed.

The size of the supercell that is sufficient for a certain defect calculation can not be known in advance. Convergence of the formation energy with respect to the supercell size \([28]\) and shape is required. According to Oikkonen et al. \([28]\), even a small supercell size is sufficient for calculations for neutral defects in CIS. However, the formation energy of a charged defect converges slowly as a function of the supercell of a linear size \(L\). In this case the formation energy can be corrected by a finite-size-extrapolation method \([82]\). However, the choice of the extrapolation function is not always straightforward.

Another way for correcting the formation energies of charged defects is through various correction schemes, the most commonly used of which are those of Makov and Payne (MP) \([83]\), Lany and Zunger (LZ) \([84]\), and Freysoldt, Neugebauer and Van de Walle (FNV) \([85]\). In an ideal case, the correction energy for a periodically repeated point charge depends on the Bravais lattice and supercell size. The electrostatic energy, \(i.e.\) the Madelung energy, shows, in the case of a cubic supercell, a dependence on \(L^{-1}\), where \(L\) is the length of the cube edge.

The MP scheme is an extension of the Madelung-type correction. It gives a reasonable correction for a charged defect, if the extra charge is well localized \([83]\). The lowest-order terms in the MP scheme scale as \(L^{-1}\) and as \(L^{-3}\) and, therefore, most supercell scaling approaches fit formation energies to the form \(aL^{-1} + bL^{-3}\). If the extra charge of the defect is not well-localized, either the LZ or FNV scheme can be used. The LZ correction is the second MP correction term calculated using the charge difference directly obtained from the total charge densities between the charged and neutral DFT calculations, which in the case of homogeneous screening charge reduces to the Madelung energy multiplied by a constant (2/3). The FNV scheme consists of two terms. The first term takes into account the interaction of the sum of the defect charge density and background charge with the artificial periodic potential. The second term removes the interaction between the background charge and the electrostatic potential from a single defect. The advantage of the FNV scheme is that it can be easily applied for supercells of arbitrary shapes, often allowing the use of smaller supercells.

The defect concentration in the dilute limit \((c_i)\) can be estimated from the following expression

\[
c_i \approx \exp(-E_f/k_BT) \tag{3.11}
\]

where \(k_B\) is the Boltzmann constant and \(T\) is the temperature. The concentrations of all abundant defects and the Fermi levels should be determined self-consistently. The self-consistency requires that the Fermi level is chosen so
that charge neutrality in the sample is maintained.

### 3.2.2 Migration energy barrier

The migration energy barrier for a point defect or an impurity corresponds to the energy needed for a jump of an individual atom between two lattice sites. In the thesis, the vacancy and interstitial migration mechanisms for AM impurities in CIS are considered. The migration barriers and positions of saddle points can be predicted by using the climbing image nudged-elastic-band method (CI-NEB) [86]. In practice, this means that the total energy of the system has been calculated for a discrete set of atomic configurations, that lie on the minimum energy path. The climbing image method ensures that the saddle point of the path is reached. The migration barrier is the difference between the total energies at the initial point and at the saddle point.

Due to the high computational cost, the calculation of the migration barrier is usually performed for a smaller supercell than that for the formation energy. Moreover, the migration barrier can be obtained in practice fully self-consistently only with a local or semilocal approximation for the exchange-correlation functional. Fortunately, in most cases, an additional check of the migration barrier with the HSE06 functional shows that the maximum difference between the PBE and HSE migration barriers in CIS is around 0.07 eV [28]. Thus, in this thesis the PBE functional and the supercell of 64 atoms have been used.

### 3.3 Calculation of secondary phases and interfaces

The second part of the thesis concerns secondary phase formation and characterization of interface properties between a secondary phase and the absorber layer. Below, information about two methods can be found: 1) how to predict stabilities of secondary phases under the given experimental conditions and 2) how to calculate band offsets between two materials.

#### 3.3.1 Secondary phase formation

Chemical processes occurring in the solar cell absorber layer during PDT can be predicted theoretically by calculating chemical reaction enthalpies. For instance, the enthalpy (\(\Delta H\)) of the reaction

\[
A + B \rightarrow C + D
\]  

(3.12)

can be determined from the equation

\[
\Delta H = \Delta H_f(A) + \Delta H_f(B) - \Delta H_f(C) - \Delta H_f(D). 
\]  

(3.13)

In 3.13, \(\Delta H_f(A)\), \(\Delta H_f(B)\), \(\Delta H_f(C)\), and \(\Delta H_f(D)\) are the formation enthalpies of the corresponding species (A, B, C, and D). Accordingly, the reaction can spontaneously occur only if the reaction enthalpy is positive.
In order to compare results with experiments, one must calculate the temperature dependence of the miscibility between two phases. *i.e.*, we consider the reaction

\[ xA + (1-x)B \rightarrow A_xB_{1-x} \]  

(3.14)

between the phases A and B forming the mixed phase \( A_xB_{1-x} \). Based on the mixing enthalpy one can conclude about stability of the mixed phase. The concept of the mixing parameter \( \Omega \) for an alloy with a small concentration of a given impurity has been used in this thesis [87]. We assume that \( \Omega \) is constant through the concentration region considered, and it is defined for an alloy by the equation

\[ \Delta H_{\text{mix}} = x(1-x)\Omega, \]  

(3.15)

where \( \Delta H_{\text{mix}} \) is the mixing enthalpy obtained by applying Equation 3.13 for the reactants A and B and the product \( A_xB_{1-x} \). The pressure-volume term \((pV)\) in the enthalpy is neglected [51, 87].

Within the mixing parameter model of Equation 3.15, the free energy \( F(x, T) \) of the system of the mixed phase can be calculated analytically by adding the entropy contribution:

\[ F(x, T) = \Delta H_{\text{mix}} - TS(x) \]  

(3.16)

where \( T \) is the temperature and \( S(x) \) is the configuration entropy for a random binary alloy

\[ S(x) = -k_B[x\ln(x) + (1-x)\ln(1-x)] \]  

(3.17)

where \( k_B \) is the Boltzmann constant. The boundary for the phase separation on the \((x, T)\)-plane is obtained by calculating the binodal curve, *i.e.*, requiring that the derivative of the free energy in Equation 3.16 with respect to \( x \) is zero [88].

### 3.3.2 Band offset calculations

In the present work, the interface between an alkali metal secondary phase and the CIS absorber layer consists of two semiconductors. The band offsets at an interface between two semiconductors can be obtained by using the method of Van de Walle and Martin [89]. A recent tutorial review of the method is given in Reference [90]. The four steps below are performed.

1. Calculation of the macroscopic average electrostatic potentials, as shown in Figures 3.2 (a) and (b).

2. Calculation of the average electrostatic potential energies in the bulk-like regions of the interface system as shown in Figure 3.2 (c). The macroscopic averages \( \overline{V} \) are obtained by integrating the electrostatic potential energy \( V(x, y, z) \) over a volume in two steps as

\[ \overline{V}(z) = \frac{1}{A} \int_A \int A V(x, y, z) dx dy, \quad \overline{V} = \frac{1}{L} \int L \overline{V}(z) dz. \]  

(3.18)

Above, \( A \) is the cross sectional area of the supercell parallel to the interface and \( L \) is the period of the planar average potential energy \( \overline{V}(z) \) in the \( z \) direction.
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Figure 3.2. Plane averaged electrostatic potential $\overline{V}(z)$ of (a) the KInSe$_2$ and (b) CIS bulk along the $z$-direction, (c) Plane average electrostatic potential of a slab comprising CIS and AlkInSe$_2$ with the (001) interface orientation, and (d) band offsets between CIS and AlkInSe$_2$ phases. The $z$-axis is along the (001) direction. The horizontal straight lines on the plots (a–c) indicate average values of the local potential for the AlkInSe$_2$ and the CIS parts.

perpendicular to the interface. In the bulk-like regions $\overline{V}$ saturates to the average electrostatic potential energy in the bulk material.

3. Calculation of the VBM and CBM for the bulk materials with respect to the macroscopic average electrostatic potential energies. The calculation of bulk average potential is done using Equation 3.18 extending the integrations over the unit cell used in the bulk material calculations as shown in Figures 3.2 (a) and (b). In VASP code the average potential in the bulk is zero by convention.

4. Aligning the bulk VBMs and CBMs over the interface according to the potential energy step determined in point 2 and using the distances of VBMs and CBMs from the macroscopic average potential energies in the bulk materials determined in steps 1 and 3. The differences in VBM and CBM over the interface give the valence band (VBO) and conduction band (CBO) offsets, respectively, as shown in Figure 3.2 (d). In this thesis, the HSE06 functional which gives accurate predictions for the band gap was used consistently in all the step above.

3.3.3 Density of states calculations

In this thesis, first-principles modelling was done to analyse measured HAXPES valence band spectra of the CIGS absorber surface for which no PDT or NaF/KF PDT was performed as part of the preparation process [91]. The ultimate goal
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was to reveal the chemical and electronic structures of the absorber layer and how it is impacted by AM PDT. Of particular relevance would be any insight into whether or not a K-In-Se-type species is formed on top of the NaF/KF PDT CIGS even in cases where the absorber is treated with moderate or low amounts of K. To do so, simulated HAXPES valence band spectra were derived by using first-principles DFT electronic structures of crystalline Cu-In-Se phases with different compositions as well as those of potentially formed (K-)In-Se secondary phases.

The atomic orbital basis used in FHI-aims provided a straightforward way to decompose the total DOS into its atom- and orbital-projected contributions (PDOSs). To compare theoretical results with experimental HAXPES spectra, PDOSs were weighted with atom- and orbital-dependent photoionization cross sections. For each core level at each excitation energy the photoionization cross section has been calculated according to the References [92, 93]. The experimental spectra can be represented by a combination of calculated, photoionization cross section-corrected DOSs. The total corrected DOSs are linear combinations of the DOSs for all contributing phases, i.e.

\[ g_{\text{tot}} = \sum a_i g_i(E - b_i), \]  

where \( g_i \) is the cross section-corrected DOS for the sample component \( i \), and \( a_i \) is its relative concentration. The shifts \( b_i \) along the energy axis \( E \) account for the expected differences in energy level positions with respect to the experimental spectrum and give the (unknown) band alignment between the contributing phases. The coefficients \( a_i \) and \( b_i \) were determined by minimizing the mean square error between experimental and simulated intensities. The goodness of the fit was obtained as the normalized mean square error of the fit as

\[ G = 1 - \frac{\| g_{\text{ref}}(E) - g_{\text{tot}}(E) \|}{\| g_{\text{ref}}(E) - \langle g_{\text{ref}}(E) \rangle_E \|}. \]

Above, \( g_{\text{ref}} \) is a HAXPES data vector, \( \langle \cdot \rangle_E \) gives the mean value of the data, and \( \| \| \) indicates the 2-norm of a vector. Thus, a \( G \) value between 0.7 and 1.0 indicates a good fit. To obtain significant fits, we kept the fitting parameters to a minimum and assumed that each experimental spectrum is constituted of a maximum of two phases.
4. Results

4.1 Simulation of point defect properties

4.1.1 Native point defects and their complexes in CuInSe$_2$

An important step in gaining an understanding of the properties of CIGS materials is the investigation of point defects and their complexes. As already discussed above, point defects can be classified as either native point defects (or intrinsic defects) or impurities (or extrinsic defects). The electronic properties of intrinsic point defects and their complexes are studied in this chapter.

During the manufacture of solar cells, different types of point defect can arise. The chalcopyrite CIGS contains vacancies, interstitials, antisites, and their complexes in abundance. These defects affect the electrical properties of the CIGS absorber layer. A point defect can either act as a donor, contributing an electron to the conduction band, or as an acceptor, creating a hole in the valence band. Depending on the concentration of donors and acceptors, a semiconductor can be classified as $p$- or $n$-doped. Concentrations of donors and acceptors can be calculated from defect formation energies.

In this work, the formation energies of intrinsic point defects in CIS were obtained by using Equation 3.6. In previous theoretical studies [23, 24, 79, 28, 25, 26, 27], formation energies of intrinsic point defects were calculated, but the results disagree in some important respects. In order to form our own opinion, we revisited the case of native point defect calculations.

In the present work, a chemical potential stability diagram for CIS was calculated based on formation enthalpies of different binary and ternary compounds (for more details see Section 3.2.1). The formation enthalpies were calculated using the PBE and HSE06 functionals, and compared with previously measured and calculated results (Table 4.1). The PBE functional always underestimates the formation enthalpies of all compounds, while the HSE06 functional slightly overestimates them, except for the In$_2$Se$_3$ compound. However, the HSE06
Results

Figure 4.1. Stability diagram for CIS constructed by using the heats of formation calculated with the HSE06 functional and presented in Table 4.1. Point D corresponds to point A in Figure 1 in the paper by Pohl and Albe [79]. The figure is reproduced from Publication I.

functional gives results in much better agreement with experiments. The resulting stability phase diagram is shown in Figure 4.1. We extend the range of chemical potentials beyond the stability region of CIS, in order to get insight into out-of-equilibrium growth conditions, i.e., conditions where the secondary phases should form.

Table 4.1. Formation enthalpies $\Delta H_f$ (eV) calculated using the PBE and HSE06 functionals as well as the corresponding experimental values. The table is reproduced from Publication I.

<table>
<thead>
<tr>
<th>Compound</th>
<th>PBE</th>
<th>HSE06</th>
<th>Experiment</th>
</tr>
</thead>
<tbody>
<tr>
<td>CuSe</td>
<td>−0.27</td>
<td>−0.45</td>
<td>−0.42 [94]</td>
</tr>
<tr>
<td>In$_2$Se$_3$</td>
<td>−2.45</td>
<td>−2.99</td>
<td>−3.57 [94]</td>
</tr>
<tr>
<td>CuInSe$_2$</td>
<td>−1.77</td>
<td>−2.40</td>
<td>−2.12 [94], −2.77 [95]</td>
</tr>
<tr>
<td>Cu$_2$Se</td>
<td>0.01</td>
<td>−0.65</td>
<td>−0.42 [94]</td>
</tr>
<tr>
<td>InSe</td>
<td>−1.05</td>
<td>−1.28</td>
<td>−1.22 [94]</td>
</tr>
<tr>
<td>CuIn$_5$Se$_8$</td>
<td>−7.08</td>
<td>−8.93</td>
<td>−</td>
</tr>
</tbody>
</table>

Point D in the chemical potential diagram 4.1 was chosen for the calculation of defect formation energies in order to compare our values with previously published results. Point D corresponds to the Se-rich, In-poor, and Cu-poor chemical conditions. Figure 4.2 shows formation energies as a function of the Fermi level for the most important point defects in CIS. According to the formation energy calculations, the Cu vacancy ($V_{Cu}$) with the $−1$ charge state and Cu substituting In, i.e., the antisite Cu$_{In}$ with the $−1$ and $−2$ charge states are the most prominent acceptors under the given Se-rich and Cu-poor conditions.
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Figure 4.2. Point defect formation energies in CIS as a function of the Fermi level. The chemical potentials correspond to the point D in Figure 4.1. The figure is reproduced from Publication I.

The Cu interstitial (Cu_{int}) and the In substituting Cu antisite (In_{Cu}) with the +1 and +2 charge states can act as donors, because they have low formation energies. The concentrations of other point defects in these conditions are small, because of high formation energies. Note that CIGS absorbers are usually p-type and thus the most relevant Fermi level region is close to VBM.

Figure 4.3. Point defect formation energies along the green line in the stability diagram of Figure 4.1. The energies are calculated for the position of the Fermi level ($E_F$) at (a) VBM and (b) CBM. The dashed lines correspond to donor and the solid lines to acceptor defects. The figure is reproduced from Publication I.

In order to discuss the trends in the formation of point defects in CIS with respect to the Cu concentration, six combinations (A–F) of chemical potentials were specified, as shown in Figure 4.1. Since high-efficiency CIGS solar cells were prepared in the selenium atmosphere (Se-rich condition), all the points were chosen close to the border between the CIS and Se phases. Point A corresponds to extremely Cu-rich conditions, and point F to extremely Cu-poor conditions. Formation energies for the most important point defects are

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Results

presented in Figure 4.3 as a function of the In chemical potential. Figure 4.3 shows defect formation energies obtained with the Fermi level at VBM (a) and at CBM (b).

In high-efficiency CIGS solar cells the CIGS absorber has usually an n-type surface layer and a p-type bulk region. V\textsubscript{Cu} has a low formation energy under most of the chemical conditions in both n- and p-type materials, and makes a material more p-type. Cu\textsubscript{In} can also act as an acceptor, but only for some positions of the Fermi level, because its transition level from the neutral to the negative state is inside the band gap. The formation energy of V\textsubscript{In} is low in Cu-rich n-type CIS. In other cases V\textsubscript{In} has a high formation energy and its concentration in CIS is negligible. In\textsubscript{Cu} and Cu\textsubscript{int} are the most important donors with the +2 and +1 charge states, respectively. Worth noting is that both Cu\textsubscript{int} and V\textsubscript{Cu} have low formation energies in the p-type material as shown in Figure 4.3 (a). This corresponds to the facts that the Cu-Se bonds are weak and the Cu ion has a small ionic radius. Thus, one can also conclude that the interstitial Cu atom is very mobile. Despite the fact that the formation energies of V\textsubscript{Cu} and Cu\textsubscript{int} in p-type CIS are similar (points C–D), the interstitial Cu atom diffuse faster than Cu on a Cu sublattice because the migration barrier for the interstitial mechanism is smaller [28]. Moreover, Cu\textsubscript{In} and Cu\textsubscript{int} have relatively low formation energies in n- and p-type Cu-rich CIS leading to precipitation of CuSe and Cu\textsubscript{2}Se secondary phases.

Individual point defects can diffuse and bind together in highly doped materials. Thus, different point defect complexes can be created. In this thesis, acceptor-type complexes are considered, because a PL study of Cu-rich CIS indicated the presence of three acceptors [13], but their identities were unknown. The first two are V\textsubscript{Cu} and Cu\textsubscript{In} (Figure 4.3). The third acceptor should have a low concentration. The most stable acceptor-type complex should consist of both donors and acceptors feeling a strong Coulomb interaction. In CIS, only two donors have low formation energies, they are: Cu\textsubscript{int} and In\textsubscript{Cu}. In this work, we choose to examine only complexes with Cu\textsubscript{int}, because complexes with In\textsubscript{Cu} have been studied already [28, 23, 96]. In this thesis, the formation and binding energies of Cu\textsubscript{int}-2V\textsubscript{Cu}, Cu\textsubscript{int}-V\textsubscript{In}, Cu\textsubscript{int}-Cu\textsubscript{In} were calculated (Figure 4.4).

Concentrations of Cu\textsubscript{int} and V\textsubscript{Cu} are high in Cu-rich material (Figure 4.3), and formation of the Cu\textsubscript{int}-2V\textsubscript{Cu} complex is possible in the −1 charge state for all Fermi level positions. Cu\textsubscript{int} and V\textsubscript{Cu} can annihilate each other if they are too close, but the combination of Cu\textsubscript{int} with two V\textsubscript{Cu} defects is more stable. Surprisingly, the binding energy of the Cu\textsubscript{int}-2V\textsubscript{Cu} complex is low (−0.36 eV). Thus, this complex is not strongly bound. The second complex, Cu\textsubscript{int}-V\textsubscript{In}, can also act as an acceptor. This complex has two transition levels in the band gap, as does its constituent V\textsubscript{In}. Its charge state varies from 0 to −2. The neutral complex has a high formation energy and a high binding energy of −0.9 eV. The Cu\textsubscript{int}-V\textsubscript{In} complex becomes an acceptor, when the Fermi level rises 0.1 eV above the VBM. Also Cu\textsubscript{int}-Cu\textsubscript{In} has two transition levels, (+1/0) and (0/−1). This means that this complex can act as an electron trap in p-type CIS, and can act as
Figure 4.4. Formation energies of defect complexes at point D on the chemical potential stability diagram of Figure 4.1. The figure is reproduced from Publication I.

an acceptor in $n$-type CIS. The formation energy for the Cu$_{\text{int}}$-Cu$_{\text{In}}$ complex in the $-1$ charge state is the lowest among the other considered complexes and the binding energy of $-0.7$ eV indicates the stability of the complex. However, one has to take into account the limitations of the computational approach. Note, the use of the hybrid functional results in an accuracy of $0.12$ eV for charge transition levels [81, 97].

4.1.2 Alkali metal impurities in Cu(In,Ga)Se$_2$

During the manufacturing process of CIGS solar cells, AM atoms dissolve into the solar cell absorber layers creating extrinsic point defects. In this section, the effects of AM impurities on the CIGS constituents, such as CIS and CGS semiconductors, are considered.

As in the case of native point defects, a key factor in characterizing an AM impurity is its formation energy. The defect formation energy is very sensitive to the choice of the chemical potentials. They can be chosen from a chemical potential stability diagram like the one obtained here by using the formation enthalpies of 16 possible compounds (Table 4.1 and 4.2).

Experimental formation enthalpies for AM compounds are not available, so one can only compare the calculated values with each other. NaInSe$_2$ has the highest formation enthalpy among the AlkInSe$_2$ compounds. LiInSe$_2$ has a lower formation enthalpy than NaInSe$_2$. The formation enthalpies of other Alk-In-Se compounds decrease monotonously from KInSe$_2$ to CsInSe$_2$. The formation enthalpies of Alk$_2$Se compounds are very similar with the exception of Li$_2$Se, which clearly has the lowest formation energy.

Chemical potential stability diagrams for Alk-In-Se and Cu-In-Se systems are shown in Figure 4.5. The stability diagrams illustrate which compounds will be the most stable ones at 0 K under the given combination of chemical potentials.
Table 4.2. Formation enthalpies (eV) and band gaps (eV) for AM (indium) selenides (AlkInSe₂ or Alk₂Se) calculated using the HSE06 functional (Publication II).

<table>
<thead>
<tr>
<th>Crystal structure</th>
<th>ΔH_f (HSE06)</th>
<th>Band gap (E_g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiInSe₂ chalcopyrite</td>
<td>-4.05</td>
<td>2.60</td>
</tr>
<tr>
<td>NaInSe₂ delafossite</td>
<td>-3.73</td>
<td>2.16</td>
</tr>
<tr>
<td>KInSe₂ monoclinic</td>
<td>-4.17</td>
<td>2.53</td>
</tr>
<tr>
<td>RbInSe₂ monoclinic</td>
<td>-4.23</td>
<td>2.57</td>
</tr>
<tr>
<td>CsInSe₂ monoclinic</td>
<td>-4.34</td>
<td>2.66</td>
</tr>
<tr>
<td>Li₂Se cubic</td>
<td>-4.19</td>
<td>3.84</td>
</tr>
<tr>
<td>Na₂Se cubic</td>
<td>-3.55</td>
<td>3.01</td>
</tr>
<tr>
<td>K₂Se cubic</td>
<td>-3.62</td>
<td>2.96</td>
</tr>
<tr>
<td>Rb₂Se cubic</td>
<td>-3.49</td>
<td>2.69</td>
</tr>
<tr>
<td>Cs₂Se cubic</td>
<td>-3.47</td>
<td>2.74</td>
</tr>
</tbody>
</table>

Previous experimental studies [19, 47, 48] have shown that Alk₂Se and AlkInSe₂ secondary phases may form after AM PDT. In order to get all relevant variations of formation energies under different preparation conditions, three sets of chemical potentials at the different corners of the AlkInSe₂ stability area were chosen. The combinations of the chemical potentials (A, B, and C) considered in Publication II are shown in Figure 4.5.

CIGS solar cell devices with the highest efficiencies are usually Cu-poor and grown in an Se atmosphere. In the present chapter, chemical conditions close to the experimental conditions have been chosen, e.g., Cu-poor, Alk-poor, In-rich, and Se-rich (points B in Figure 4.5). The formation energies of AM impurities at this point with respect to the Fermi level position are shown in Figure 4.6. The formation energies of the AM impurities in other chemical conditions can be found in Figure 2 in Publication II.

All the AM atoms prefer to accumulate on the Cu sublattice for the chemical potential set considered. It should be pointed out that all the AM atoms on the Cu sublattice are always neutral. However, one should take into account that V_Cu is the most stable acceptor in CIS. Thus, AM impurities could affect the charge carrier concentration in CIS by creating new V_Cu after a washing process [27]. Li-Se bonds are the strongest ones as one can see from Figure 4.9 (a) below. Going to the heavier alkali metal atoms, the bonds weaken and the core-core repulsion increases, so therefore the formation energies increase.

AM atoms on In sites in CIS are acceptors and may influence the Fermi level position. These defects produce two transition levels in the band gap and may act as electron traps, which can be detrimental to device properties. These results are in contrast with the previous results by Oikkonen et al. and by Ghorbani et al. [43, 44]. They observed that Na_In produces just one transition level or has only one stable charge state. The differences can be explained by the different supercell sizes and electrostatic correction schemes used.

Light AM atoms can accumulate on octahedral interstitial sites. As expected
Results

Figure 4.5. Stability diagrams for (a) Cu-In-Se, (b) Li-In-Se, (c) Na-In-Se, (d) K-In-Se, (e) Rb-In-Se, and (f) Cs-In-Se systems. All the panels are reproduced from Publication II.

from the electronic configurations of the AM atoms, they can easily donate their lone s-electrons and always have the +1 charge state on the interstitial positions. AM defects on the Se site have higher formation energies than all the other AM defects considered. The formation energies for the AM atoms on Se sites are similar for all the AM atoms due to the similar relaxations they cause in the CIS lattice.
Results

Figure 4.6. Formation energies for different (a) Li, (b) Na, (c) K, (d) Rb, and (e) Cs impurities in CIS as a function of the Fermi level position. The formation energies correspond to the points B in the stability diagrams in Figure 4.5.

4.1.3 Effect of Ga alloying on alkali metal impurity formation energies

In order to understand how Ga alloying affects the outcome of the AM PDT process, hybrid DFT calculations for bulk CGS and substitutional AM impurities on Cu sites in CGS were performed. According to the calculations, the lattice constants of the chalcopyrite structure decrease from CIS to CGS. The $a$ lattice constant for CIS is 0.07 Å larger than that for CGS and the $c$ lattice constant is as much as 0.61 Å larger. Experimental structural parameters $a$ and $c$ of CIS are larger than those of CGS by 0.17 Å and 0.6 Å, respectively [98].

Figure 4.7. Stability diagrams of CIS and CGS superimposed. The highlighted areas give the chemical potential regions where the stoichiometric phases and the ODCs CuIn$_5$Se$_8$ and CuGa$_5$Se$_8$ are stable.

By calculating the heats of formation of different compounds which can occur in experiment (CIS, CGS, CuIn$_5$Se$_8$, CuGa$_5$Se$_8$, Ga$_2$Se$_3$, In$_2$Se$_3$, InSe, and
Results

GaSe) and the cohesive energies of the elemental phases (Cu, In, Ga, and Se), the phase stability diagrams for CIS and CGS have been obtained following the procedure described in Section 4.1.1. The superimposed phase diagrams in Figure 4.7 indicate that the Cu(In/Ga)5Se8 region increases from CIS to CGS. This means that the (In/Ga)Cu + 2V_{Cu} defect complex constructing the ordered defect compounds (ODCs), such as Cu(In,Ga)5Se8 is stabilized by Ga alloying.

The CGS stability diagram, and those for the AM compounds (including the secondary phases AlkGaSe2), have been used to determine the formation energies of substitutional AM impurities on Cu sites. The stability diagrams for the AlkGaSe2 systems have been calculated as discussed in Section 4.1.2. Heats of formation for the AlkGaSe2 compounds are listed in Table 4.3. The chemical potential sets have been chosen from the different corners of the AlkGaSe2 stability area. The use of three different chemical potential sets gives a range of possible formation energies for a defect.

Table 4.3. Formation enthalpies (in eV) and band gaps (eV) for AM gallium selenides (AlkGaSe2) calculated using the HSE06 functional.

<table>
<thead>
<tr>
<th>crystal structure</th>
<th>ΔH_f (HSE06)</th>
<th>Band gap (E_g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiGaSe2 wurtzite</td>
<td>-4.25</td>
<td>3.25</td>
</tr>
<tr>
<td>NaGaSe2 delafossite</td>
<td>-3.41</td>
<td>2.09</td>
</tr>
<tr>
<td>KGaSe2 monoclinic</td>
<td>-4.53</td>
<td>3.02</td>
</tr>
<tr>
<td>RbGaSe2 monoclinic</td>
<td>-4.48</td>
<td>2.85</td>
</tr>
<tr>
<td>CsGaSe2 monoclinic</td>
<td>-4.56</td>
<td>3.49</td>
</tr>
</tbody>
</table>

Figure 4.8. Formation energies for substitutional Li, Na, K, Rb, and Cs impurities in CIS and CGS. In each case, the formation energy range contains the formation energies for points A–C in the chemical potential stability diagram in Figure 4.5.

The ensuing CIS and CGS results are compared in Figure 4.8 in the case that the chemical potentials of the Cu, Se, and AM atoms are the same in CIS.
Results and CGS. There is a little change in the formation energies for the light AM atoms. The effects of Ga alloying on the formation energies of substitutional heavy AM atoms are larger, but because of their larger magnitudes, heavy AM concentrations in both bulk CIS and CGS are negligible. This is the effect of core-core repulsion that is larger in CGS due to its smaller lattice constant.

According to the results, the effects of light alkali metal atom doping in CIS and CGS are similar. Thus, one can conclude that the compositional effects of Ga alloying in bulk CIGS for the outcome of AM PDT are rather small.

4.1.4 Migration of alkali metal atoms in CuInSe$_2$

To understand the evolution of AM atom distributions in the absorber layer during the PDT process, we calculated migration barriers for AM atoms. The vacancy migration mechanism requires the presence of a Cu vacancy close to the substitutional AM atom on the Cu site. The migration barriers for the AM atoms from one Cu site (relative coordinate 0.0) to the nearest Cu vacancy (relative coordinate 1.0) through an interstitial tetrahedral site (relative coordinate 0.5) are shown in Figure 4.9 (a). Li has the highest migration barrier among the AM atoms. The obtained value of 0.62 eV is in good agreement with the previous study by Maeda et al. [42]. The migration path for Na has the same shape as that for Li. However, Na diffusion is faster than Li diffusion, as one can infer from Figure 4.9. The migration barrier for Na correlates well with previous theoretical [42, 43] and experimental studies [18, 20]. The migration barriers for K, Rb, and Cs increase from 0.18 to 0.37 eV. Note that the migration barriers for the AM atoms show a non-linear trend from Li to Cs. Moreover, the shapes of the migration barriers for light AM atoms are different from those for heavy AM atoms. These findings can be explained by the fact that Li and Na have a tendency towards the formation of bonds with the nearest Se atoms, as one can see from Figure 4 Publication II. In contrast, the Alk-Se bonds are weaker for the heavy AM atoms than for the light AM atoms, and there is therefore practically no energy increase along the migration path before the ion cores start to overlap.

The migration barriers for the AM atoms within the interstitial mechanism between two interstitial tetrahedral sites (relative coordinates 0.0 and 1.0) via an interstitial octahedral site (relative coordinate 0.5) are shown in Figure 4.9 (b). The migration barriers for Na, K, Rb, and Cs exhibit an increasing trend with respect to the atomic number, i.e. 0.53, 0.61, 1.14, and 1.65 eV, respectively. Li has a migration barrier of 0.64 eV, i.e. higher by 0.11 eV than that for Na, because of the deep minimum energy at the interstitial octahedral site. The migration barrier for Na correlates well with the value obtained by Oikkonen et al. [43]. The migration paths for Li and Na atoms have two saddle points, and one minimum at the interstitial octahedral site. The migration barriers in these cases are the difference between the saddle point and the minima at the octahedral or tetrahedral site. In contrast, the migration barriers for
the heavier AM atoms have only one maximum at the interstitial octahedral site. The difference between the light and heavy AM atoms with respect to the migration barrier shapes is due to the different atomic radii and different bond formation properties.

### 4.2 Formation of alkali metal secondary phases

The diffusion of AM atoms may lead to the accumulation of AM atoms in some parts of the material and, as a consequence, it can lead to formation of AM secondary phases. In this section, a model for secondary phase formation is considered. The possible chemical processes which occur during PDT are predicted by theoretical calculations of formation enthalpies for reactants and products (Equation 3.13). Note that the calculations do not take into account the reaction barrier. Thus, reaction rates are not calculated.

The first step in the PDT process is deposition of AM fluorides onto the absorber surface in an Se atmosphere. AM fluorides can react with Se as

\[
6\text{AlkF} + 4\text{Se} \rightarrow 3\text{Alk}_2\text{Se} + \text{SeF}_6 + \Delta H
\]  

(4.1)

The enthalpy \(\Delta H\) of this reaction is 2.93, 3.95, 2.12, 1.49, and 0.27 eV for Li, Na, K, Rb, and Cs, respectively. The positive reaction enthalpies mean that all these reactions will occur in an Se atmosphere.

Selenium fluorides do not adsorb to the CIGS surface [20], thus the next step is the reaction between \(\text{Alk}_2\text{Se}\) and the absorber. As shown in Section 4.1.2, AM atoms prefer to accumulate on the Cu sublattice, leading to the possible formation of the AlkInSe\(_2\) phase on the absorber surface

\[
\text{Alk}_2\text{Se} + 2\text{CuInSe}_2 \rightarrow 2\text{AlkInSe}_2 + \text{Cu}_2\text{Se} + \Delta H
\]  

(4.2)

The formation of AlkInSe\(_2\) and Cu\(_2\)Se is possible for K, Rb, and Cs with reaction
Results

enthalpies of 0.61, 0.85, and 1.10 eV, respectively. KInSe$_2$, RbInSe$_2$, and CsInSe$_2$

have similar crystal structures and band gaps of 2.53 eV, 2.57 eV, and 2.66 eV,

respectively, as shown in Figure 4.10 (c). In contrast, Reaction 4.2 is suppressed

for light AM atoms, because of negative reaction enthalpies of −0.22 for Li and

−0.21 eV for Na. The LiInSe$_2$ lattice structure is similar to that of CIS, but

the lattice constant is larger by 0.17 Å in the a-direction and by 0.03 Å in the c-direction as shown in Figure 4.10 (a). NaInSe$_2$ has the delafossite structure as shown in Figure 4.10 (b), which is very different from the chalcopyrite structure of CIS. Thus, the formation of a NaInSe$_2$ phase is unlikely.

If AM atoms substitute only a small fraction of Cu atoms in the absorber

layer, a mixed (Alk,Cu)InSe$_2$ phase can occur. The concentration of AM atoms
eoveaporated during the PDT process is only up to 0.1 at. %, meaning that the

mixed phase is bulk CIS with AM impurities. The reaction for the mixed phase

formation reads as

\[
\frac{x}{2} \text{Alk}_2\text{Se} + \text{CuInSe}_2 \rightarrow \text{Alk}_x\text{Cu}_{(1-x)}\text{InSe}_2 + \frac{x}{2} \text{Cu}_2\text{Se} + \Delta H \quad (4.3)
\]

The calculated reaction enthalpies (per one AM atom) are now 0.90, 0.62, −0.20,

−0.56, and −1.07 eV for Li, Na, K, Rb, and Cs, respectively. This reaction agrees

with calculations of the formation energy of AlkCu. The positive values for Li

and Na mean that they will readily fill all the available Cu vacancies. But

concentrations of heavy AM atoms are negligible even at the PDT temperature.

In order to understand better which of the phases (mixed or secondary) will

be stable in the PDT conditions, dissociation of the mixed phase has been

considered.

\[
\text{Alk}_x\text{Cu}_{(1-x)}\text{InSe}_2 \rightarrow x\text{AlkInSe}_2 + (1-x)\text{CuInSe}_2 + \Delta H \quad (4.4)
\]

The enthalpies of this reaction (for x=0.03 and T = 0 K) are 0.0013, 0.0102,

0.0488, 0.0637, and 0.0836 eV per formula unit for Li, Na, K, Rb, and Cs, re-

spectively. Temperature-dependent miscibility of AlkInSe$_2$ and CIS in different

proportions is shown in Figure 4.10 (d). In this calculation, the concept of the

mixing enthalpy has been used (for more details see Section 3.3.1 ). The typical

PDT conditions are 0.1 at. % of AM atoms and 650 K. Li$_x$Cu$_{(1-x)}$InSe$_2$ is stable

in all concentrations, whereas the mixed Na$_x$Cu$_{(1-x)}$InSe$_2$ is stable only for small

concentrations of Na atoms (x < 10$^{-2}$) or for T > 650 K. For heavy AM atoms, on

the other hand, AlkInSe$_2$ secondary phases are formed in the PDT conditions.

Thermodynamic limitations for AM in CIGS solar cell have been discussed also

by Hariskos [99].

The effect of additional Ga has been studied by performing calculations also for

CGS as the host matrix. The results are shown in Figure 4.11 and they should

be compared to those for the In-based alloys in Figure 4.10. One can see that the

regions of mixed phases are smaller for the Ga-based compounds than those for
the In-based compounds in the case of Li, K, Rb, and Cs. This is related to the smaller lattice constant and, as a consequence, the larger formation energies of the substitutional AlkCu defect (see Section 4.1.3). In the case of Na, the lattice structures of the secondary phases NaInSe2 and NaGaSe2 are very different, which explains the decrease in the size of the region for the secondary phase from the In- to the Ga-based compound. The present calculations predict band gaps that are between 0.28 and 0.83 eV larger for the relevant secondary phases KGaSe2, RbGaSe2, and CsGaSe2 than for their In-based counterparts. Thus, precipitation of the AlkGaSe2 phase might affect the electronic structure of the CIGS absorber layer.

Figure 4.10. Atomic structure of (a) chalcopyrite LiInSe2 viewed along the [110] direction; (b) delafossite NaInSe2; (c) monoclinic KInSe2, RbInSe2, and CaInSe2 viewed along the [110] and [010] directions; (d) phase diagram for the AlkCu1−xInSe2 alloy. The dashed horizontal and vertical lines mark typical PDT conditions. In the regions above the colored curves, the mixed alloys are stable, whereas the regions under the curves correspond to the coexistence of CIS and the secondary phase AlkInSe2.

Figure 4.11. Phase diagram for the mixed AlkCu1−xGaSe2 alloy. In the regions above the curves, the mixed alloys are stable, whereas the regions under the curves correspond to the coexistence of CIS with the secondary phase AlkGaSe2. The dashed horizontal and vertical lines mark typical PDT conditions.
4.3 Electronic structure of the interface between CuInSe$_2$ and AlkInSe$_2$

Experiments [47, 46] have revealed that heavy AM PDTs induce shifts of the VBM and CBM away from the Fermi level, leading to the widening of the surface band gap. In order to understand the chemical and electronic structure of the absorber layer after heavy-AM PDT, the results of hard X-ray photoelectron spectroscopy (HAXPES) measurements and those of the DFT calculations are compared, with the KF PDT on CIS as a case study (Publication III). We omit Ga in our simulations, because it is depleted at KF-PDT CIGS surfaces [45].

A comparison between HAXPES spectra of the valence band region for K-free, K-poor, and K-rich samples measured with the 2 keV excitation energy and simulated spectra, each consisting of two possible compounds, is shown in Figure 4.12. K-poor and K-rich samples were prepared by employing a combined NaF/KF PDT with different KF deposition rates (for more details see References [45, 91]).

![Figure 4.12. Photoionization cross section-weighted DOSs and experimental HAXPES spectra for (a) K-free, (b) K-poor, and (c) K-rich CIGS samples measured with an excitation energy of 2 keV. G is the goodness of the fit (as defined in Equation 3.20). The fractions of the calculated and corrected component DOSs (to give the best fit for the respective compound combination) are displayed as filled areas under the curves (adopted from Publication III).](image)

A linear combination of CIS and CuIn$_5$Se$_8$ phases closely reproduces the shape and the width of the experimental valence band for the K-free sample (Figure 4.12 (a)). The resulting stoichiometry of the K-free sample corresponds to the formula Cu$_{1.14}$In$_{2.95}$Se$_5$, which is very close to the much-discussed CuIn$_3$Se$_5$ ODC [100]. Figures 4.12 (b) and (c) show that the valence band structures of the K-poor and K-rich samples can be explained by combinations of Cu$_{1.14}$In$_{2.95}$Se$_5$ and KInSe$_2$ DOSs. The contribution of the KInSe$_2$ phase is clearly larger in the case of the K-rich sample. The mean VBOs for the CIS/CuIn$_5$Se$_8$ interface and Cu$_{1.14}$In$_{2.95}$Se$_5$/KInSe$_2$ interface obtained from the fittings to the HAXPES spectra are $-0.4$ eV and $-0.5$ eV, respectively. The VBOs are similar to experimental values of $-0.55$ and $-0.6$ eV for the interface between CIS and ODC, and for the interface between ODC and KInSe$_2$, respectively [47].

The potential line-up method described above in Section 3.3.3 can be used to calculate band offsets between phases in contact for comparison with experimental findings. Unfortunately, in the above case of the CuIn$_3$Se$_5$ and KInSe$_2$ interface a direct comparison is not possible because there is no simple structural
model for the CuIn$_3$Se$_5$ phase due to the inherent randomness in Cu and In positions [101]. Therefore, calculations for the CIS/AlkInSe$_2$ (Alk = K, Rb, and Cs) interfaces with the (001) surface orientation are presented in this thesis. Previously, similar calculations have been performed to estimate VBO and CBO of CdS/CIS interfaces [102, 103].

The CBOs and VBOs obtained in this thesis for the (001) CIS interfaces with the heavy AM secondary phases (AlkInSe$_2$) are shown in Figure 4.13. Heterojunctions have type-II alignment in all cases. Electrons excited from the CIS conduction band transfer to the AlkInSe$_2$ conduction band without any barrier. The hole transport from AlkInSe$_2$ to CIS is likely in all cases. This helps the charge separation at the interface, and it decreases interface recombination. Of course, the interface between AlkInSe$_2$ and CdS can still have a barrier. However, band gaps and band positions of AlkInSe$_2$ and CdS are similar [91], so we can expect that AlkInSe$_2$ secondary phases are not harmful for solar cell devices.
5. Discussion and outlook

5.1 Benchmarking of the computational approach

DFT calculations are usually very successful in predicting material properties. However, the results of the DFT calculations remain very sensitive to the choice of calculation parameters. We can distinguish three types of errors:

1. Model errors, i.e., errors arising already on the level of continuous, infinite-dimensional equations. For instance, in choosing the exchange-correlation functional or supercell size.

2. Discretization errors, i.e., errors arising from the discretization of the equations when projecting them from infinite to finite dimensions. Typical factors are the choice of the basis functions and the number of grid points.

3. Round-off errors, i.e., errors arising from the use of floating point numbers which cause inaccuracies when dealing with the discretized equations.

Point defect formation energies in CIS have been calculated in many previous theoretical studies [23, 25, 79, 27, 84, 26]. The remarkable differences in the results for the point defect formation energy can be associated with three types of model error related to the choice of the exchange-correlation functional, to the choice of the chemical potential set, and to the choice of the supercell size.

First, PBE, LDA, and LDA+U functionals usually underestimate formation enthalpies of compound semiconductors, resulting in discrepancies in the stability diagrams used for choosing chemical potentials to calculate defect formation energies. Moreover, local and semilocal functionals usually underestimate band gaps in semiconductors (see Section 2.2). The HSE06 functional gives remarkably accurate predictions for the formation enthalpies of all considered compounds (Tables 4.1–4.3) and band gaps. As was shown in Section 4.1, chemical potential stability diagrams are constructed based on the formation enthalpies of different compounds. CIS stability diagrams obtained with the HSE06 functional agree very well with each other [25, 79, 27, 26, 104], and with the diagrams presented in Figure 4.1. The exact experimental band gap can be achieved by tuning the portion of the Hartree–Fock exchange and its inverse
Discussion and outlook

screening length [29]. The underestimated band gap does not directly affect the
defect formation energy, but it can reduce the number of transition levels and
thereby affect it through the details of the electron density. In order to get an
unbiased comparison with previously published results for formation energies of
point defects [23, 25, 79, 27, 84, 26], default parameters for HSE06 are used in
this thesis.

Second, in order to get accurate results for defect formation energies one has
to take into account experimental conditions. High-efficiency CIGS solar cells
are grown in a Se atmosphere with different concentrations of In and Cu. Thus,
an experimentally relevant chemical potential set is in the CIS stability area
close to the boundary with the bulk Se phase. In order to understand which
of the point defects are likely to form in non-stoichiometric CIS, a chemical
potential set with an extended range was used (this was done by stretching the
Cu chemical potential from extremely Cu-poor to extremely Cu-rich). Point
defects were then compared with PL and Hall measurement (Section 5.2).
Thus, by carefully considering experimentally relevant chemical potential limits,
thetheoretical predictions of abundances of donors and acceptors are possible.

Third, still another source of error in the calculations of point defects and
impurities is the artificial interaction between a defect and its periodic images.
A convergence test presented in Figure 5.1 shows only minor variations in the
formation energies and charge transition levels of the CuIn antisite in CIS for
supercells larger than 64 atoms. Thus, a 128-atoms supercell was sufficient for
this calculation. Worth noting is that the FHI-aims and VASP codes give similar
results for the defect formation energies and transition levels. However, the
band gap obtained by FHI-aims is 0.06 eV smaller than that obtained by VASP.

![Figure 5.1. Formation energy of the CuIn antisite in CIS as a function of the Fermi level position for different supercell sizes. The chemical potentials correspond to point D in Figure 4.3. The calculation are performed with FNV correction scheme.]
As was shown in Reference [28], formation energies for some defects converge very slowly with respect to the supercell size. Thus, the formation energy should be corrected by using a finite size correction scheme (see Section 3.2.1). The LZ and FNV correction schemes give similar results for formation energies of well-localized defects in CIS (Publication I). The advantage of the FNV correction scheme [85] is that it can be used for arbitrary supercell shapes.

There is no doubt that during the last decade, calculations of point defects in semiconductors have achieved a high degree of accuracy, thanks to various correction schemes and new exchange-correlation functionals. However, there are no general recommendations for the choice of computational parameters, such as the supercell size, the number of \( k \)-points in sampling the first Brillouin zone, cut off energy for the plane wave expansion, the total energy correction scheme, or the mixing parameters for HSE06 calculations. All these parameters have to be verified by repeating calculations and by varying the parameters one by one. Otherwise, calculations do not give reliable results. One should also note that, each material has to be considered individually, by making numerous convergence tests.

5.2 The role of native point defects and alkali metal impurities in Cu(In,Ga)Se\(_2\) solar cell performance

DFT can be used not only for accurate predictions of material properties, but theoretical calculations may also help to analyse experimental results. In this section, theoretical calculations of native point defects and AM impurities (Section 4.1) are compared with various experiments.

Understanding point defect properties is necessary for controlling semiconductor doping. Experimentally, information about acceptors and donors in semiconductors can be obtained, for example, from PL or Hall measurements. These measurements have been performed on CIS samples with different CIS stoichiometries [13, 14]. The amounts of acceptors and donors and their ionization energies vary when the temperature and composition of the CIS samples change.

In order to make quantitative comparison of our DFT results for point defects with PL peaks, formation energies at chemical potential values, corresponding to the experimental conditions have been calculated (see Section 4.1.1). Our thermodynamic charge transition levels cannot be directly compared to the optical charge transition levels probed in PL, and thus we just look for which defects are acceptors/donors. According to the calculations, the abundant donor seen in the experiment in the Cu-rich CIS is In\(_{\text{Cu}}\) and the three abundant acceptors observed could be V\(_{\text{Cu}}\), Cu\(_{\text{In}}\), and V\(_{\text{In}}\). Due to the low formation energies of these defects, their concentrations should be significant and consequently lead to the formation of defect complexes. In this thesis three possible complexes (Cu\(_{\text{int}}\)-2V\(_{\text{Cu}}\), Cu\(_{\text{int}}\)-V\(_{\text{In}}\) and Cu\(_{\text{int}}\)-Cu\(_{\text{In}}\)) have been considered. Cu\(_{\text{int}}\)-Cu\(_{\text{In}}\) has the lowest
formation energy among the considered complexes, with the formation energy of 0.6–1.2 eV, depending on the Fermi level position (Figure 4.4). However, this complex can act as an acceptor only at Fermi level positions higher than 0.4 eV. In summary, the Cu\textsubscript{int}-CuIn complex could act as an acceptor in \textit{n}-type material. But a conclusive study would also require the study of the kinetics of the native point defects, which is beyond the scope of the present thesis.

Extrinsic point defects can also affect the defect structure of the CIGS absorber. AM atom concentrations in CIGS after the PDT process are around 0.1 at. % [19]. However, for CIGS absorber layers grown on soda-lime glass, Na and K concentrations inside grains are even less than 0.1 at. % [39, 105].

According to the formation energy calculations in Section 4.1.2, the equilibrium concentrations (Equation 3.11) of AM atoms accumulated on Cu sites in the bulk CIS at the PDT temperature are estimated as 0.02 at. % for Na, $2 \times 10^{-9}$ at. % for K, and negligible for Rb and Cs. The concentration of Li\textsubscript{Cu} in CIS is expected to be even larger than that for Na because its formation energy is practically zero. Additional Ga can decrease the concentrations of heavy AM atoms on Cu sites, however, Li and Na concentrations remain the same (see Section 4.1.3). Concentrations of AM atoms also depend on kinetic factors, such as migration barriers. AM atoms may diffuse via the vacancy mechanism, as shown in Figure 4.9 (a). However, it requires a high concentration of V\textsubscript{Cu} along the diffusion path. Thus, the vacancy diffusion mechanism is expected to be dominant only in Cu-poor CIS. Note that Li, Na, and K also have low migration barriers for diffusion via the interstitial mechanism. This finding agrees with the APT measurement [38], where Li, Na, and K have also been found in the more stoichiometric grain interiors.

In early experimental studies [19, 106, 107, 50] the positive effect of Na and K impurities on the electronic structure of the CIGS absorber layer was associated with 1) the annihilation of compensating donor defects, such as In\textsubscript{Cu}, 2) the enhancement of the acceptor-type defect concentration, or 3) the increase of the Cu-vacancy concentration. To the best of our knowledge, the effect of other impurities is not clear [9]. According to Figure 4.3, the In\textsubscript{Cu} antisite concentration is high in Cu-poor CIS. If AM atoms replace In in In\textsubscript{Cu} antisites, the concentration of holes in the absorber layer increases because of the changes in the charge state of the defect. AM atoms on the In site may act as acceptors. However, according to our calculations the maximum concentrations of Li\textsubscript{In} and Na\textsubscript{In} are only about $8.2 \times 10^{-7}$ at. % (estimated from Figure 4.6), and the concentrations of the other AM atoms on the In site are even smaller under all possible chemical conditions. AM atoms may also contribute, by the increase of the Cu-poor region, suggested by Maeda \textit{et al.} [42] and Yuan \textit{et al.} [108]. The calculation of the AM atom migration barriers via the vacancy diffusion mechanism (Section 4.1.4) supports this explanation. Worth noting is that the concentrations of AM atoms on the Cu site are much higher than those on the interstitial positions and therefore diffusion in stoichiometric regions is limited.
5.3 The role of the secondary phase formation in Cu(In,Ga)Se$_2$ solar cell performance

Concentrations of AM atoms at the surface or at grain boundaries in CIGS are much higher than those in grain interiors. APT measurements have revealed that at grain boundaries the concentration of Na is up to 20 at. % [109] and the concentration of Rb is 1.5 at. % [38]. Thus, these regions can be unstable against formation of secondary phases.

AM atoms can easily diffuse in Cu-poor regions via the vacancy diffusion mechanism (Section 4.1.4) and extensively occupy Cu vacancies in CIGS. This can lead to the formation of mixed Alk$_x$Cu$_{(1-x)}$InSe$_2$ compounds. As was shown in Section 4.2, the mixed phase is stable for Li and Na. However, for Na the mixed phase is only stable for Na concentrations smaller than 0.1 at. %. For the heavy AM atoms, segregation of the AlkInSe$_2$ secondary phases is expected and supported by experimental evidence. For instance, the surface band gap measured with XPS after KF PDT [47] is in good agreement with estimated values for KInSe$_2$ [53]. Moreover, a recent TEM measurement has shown the formation of a Rb-contained secondary phase with a layered monoclinic structure [52]. These observations are consistent with the mechanism for the secondary phase formation considered in this thesis. Motivated by this, we focused more on the AlkInSe$_2$ properties.

The calculated band gaps for the AlkInSe$_2$ phases are larger than those for CIS, CGS, and CuIn$_5$Se$_8$. The formation of secondary phases can explain the surface band gap widening and changes in the morphology of the absorber layer after heavy-AM PDT [91, 19, 110, 52]. The valence band structure is also changed after AM PDT (Section 4.3).

The results of calculations presented in Figure 4.12 show that the valence band structures of the K-poor and K-rich samples can be explained by the combination of the Cu$_{1.14}$In$_{2.95}$Se$_5$ and KInSe$_2$ phases. The formation of a pronounced KInSe$_2$ phase contribution might depend on the amount of K available during PDT. Although the experimental valence band structures for samples after RbF PDT and CsF PDT are not available at this moment, the formation of RbInSe$_2$ and CsInSe$_2$ phases on the absorber surface is expected. The AlkInSe$_2$ secondary phases have different optoelectronic properties from the Cu-deficient CIGS variants, which may affect (and thus open a route to deliberately tune) the energy level alignment at the buffer/absorber heterointerface.

The best fits for the K-free experimental spectra with excitation energies of 2 keV can be achieved with the VBO between CIS and CuIn$_5$Se$_8$ of $-0.4$ eV as shown in Figure 4.12 (a). For comparison, the experimentally determined VBO between CIS and the Cu-depleted region is $-0.55$ eV. The shift between the Cu$_{1.14}$In$_{2.95}$Se$_5$ and KInSe$_2$ VBMs is about $-0.6$ eV. The theoretical calculation of the band offset between stoichiometric CIS and KInSe$_2$ shows a VBO of $-2.10$ eV (Figure 4.3).

In summary, heavy-AM PDT broadens the band gap and lowers VBM at the
absorber surface because of the formation of AlkInSe$_2$ secondary phases. This can lead to the passivation of the surface and grain boundaries, by hindering the atomic diffusion into the Cu sublattice. Heterojunctions have type-II alignment in all cases. Electrons excited from the CIS conduction band transfer to the AlkInSe$_2$ conduction band without any barrier. Hole transport from AlkInSe$_2$ to CIS is strongly favoured in all cases. Thus, the formation of secondary phases would increase the charge separation at the absorber-buffer interface, decrease recombination, and increase open-circuit voltage.
6. Conclusions and perspectives

Efficiencies of CIGS solar cells have been recently improved by incorporation of small amounts of AM atoms in PDT to the absorber layer. A further increment of the CIGS conversion efficiencies requires good understanding of changes in the defect microstructure during the manufacturing process of the CIGS absorber and after AM PDT.

In this thesis, fundamental properties of native point defects, AM impurities, and secondary phases have been obtained by using DFT employing the supercell approximation and the HSE06 functional. Since the ability to compare with experimental results is very important, the computational approach must be chosen carefully. The choice of the chemical potentials is the most important problem. The chemical potential set must be chosen based on the experimental conditions, taking into account the formation of secondary phases. Another well-known problem is the finite size problem for charged defects in semiconductors. This can be solved by increasing the size of the supercell and/or by implementing a correction scheme.

Depending on experimental conditions, the composition of the CIGS absorber layer varies from Cu-rich to Cu-poor. Concentrations of the most abundant internal point defects in Cu-rich and Cu-poor samples have been found experimentally. In this thesis, formation energies of native point defects in various chemical conditions have been calculated and compared with the results of PL measurements. It is found that some native point defects have a very strong tendency towards formation of point defects complexes. These complexes can also act as donors or acceptors. The present calculations show that $V_{\text{Cu}}$ and $\text{Cu}_{\text{In}}$ are two acceptors, observed in PL measurement. $V_{\text{In}}$ or $\text{Cu}_{\text{int}}$-$\text{Cu}_{\text{In}}$ complex are the most probable candidates for the third acceptor observed in Cu-rich CIS.

Knowledge about external point defects is also very important. According to experimental results, device parameters, such as the open-circuit voltage, short-circuit current, fill factor, and conversion efficiency of the CIGS solar cell strongly depend on which AM atoms have been used during PDT. The main observation from the calculations of this thesis is that Li, Na, and K mostly act in grain interiors, but K, Rb, and Cs can also modify the absorber surface and grain boundary regions, through the formation of AM secondary phases. Thus,
Conclusions and perspectives

K has an intermediate effect and can act as a light or a heavy AM atom. The chemical conditions also affect the electronic structure of CIGS after AM PDT. For instance, an AM atom on the In site is an acceptor and in In-poor conditions, these defects may form due to their low formation energy. However, in In-rich conditions, the concentration of the defect is negligible and it will not affect the electronic properties of the absorber.

The distribution of AM atoms in the absorber layer strongly depends on kinetic factors. Li, Na, and K migrate via the vacancy and interstitial diffusion mechanisms. In contrast, Rb and Cs diffuse only via the vacancy mechanism. Thus, Li, Na, and K are able to penetrate deeper into the absorber layers and can even be found in near-stoichiometric CIGS regions. Worth noting is that the shapes of the diffusion barriers are different for light and heavy AM atoms. The predicted trends in the vacancy and interstitial diffusion mechanisms reflect the different abilities of bond making and breaking for light and heavy AM atoms.

Since grain boundaries and the surface of the CIGS absorber layer are Cu-depleted, AM atoms can easily occupy Cu sites in those regions. If concentrations of heavy AM atoms are large, then formation of AlkInSe₂ phases are expected. These phases are known to lower the valence band maximum. Local lowering of the valence band maximum in the regions close to grain boundaries and the absorber surface repels holes and reduces grain boundary and surface recombination.

The use of heavy AMs results in modifications of the absorber surface leading to wide surface band gaps. On the basis of the calculated heats of formation and free mixing energies, the formation of the AlkInSe₂ secondary phases has been suggested. The analysis of HAXPES data for K-treated samples with theoretical predictions demonstrates that the surface region is mainly composed of the KInSe₂ and Cu-poor phases. The band offset calculations show that VBOs for the CIS-AlkInSe₂ interfaces with Alk = K, Rb, or Cs are large and favour the separation of holes towards the bulk absorber and electrons towards the buffer layer.

Although the present calculations can be used to explain most of the AM effects
in the CIGS absorber layers, there are still some open questions (Figure 6.1). The possible native point defects and their complexes have been considered in both prior and during the present theoretical calculations. However, there are still many complexes that must be considered. There is also a lack of knowledge about the diffusion of point defect complexes and their interactions with AM atoms. In this thesis, possible distributions of light and heavy AM atoms have been suggested. However, comprehensive information about the AM diffusion in the CIGS absorber layer can be obtained only after comparing AM atom formation energies and migration barriers in the grain interiors and close to the grain boundaries. In addition, the properties of the interface between the absorber and the buffer layer remain unclear and must be studied.

This work is a step toward a full understanding of the effect of AM PDT on CIGS solar cell efficiency. The results presented in this thesis summarize the properties of native point defects and AM impurities examined from first-principles. The direct comparison between theory and experiment helps in understanding the physics of defects in the CIGS solar cell. The author believes that a new record in CIGS solar cell efficiency will come soon, thanks to the detailed analysis of the CIGS defect structures provided by theoretical and experimental groups all over the world.
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Errata

Publication I

The CuInSe$_2$ lattice constants should be 5.82 Å and 11.71 Å. The In chemical potential in the M point should be -1.87 eV, instead of -0.87 eV

Publication II

The Equation 9 should not have the multiplayer (1-x) on the left hand side.
The aim of this work is to understand the effect of native point defects and alkali metal impurities on the electronic structure of the Cu(In,Ga)Se₂ absorber layer in order to improve the solar cell efficiency. Especially, it is found that the positive effect of light alkali metal (Li, Na) treatment is associated with the increase of the p-type conductivity, open-circuit voltage, and fill factor. The benefit of heavy alkali metal (K, Rb, and Cs) treatment is mainly the improvement the surface morphology, which allows a thinner and optically more transparent n-type material layer on the absorber. The different effects of the light and heavy alkali metals are shown to arise from the tendency of the light alkali metal atoms prefer to accumulate on the Cu sublattice as impurities whereas incorporation of heavy alkali metal atoms contribute mostly by separation of alkali metal containing secondary phases.