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# Computational Investigation of the Properties and Performance Bottlenecks of Selected Metal Sulfides for Use as Solar Absorber Materials

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i



## Abstract

- Why metal sulfides - some have ideal optical properties and some are earth abundant?  
(look for book on sulfide minerals)
- $\text{Cu}_2\text{ZnSnS}_4$  as a promising earth-abundant non-toxic solar absorber material for thin-film photovoltaic devices, theoretical conversion efficiency of 28% but major bottleneck of low open circuit voltage ( $V_{OC}$ ) relative to the band gap of the material.
- CZTS bottlenecks we address in this study
- Candidate photoferroelectric materials from screening process and properties for PV that we predict + novel properties of FE (Rashba splitting and FE domains for reduced recombination)

Add appendix section for convergence tests for DFT calculations?

**Include multiscale modelling in title? (especially if main project of yrs 2 and 3 will be to build QM/MM model for CZTS surfaces)**

## **Acknowledgements**

I would like to express (whatever feelings I have) to:

- My supervisor
- My second supervisor
- Other researchers
- My family and friends

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# Chapter 1

## Introduction

### 1.1 The Case for New Solar Absorber Materials for Photovoltaic Devices

#### 1.1.1 Terawatt-Scale Power Production from Renewable Resources

It is now widely accepted that the world is heading towards a major energy crisis, where there will come a point that the current major sources of energy (namely fossil fuels) will be unable to meet increasing global demand for energy as they are not a limitless supply. Furthermore, there is the ever present worry of climate change linked to increased carbon dioxide emissions from the burning of fossil fuels. Renewable, low-carbon alternative energy sources are therefore clearly desirable. From purely environmental considerations, it seems clear that fossil fuels should no longer be used and we should meet our energy needs solely from renewable, low-carbon energy resources such as solar power. However, it is not only environmental sustainability that must be considered, we must also consider the economic feasibility of solar power for large-scale projects. Germany is an example of a country making considerable efforts to increase the percentage of their energy supplied by solar power. On 9 June 2014 Germany even generated over 50% of its electricity demand from solar for the first time [135]. Although on average the country is not able to produce such a large portion from solar power, with solar-generated power providing

approximately 7.5% of net electricity consumption in 2015 [139]. To facilitate the growth of the solar power capacity in Germany a number of schemes and financial incentives to encourage investment were introduced, such as feed-in tariffs (FiTs). The German government first introduced FiTs in their Grid Feed-In Law (the Stromeinspeisegesetz), which came into force in 1991 [71]. FiTs are intended to support new developments in renewable energy supply by providing investor certainty. They set the rate a utility company must pay for renewable generated energy and guarantee the provider of renewable energy a specific rate for a long period of time, typically fifteen to twenty years. As this cost is higher than fossil fuel based electricity, the higher price is then passed on to all customers of the utility company to spread out the higher costs so that buyers of renewable energy do not pay higher prices. In Germany, this has resulted in an increase of 6% on the average electricity bill for users in a specific region [92]. The social implications of such a cost increase must also be considered in assessing the viability of a particular power source.

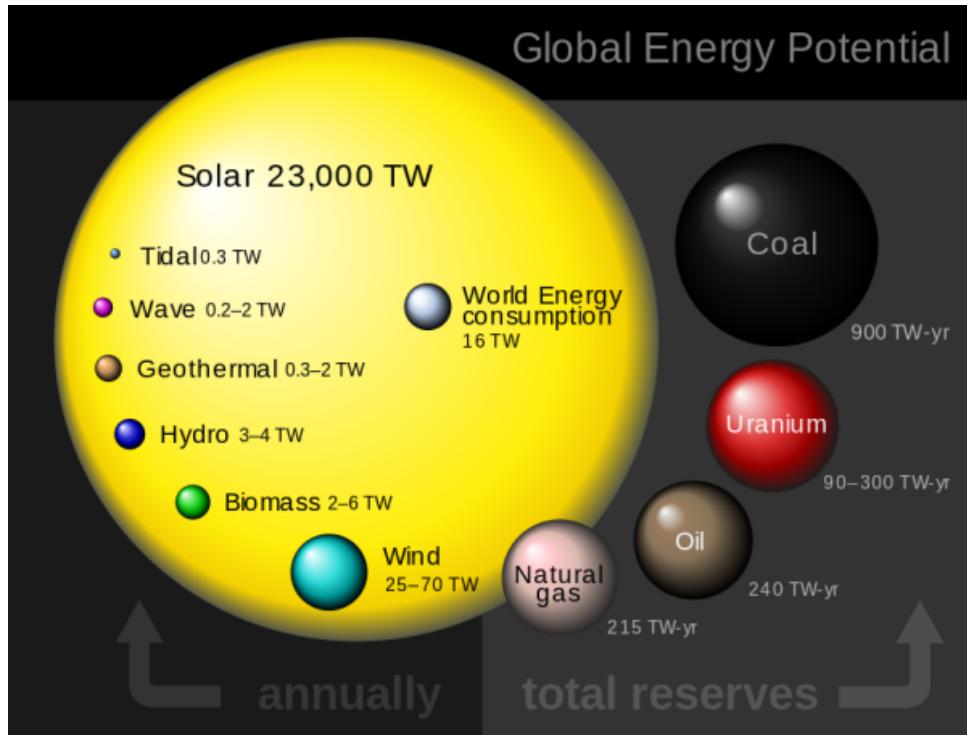


Figure 1.1: Illustration of power available annually from various renewable energy resources, annual world energy consumption and total reserves of various non-renewable energy resources. Figure take from reference 131.

However if solar power, in combination with proper energy transport, storage and secondary

conversion into heat and fuels, could be made to be economically feasible; it is a realistic candidate for replacing fossil fuels as a major supply of global energy. It is by far the largest source of energy available to us, as illustrated in figure 1.1, and it is also the most widely geographically distributed [58]. The Sun supplies  $3 \times 10^{24}$  J of energy to the Earth each year, which is around  $10^4$  times more than mankind's current annual energy consumption. Assuming a fairly modest module efficiency of 20%, a system capacity factor of 15%, an average ground cover ratio of 50%, and 50% losses related to storage and secondary conversion, 1.6% of the Earth's land area would be required for solar-generated power to meet current world energy needs [103]. Although this would be a fairly large area, it would not be completely unrealistic. For instance, this area would be less than 5% of the area used for agriculture worldwide [103]. The area required could also be reduced further through improvements in the efficiency of PV module and by making use of building-integrated PV (BIPV) innovations, largely made possible by flexible, thin-film second generation PV technologies which are discussed further in section 1.1.4. An example of a BIPV project is shown in figure 1.2, where solar panels are not only placed on the roof of a building but can also placed on the windows and outer walls.



Figure 1.2: A building integrated photovoltaics (BIPV) project fitted in the United States by BISEM-USA [12].

Recent years have seen a rapid increase in the installed solar generation capacity, with the

global grid-connected PV capacity growing from 1.3 GW in 2000 to 139 GW in 2014 [7], with approximately a doubling in the cumulative installed capacity every two years [62]. Additionally, creative business models have spurred investment in residential solar systems [93]. Great improvements in technology, price and performance have helped to facilitate this growth, but solar energy still only provides a minor fraction of the world's energy. In 2013 solar power only provided 0.87% of the world's electricity [104]. Further advances are required to enable a dramatic increase in the contribution from solar power at socially acceptable costs [93]. Ultimately, solar power-generation technologies must become cost-competitive with conventional fossil-fuel based power sources.

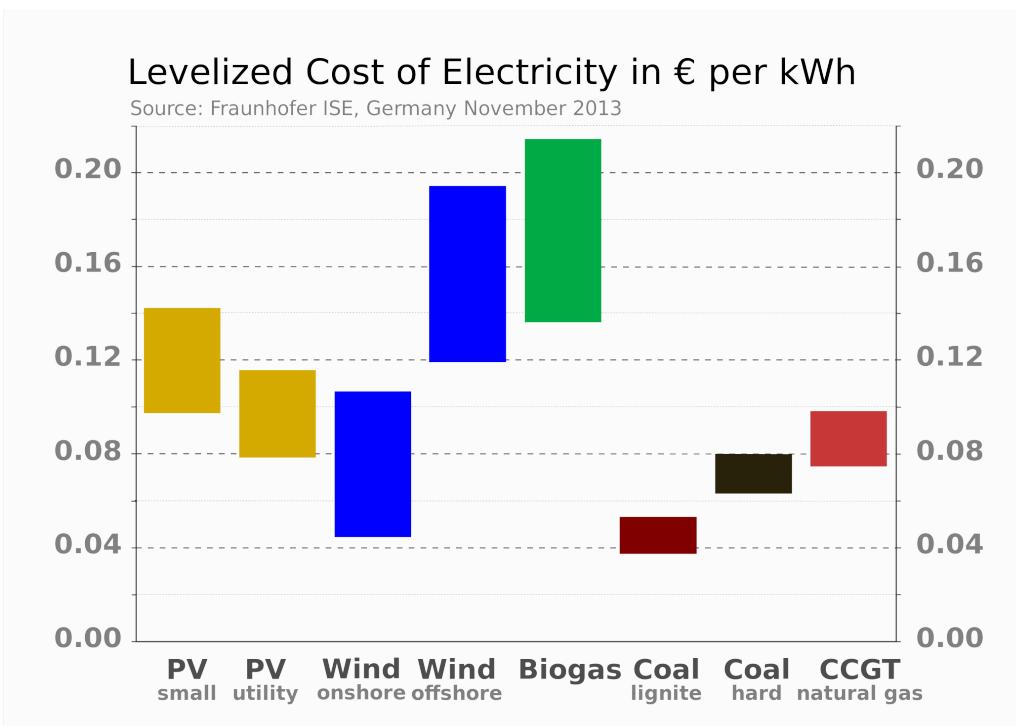


Figure 1.3: Levelized cost of electricity (LCOE) of renewable energy technologies and conventional power plants at locations in Germany in 2013. Specific investments are taken into account with a minimum and maximum value for each technology. Figure taken from reference 38.

Levelized cost of energy, or electricity, (LCOE) is a common way to assess how cost competitive renewable energy sources are with their non-renewable counterparts. LCOE allows for the measurement of the performance of different power generating technologies, which may have unequal lifetimes and differing capacities. It is calculated by summing all costs incurred during

the lifetime of the technology and dividing this value by the units of energy produced during the lifetime, with units of energy expressed as dollars per kilowatt hour (\$/kWhr) [77]. This measure is also used as the key selling point for a number of commercial solar cell manufacturers such as First Solar Inc., who market their product as being able to generate electricity at an average of \$0.63 per Watt as stated in their 2013 Annual Report [57]. Using the LCOE, comparisons of grid competitiveness for renewable energy sources can be made [77]. Figure 1.3 shows the LCOE of renewable energy technologies and conventional power plants at locations in Germany in 2013, enabling an assessment of the cost-competitiveness of PV power generation at this location, accounting for, for example, typical solar irradiation at the given locations [38]. As the figure shows, both small-scale and large-scale utility solar power are still not cost competitive with the cheapest non-renewable resources.

### 1.1.2 Basic Operating Principles of a Solar Cell Device

Refer to: pg 5 [16], pg 11 + 18 [45]

A solar cell device converts solar energy directly into electrical energy, where solar energy can be described as either a spectrum of electromagnetic radiation or a flux of photons ???(and electrical energy is a flow of charge carriers able to do work in an external circuit.)??? [16] Voltage is generated in a solar cell device by the photovoltaic effect. The terms ‘solar cell’ and ‘photovoltaic (PV) cell’ are therefore often used interchangeably.

Semiconducting materials are usually utilized in a PV device. A semiconductor is described by its valence and conduction energy bands i.e. a group of energy levels, which electrons may occupy, and a gap in between with no available energy levels called the bandgap. In thermal equilibrium at a 0 K, all the energy levels in the valence band are occupied by electrons while all energy levels in the conduction band remain unoccupied. Energy level occupancy at temperais usually described by the Fermi-Dirac distribution [1]. [16]

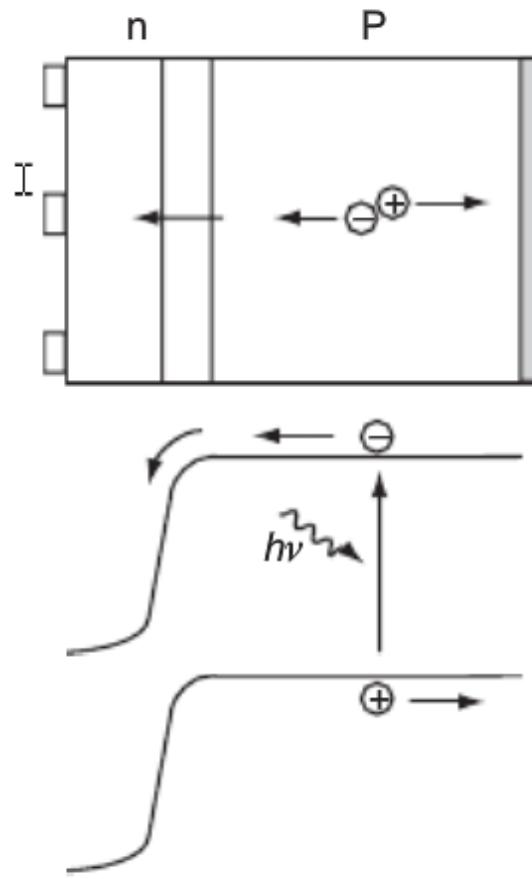


Figure 1.4: Schematic of a typical crystalline silicon solar cell device (top), where the majority of the cell consists of a thick p-type base in which most of the light is absorbed. After light absorption, the minority carriers (electrons) diffuse to the junction where they are swept across by the strong built-in electric field. The electrical power is collected by metal contacts to the front and back of the cell. Excitation of an electron-hole pair across the band gap of the p-type material (bottom). Figure taken from reference 80.

Only photons with energies higher than the bandgap can be absorbed in the perfectly pure semiconductor by exciting an electron from the valence to the conduction band, while simultaneously conserving total energy and momentum. Two types of semiconductors are distinguished with regards to the shape of the valence and conduction band in the energymomentum diagram. In a direct semiconductor, the maximum energy of the valence band and the minimum energy of the conductance band are located at the same momentum, which is not the case in an indirect semiconductor. Light absorption in a direct semiconductor occurs when the photon interacts with only an electron from the valence band. Light absorption in an indirect semiconductor requires a phonon (i.e. a quantum of thermal energy with considerable momentum, which is discernible as a crystal lattice vibration) assisted transition, where a phonon provides

or consumes the difference in momentum. [16]

When semiconducting materials absorb photons of light with energies of at least their band gap, electrons are excited to higher energy states within the material to form an electron-hole pair, as shown in figure 1.4. The excited electron-hole pair would eventually recombine and relax back to the ground state of the material with the emission of a photon of an energy equal to the energy of the electronic transition that has just occurred. However in a PV device, there is a built-in asymmetry that leads excited charge-carriers away before they can recombine back to the ground state. The extra energy of the excited electron generates a potential difference that drives electrons through a load in the external circuit to do electrical work. In the conventional PV effect, as electrons are excited across the band gap of a semiconductor, the band gap of the material sets the upper limit for the maximum voltage that can be generated. In early PV devices, the asymmetric junction was a Schottky barrier between a metal and a semiconductor but now more effective p-n junctions are used, which are formed by joining together p-type and n-type semiconductors [86].

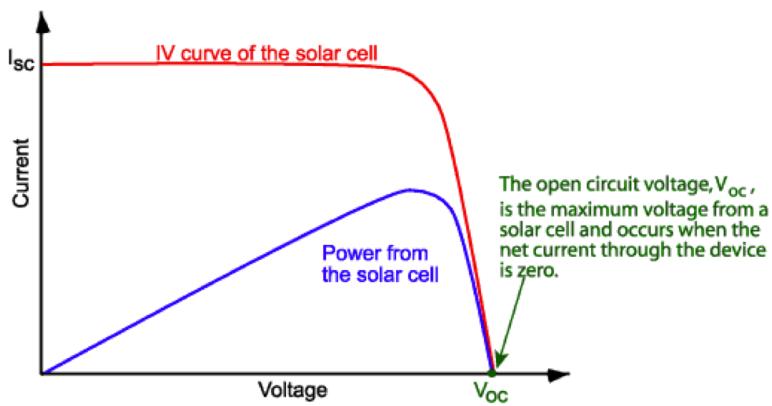


Figure 1.5: The current-voltage (I-V) curve of a solar cell showing the open circuit voltage ( $V_{OC}$ ). Figure taken from reference 54.

When a cell consisting of a p-n junction is illuminated, a voltage develops across the terminals, i.e. between the p-type and n-type semiconductors. When the terminals of the solar cell are disconnected from any external circuit, or there is an infinite load resistance, this voltage is at a maximum and is called the open circuit voltage ( $V_{OC}$ ) and no current is drawn from the solar cell. Conversely, if the terminals of the solar cell are connected together then there is

no voltage as all of the electromotive force is used to extract charge-carriers. The maximum possible current is drawn, which is called the short circuit current ( $I_{SC}$ ). For a solar cell to generate power, there must be both voltage and current generated, therefore when the cell is operating at either  $V_{OC}$  or  $I_{SC}$  the power output is zero. To generate power, a finite load resistance is added to the circuit so that some current is drawn from the solar cell and a voltage develops across the cell that is between 0 and  $V_{OC}$  [86]. There is a maximum operation point for the power output ( $P_{MP}$ ) of a solar cell in terms of I and V, as shown in figure 1.5. This can be defined in terms of  $V_{OC}$  and  $I_{SC}$  when used in conjunction with the fill factor (FF), which is a number less than one that describes the squareness of the I-V curve [48] shown in figure 1.5 and is given by equation 1.1. The current and voltage are determined by the load and illumination so the load can be tuned such that maximum power output is achieved, but the value of  $V_{OC}$  places a limit on the power output of the cell [86].

$$P_{MP} = FFV_{OC}I_{SC} \quad (1.1)$$

$$\eta = \frac{P_{MP}}{P_{in}} = \frac{FFV_{OC}I_{SC}}{P_{in}} \quad (1.2)$$

The power conversion efficiency (PCE),  $\eta$ , of a solar cell is the ratio of power output from the solar cell to the power input from the Sun. This is shown in equation 1.2, where  $P_{MP}$  has been taken from equation 1.1. For an efficient solar cell, it is desirable to have a high  $I_{SC}$ , a high  $V_{OC}$  and a FF that is as close to 1 as possible [48].

\*\*Move discussion to section on candidate new materials\*\* CZTS solar cells are known to be hampered by low  $V_{OC}$  relative to the band gap of the material [121]. Whereas in ferroelectric PV materials, photovoltages orders of magnitude larger than the band gap have been measured (a phenomena referred to as the anomalous photovoltaic effect), but very low photocurrent output is a big challenge for these devices [148].

\*\*Add figure and description of basic PV device + show basic simplified band diagram (later compare to real band structure, e.g. of Si)\*\*

A solar cell device consists of... (see Mirjana's thesis)

\*\* Explicitly discuss recombination

### 1.1.3 Key Properties for Solar Absorber Materials

A solar (or photovoltaic) cell is an example of an optoelectronic device in which the solar absorber material of choice must allow for the manipulation of light, electrical current and their interaction. Metals are excellent electrical conductors, but do not allow light to travel inside. Glass and related dielectric materials can accommodate and guide light waves, as in electrical fibres, but are electrical insulators. Semiconductors are in between these two types of material as they can carry both electrical current as well as light waves [101]. Furthermore, some semiconductors can be used to transform light into electrical current, which was described in the section above. The two vital processes that must occur in a solar absorber material were also discussed above, which were: the excitation of an electron across the band gap from the valence band into the conduction band in a semiconducting material by a photon and the subsequent collection of the photoexcited charge carriers by an external circuit before the photoexcited electron-hole pair recombine. There are certain optical and electrical properties that are necessary for these processes to occur and then there are also certain properties that indicate how well a material is likely to perform in a solar cell device. In this section the band gap, effective mass, dielectric constant and absorption coefficient of a potential solar absorber material will be discussed.

The most obvious necessary requirement for a solar absorber material is for it to be a semiconductor so that it possesses a band gap across which an electron can be excited. The value of this band gap must also be somewhere within the energy range of the solar spectrum shown in figure 1.6, so that sunlight can induce the photoexcitation of an electron-hole pair across

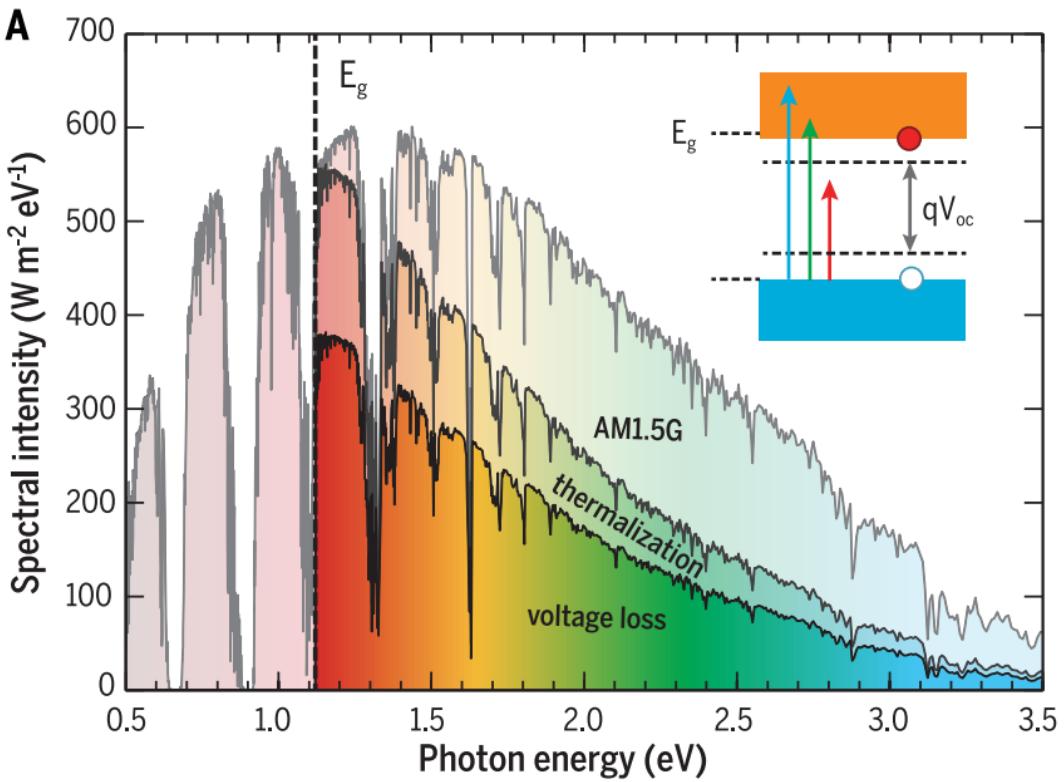


Figure 1.6: AM1.5 solar spectrum with distinct dips due to molecular absorption in Earths atmosphere. The dashed line shows the band gap of silicon and fading to the left indicates that photons with energies below the band gap will not be absorbed and other fading indicates other loss mechanisms that prevent a solar cell from being unable to convert the full incident spectrum into electricity. Figure taken from reference 103.

the band gap. Secondly the material must allow for the transport of charge carriers out of the absorber material and into a collection electrode and external circuit in order to do electrical work. Provided these necessary conditions are met and some sort of spatial asymmetry is present to drive electrons away from their point of promotion, the material should exhibit the photovoltaic effect [87]. However, how well it will actually perform in a solar cell is determined by more stringent criteria and other material properties. Firstly the actual value of the band gap within the range of the solar spectrum is of importance. It is ideal for the value to be as close as possible to the region of photon energies that make up the majority of the solar spectrum. The optimal range for the band gap under typical radiation conditions is between 1.06 eV and 1.50 eV [59]. The upper limit of the power conversion efficiency (of incident photon energy into electrical energy) by a device made from a particular absorber material based on its band gap was first calculated by Shockley and Quiesser in 1961 [117]. A plot of theoretical efficiency limit as a function of band gap is shown in figure 1.7.

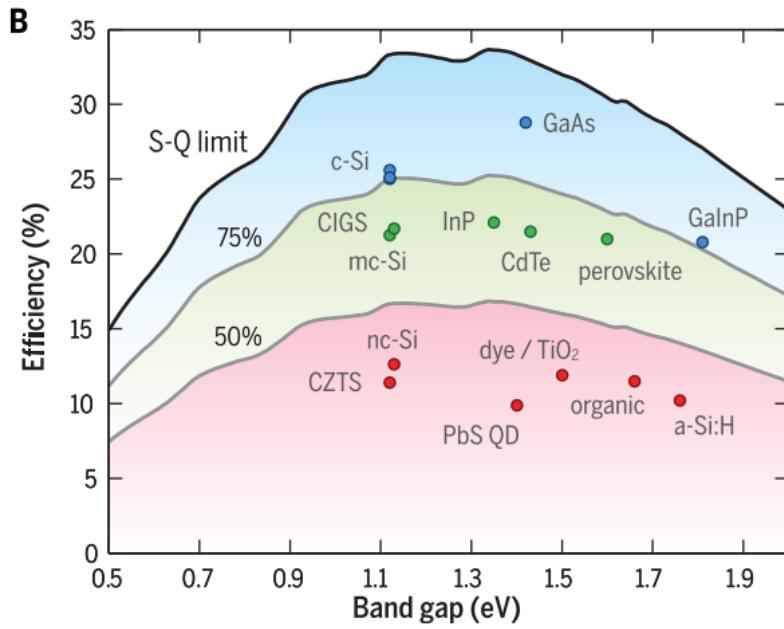


Figure 1.7: Theoretical Shockley-Queisser detailed-balance efficiency limit as a function of band gap[117] (highest black line). The record efficiencies for different materials are plotted for the corresponding band gaps, where materials below the lower two grey lines are achieving conversion efficiencies less than 75% and 50% of their theoretical efficiency limit respectively. Figure taken from reference 103.

However, it is not only the value of the band gap that is of importance. More intricate details of the band structure of the material can also impact on the performance of a solar cell device made from the material. Band theory and band structures will be discussed more in section 2.2, but it is worth noting at this point that if the band structure shows a band gap that is direct or indirect can have an impact on the performance of a solar cell made from the material. Figure 1.8 shows the band structures of Si and GaAs, where Si possesses an indirect band gap and GaAs possesses a direct band gap. The excitation of an electron directly from the valence band to the conduction band is called fundamental absorption, as there are several other optical absorption transitions that can occur in a semiconducting material, especially in a defective material, and this point will be discussed more in section 2.4.1. Both the total energy and momentum of all particles involved in the absorption process must be conserved. Photons do possess momentum ( $\frac{h}{\lambda}$ ), however this is very small compared to the range of crystal momenta and so the electron momentum is effectively conserved during photon absorption. For a direct transition, the absorption coefficient of a material for a given photon energy  $h\nu$  is proportional to the probability,  $p_{12}$ , of the transition of an electron from the initial state  $E_1$  to the final state

$E_2$ , the density of electrons in the initial state,  $g_v(E_1)$ , and the density of available final states,  $g_c(E_2)$ . This is then summed over all possible transitions between states where  $E_2 - E_1 = h\nu$ . Since the electron momentum is conserved during a direct transition, the crystal momentum in the valence band is approximately the same as that of the final state in the conduction band at energy  $E_2$  [78].

However for an indirect band gap semiconductor, such as silicon shown at the top of figure 1.8, the valence band maximum occurs at a different crystal momentum to that of the conduction band minimum. As discussed earlier, the momentum of a photon is far less than that of crystal momenta. In order to conserve the momentum of an electron during an optical transition across an indirect band gap, momentum must be either provided by the lattice or released to the lattice usually in the form of the particle representation of a lattice vibration, known as a phonon, as indicated in the top right schematic of figure 1.8. Since both a phonon and an electron are needed to make an indirect transition possible, the absorption coefficient depends not only on the density of states of the electrons, as for a direct transition, but also on the availability of emitted or absorbed phonons with the required momentum. Therefore, the absorption coefficient for an indirect transition compared to a direct transition is typically relatively small. Consequently, light penetrates more deeply into an indirect band gap semiconductor before being absorbed. In order to absorb the same amount of light therefore, the absorber layer of a device made from an indirect band gap semiconductor must therefore typically be thicker [78]. This is undesirable if the particular material contains rare or expensive components and also results in higher demands on material quality as charge carriers must be able to be transported through the absorber material in order to be collected.

Another property of importance that can be derived from the band structure of a material is the effective mass. The effective mass is related to the curvature of the band at the top of the valence band (for holes) or at the bottom of the conduction band (for electrons). The effective masses of electrons or holes are the masses they seem to carry for transport properties [8]. For example, in  $\text{ZnSnO}_3$  the hole effective mass has been calculated to be large, indicating that hole mobility will be poor in this material. Poor mobility will make carrier extraction difficult, which has been linked to the low photocurrents observed in this material [67]. Effective masses

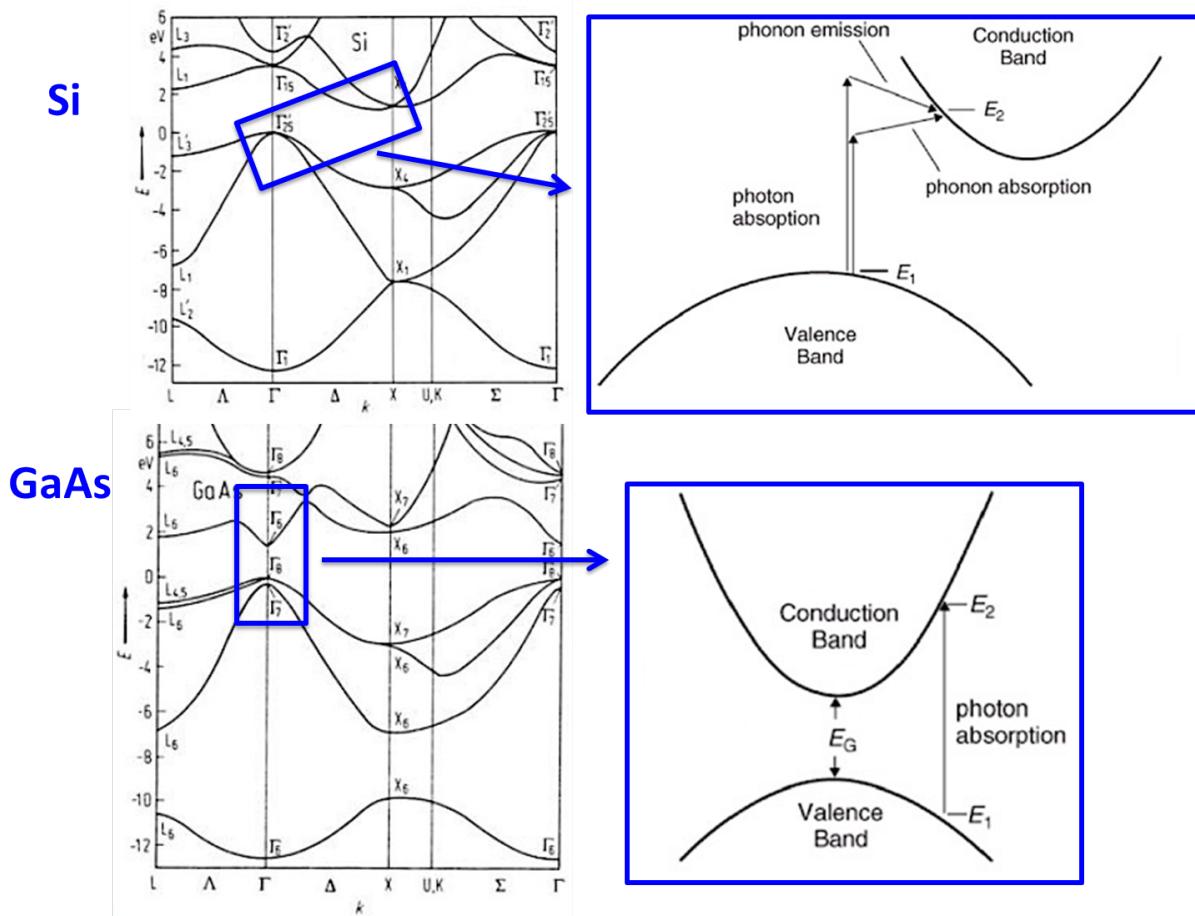


Figure 1.8: The band structure of silicon and a schematic of the absorption process in an indirect band gap semiconductor (top). The band structure of GaAs and schematic of the absorption process in a direct band gap semiconductor. Figures adapted from 49 and 78.

are calculated by fitting a formula, which will be discussed more in the methodology section 3.4. However, just from a quick inspection of the band structure of a material, a more steeply curved shape to the band extrema indicates a lower effective mass and therefore higher carrier mobility. Figure 1.9 shows a schematic of the band structure of a direct band gap semiconductor that has both heavy- and light-hole bands at the valence band extremum, where the flatter band corresponds to the heavy-hole band. Although certain thin-film technologies, which will be discussed towards the end of section 1.1.4, reduce the amount of absorber material the charge carrier must travel through before being collected. So although carriers must still travel through the material, effective mass could be considered less of a crucial parameter for this technology. Furthermore, the effect of the effective mass on the transport properties could be overshadowed by the effect of defects in a real, non-ideal material. It is the dielectric function of the material that provides more insight in this case, which is discussed below.

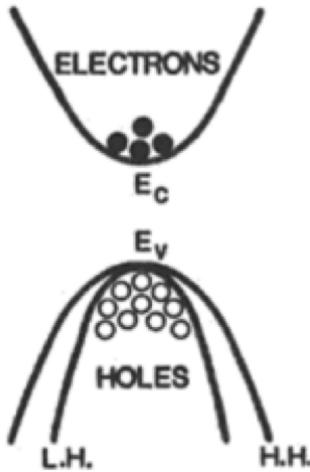


Figure 1.9: Schematic of the band structure of a photoexcited semiconductor with electrons near the bottom of the conduction band, holes near the top of the valence band, where the particular material has both heavy- and light-hole bands (labelled H.H and L.H in the figure respectively). Figure taken from reference 74.

Materials with ionic or covalent bonding, or a mixture of the two, are usually either insulators or intrinsic semiconductors. Due to this type of bonding, electrons are bound to the atomic structure and so are unable to move throughout the material when an electric field is applied as in a metal. However, these materials can be polarized by an applied electric field where electrons are displaced relative to their nuclei by small distances. When an external electric field is applied, the positive and negative charges experience electric forces tending to move them apart in the direction of the external field so that their centres of gravity no longer coincide [150]. The material is now said to be polarized and an electric displacement field ( $\vec{D}$ ) appears within it. The applied field ( $\vec{E}$ ) and displacement field are linked by the macroscopic dielectric function of the material,  $\epsilon_r$ , as shown by equation 1.3 [8], which is a function of the frequency of the applied field.

$$\vec{D} = \epsilon_0 \epsilon_r \vec{E} \quad (1.3)$$

The dielectric function indicates the ability of a material to screen the external electric field by the apparition of a polarization. In a solid, this polarization comes from the re-organization of the electronic density or from the motion the ions that make up the material. These two mechanisms are illustrated in figure 1.10a and associated frequencies of the applied field to induce particular polarization responses are shown in figure 1.10b. The contribution to the

dielectric function from the electronic density, sometimes referred to as the high-frequency dielectric function, is denoted as  $\epsilon_\infty$  and the contribution of ionic motions is denoted  $\epsilon_{vib}$  in equation 1.4 [8], and is sometimes referred to as the static or low-frequency dielectric function.

$$\epsilon_r = \epsilon_\infty + \epsilon_{vib} \quad (1.4)$$

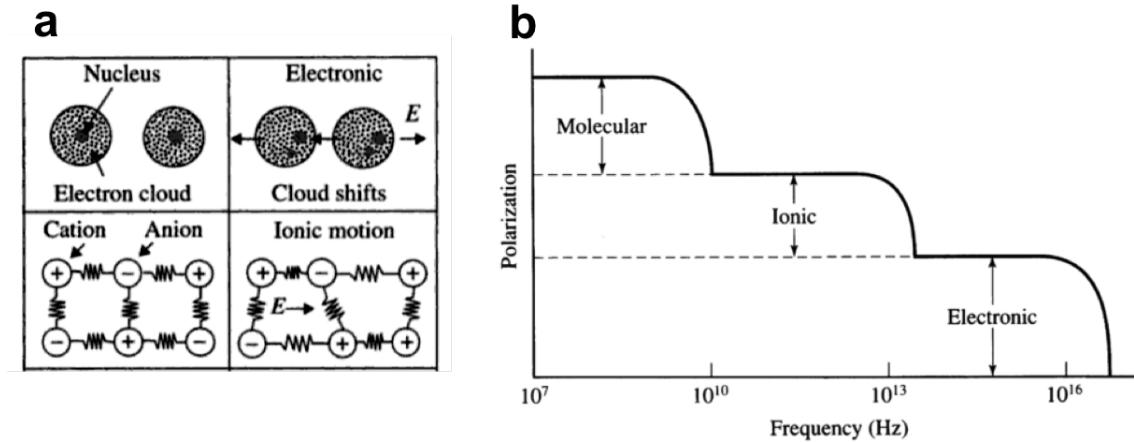


Figure 1.10: Polarization mechanisms in a crystalline solid: response of electronic density and motion of ions (a), figure taken from 90. Typical frequencies of applied electric field to induce polarization mechanisms, where the response at high frequencies is only that of the electronic density (b), figure adapted from reference 55.

The value measured for the dielectric function for various frequencies of the applied electric field can give information about different dielectric responses of the material, some of which were shown in figure 1.10. Furthermore, the dielectric function is usually a complex quantity, where the imaginary part corresponds to a phase shift of the polarization relative to the applied electric field and leads to the attenuation, i.e. a gradual loss in the intensity, of electromagnetic waves as they pass through the material. The dielectric function is an important material property for a photovoltaic material for a number of reasons. Firstly, it can be shown that the absorption of a material, which has been discussed already as a way of comparing the performance of materials with direct and indirect band gaps in a solar cell, is mainly determined by the imaginary component of the dielectric function [39]. The band gap determines the minimum energies photons must have in order to be absorbed by a material, but it does not predict how strongly that material will absorb them. In fact, it has even been suggested that when screening for

candidate solar absorber materials, a direct band gap within the optimal range for the solar spectrum is not a sufficient criteria as this does not guarantee that the onset of absorption near the band gap is strong [146]. In this particular work, instead of the Shockley-Quiesser limit mentioned earlier, they recommend an alternative screening metric, the Spectroscopic Limited Maximum Efficiency (SLME), which depends explicitly on the calculated absorption spectrum of the material.

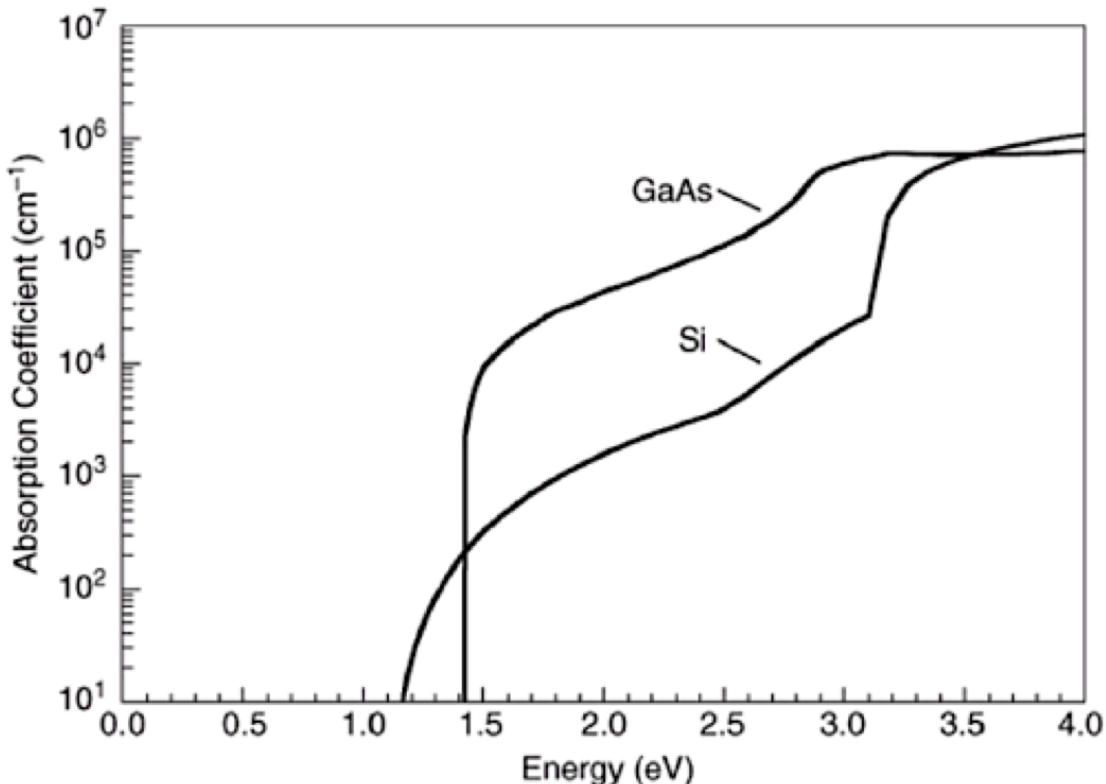


Figure 1.11: A comparison of the absorption coefficients of the indirect band gap semiconductor Si and the direct band gap semiconductor GaAs across a range of incident photon energies. Figure taken from reference 78.

The optical absorption coefficient of a material,  $\alpha$ , determines the penetration depth,  $\frac{1}{\alpha}$ , of light incident on the material [152]. Figure 1.11 shows the absorption coefficients of different semiconductors across a range of wavelengths. The figure shows a less steep onset of absorption for silicon, which as discussed earlier possesses an indirect band gap, compared to that of for example GaAs when the absorption corresponds to a direct band-to-band transition. The implication of the differing absorption coefficients and therefore different optical penetration depths of materials for solar devices is that materials which are stronger absorbers require

less material to absorb the light. This forms the basis of thin-film solar cell technologies, for which the impact of defects in the absorber layer material are typically less significant as charge carriers do not have to travel through as much of the absorber material in order to reach a collection electrode. Different solar cell technologies will be discussed further in section 1.1.4.

Secondly, the electrostatic force between an electron-hole pair is reduced when the static (or low-frequency)  $\epsilon_r$  is larger [8] due to the enhanced screening of the charge. This, therefore, will reduce the recombination of electron-hole pairs in a material. Another aspect of this property important for photovoltaic materials is that it can improve the defect tolerance of the material. In the majority of cases producing perfectly defect-free materials is impractical, if not impossible. The impact of defects in a material on photovoltaic performance will be discussed more in section 2.4.2, but for now it is just worth noting that defects can trap charge carriers, enhance electron-hole recombination (reducing carrier lifetimes in the material) and therefore have the overall effect of reducing charge collection from a PV device, thereby decreasing the efficiency of the conversion of incident photons into electrical current. In reference to modelling electronic transport in a material in the presence of defects,  $\epsilon_r$  has been referred to as the most important property of the material [19]. A higher dielectric function indicates a greater ability to screen charge. The capture cross-section for charge carriers by a charged defect will therefore be influenced by the value of  $\epsilon_r$  of the material [19]. This property can therefore indicate how well photo-excited charge carriers will be transported through a defective photovoltaic material, towards an electrode for carrier collection and on to do electrical work.

#### 1.1.4 Current Commercial Solar Cell Technologies & Limitations

It was first observed in 1839 by Edmond Becquerel that sunlight could be used to generate electricity. Becquerel discovered that if silver chloride was placed in an acidic solution, connected to platinum electrodes and exposed to sunlight, an electric current flowed. However the effect was small and poorly understood before Albert Einstein's discovery of the photoelectric effect and explanation of the phenomena by the quantum nature of light in 1904 [122]. Even then, it was not until the development of semiconductor technology during the silicon revolution of

the 1950's that solar cells were fabricated which were able to generate significant amounts of electricity. The first silicon solar cell was created in 1954 in the Bell Laboratories with cells achieving efficiencies of 6%. Originally solar cells were developed for terrestrial energy generation, such as the 108 solar cells used to supply energy to the Vanguard satellite in 1958 [122]. The first oil crisis in 1973 however highlighted the dependency of many economies on fossil fuels and the need to address the security of energy supply, in particular for Japan and West Germany which had few of their own resources. As a consequence, solar cell research was no longer limited to only high-cost crystalline silicon devices for terrestrial applications, but also into creating cheaper, commercial, thin-film solar cell technologies using absorber materials such as amorphous silicon, cadmium telluride and copper indium diselenide [70].

In spite of this, crystalline silicon is still the dominant solar cell technology with mono- and poly-crystalline silicon photovoltaic cells comprising up to 90% of all the solar cells produced in 2008 [108]. Silicon is the second most abundant element in the Earth's crust [44], making it a plausible material to use in large-scale solar power generation. Over 60 years of development have seen device efficiencies increase from 6% to 25% for the highest quality research devices and 15-18% for the more common industrial cells [108]. As can be seen from figure 1.7, the best performing silicon devices are now very close to achieving conversion efficiencies close to their theoretical limit, as predicted by Shockley-Quieser [117]. More dramatic however is the fall in manufacturing costs which have halved since 2008 and are more than a hundred times lower than they were in 1977, as shown in figure 1.12. This development was largely aided by progress in semiconductor technology driven by the silicon chip industry, with the solar industry benefiting from advances in silicon manufacturing processes and even making use of waste silicon produced that was not of a high enough grade for silicon chips [122]. Although the development of silicon-based technologies has clearly revolutionized the modern computer, the optical properties of silicon do not make it ideal for use as a solar absorber material in a photovoltaic device and despite the dramatic reduction in manufacturing costs, the technology is still not able to be cost-competitive with fossil-fuel power generation, as was shown in figure 1.3.

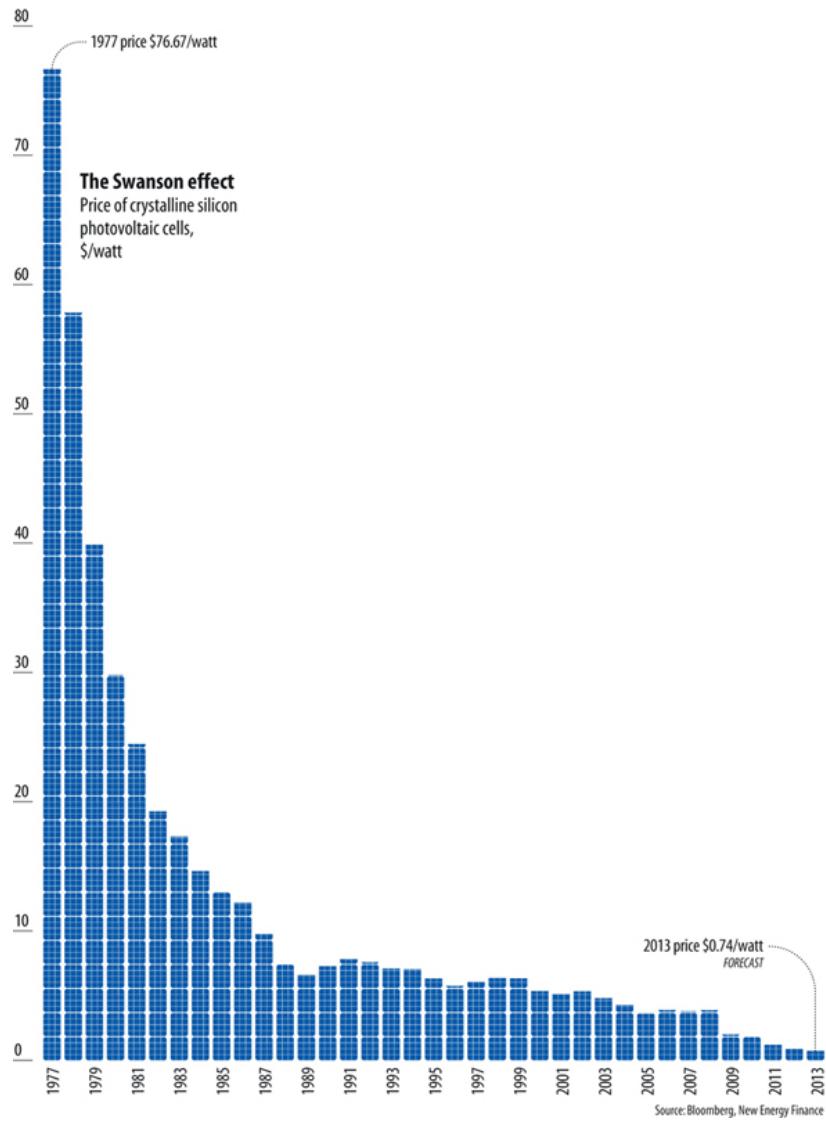


Figure 1.12: Average cost of solar panels composed of a crystalline silicon absorber layer. Figure taken from reference 116.

The primary issue with silicon is that its band gap of 1.1 eV is indirect. The key consequence of this property is that silicon is therefore not a very strong absorber of sunlight (compared to for instance newer, thin-film technologies which are discussed later), resulting in a low optical absorption coefficient compared to these newer technologies where both band gap and absorption coefficient were two of the key material properties for solar cells discussed in section 1.1.3. To absorb the same amount of sunlight with a silicon solar cell requires a thicker layer of the material than in thin-film technologies. Photovoltaic devices are very sensitive to defects and impurities. This point is discussed further in section 2.4.2, but the consequence for a thick layer of silicon is that very high quality, non-defective material is necessary to enable charge carrier

collection before recombination occurs, which results in high manufacturing costs. The devices are made from flat sheets of crystalline or multicrystalline silicon called wafers that consist of very high quality silicon (99.99999% pure) [91]. The production processes of silicon wafers have been thoroughly optimised, but are still very energy-intensive, time-consuming and complex [51] and this is reflected by the position of this type of technology on the plot of efficiency versus cost shown in figure 1.13. Despite decades of development, commercialized silicon solar panels are still too expensive to compete with fossil-fuel based power sources [115].

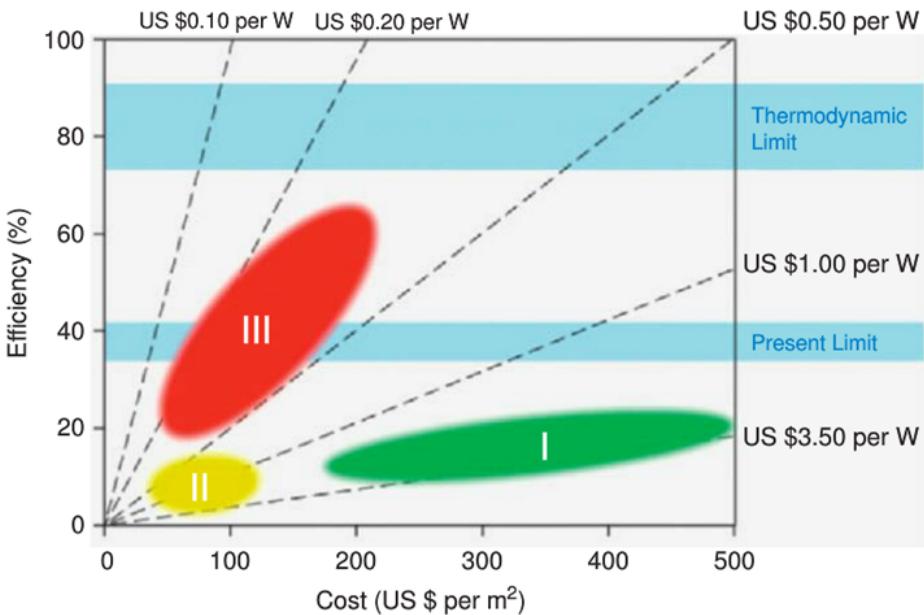


Figure 1.13: Efficiency and cost projections for first-, second- and third-generation photovoltaic technologies, which are comprised of silicon wafer, thin-film and advanced thin-film technology respectively. Figure taken from reference 43.

The ‘holy grail’ of research into new materials for photovoltaic devices would be to find materials that are strong absorbers of sunlight that could also be produced cost-effectively from materials that are abundant enough for large-scale fabrication of the devices. Then it could be possible for solar energy generation to be economically viable on a large enough scale to replace fossil fuels to meet global energy needs. Such a drive has resulted in the development of what are considered three generations of solar energy technology. These are shown in figure 1.13, where highly efficient crystalline silicon devices with high associated manufacturing costs are considered the first generation of solar cell technology. Thin-film solar cell devices are typi-

cially referred to as second-generation technology. These devices make use of materials that are much more optically thick than silicon (i.e. stronger absorbers of sunlight with higher optical absorption coefficients), which require less material to absorb the same amount of sunlight. Figure 1.14 shows a comparison between the thickness of the absorber layer in some commercial second-generation PV devices to that of first-generation silicon wafers. The consequence of the reduction in the thickness of the absorber layer is that it is then less important for the material to be of as high-quality as in crystalline silicon devices, which enables the use of low-cost and low-energy fabrication methods [51]. In the case of thin-film CuInSe<sub>2</sub> devices, it has even been found that the ‘lower quality’ poly-crystalline material has a higher performance than its single crystal counterpart [109, 105]. Theoretical studies of the electronic properties of the grain boundaries in CuInSe<sub>2</sub> have provided an explanation for this unusual observation based on beneficial band offsets at the grain boundaries [99, 100]. This effect is a special case for this particular material, but it embodies the general ideology of thin-film technology well - namely to produce materials able to convert sunlight into electricity as efficiently as possible with the simplest synthesis techniques possible. However typically the efficiencies of second-generation solar cells are less than that of the best performing first-generation devices. Examples of commercial thin-film technologies include CIGS ( $\text{Cu}(\text{In},\text{Ga})(\text{S},\text{Se})_2$ ) and CdTe and figure 1.7 shows that the best performing Si devices have higher efficiencies, which are also much closer to their theoretical limit, than these second-generation, thin-film technologies. Third-generation PV technology aims to make use of the low cost fabrication techniques of the second-generation devices but use multiple energy threshold devices to overcome the Shockley-Quieser limit for a single band gap solar cell, such as in tandem solar cells where semiconductor p-n junctions of increasing band gap are placed on top of each other in order to capture more of the solar spectrum. Typically the more complicated device architecture of third-generation devices result in higher fabrication costs. Research efforts are therefore largely focused on reducing the fabrication cost of multi-junction devices [142].

Current mainstream solar cell technologies, such as first-generation Si wafers and second-generation thin-film CdTe and CIGS solar cells, would not be able to provide solar electricity at

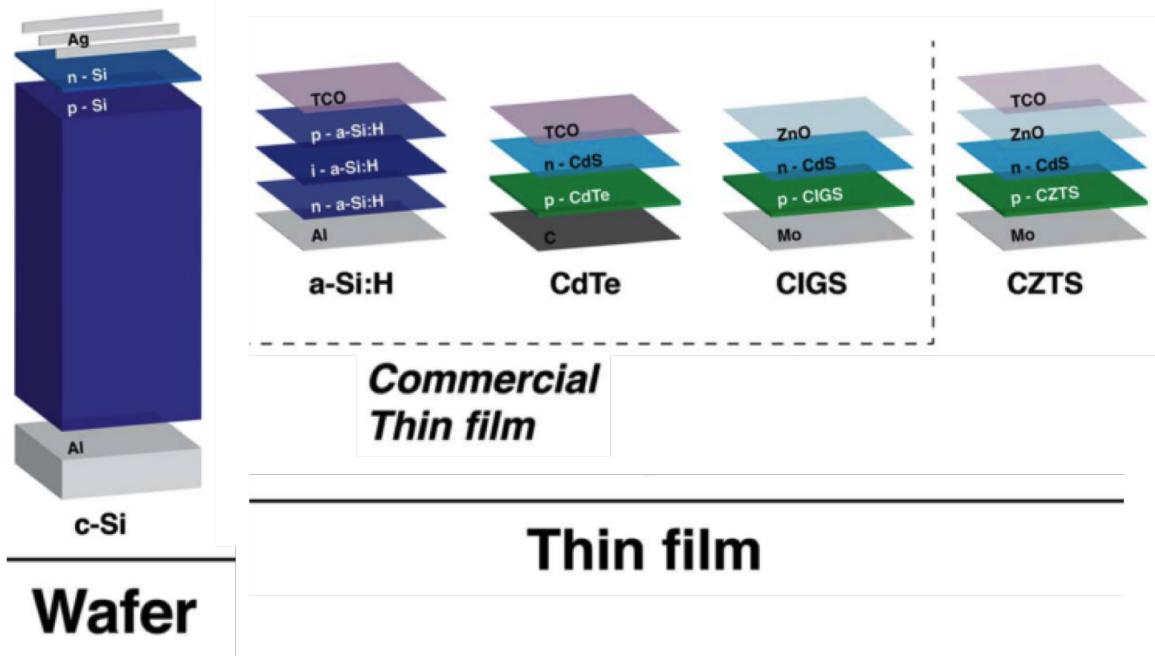


Figure 1.14: Typical structures of a commercial wafer-based PV device (first left) and commercial thin-film photovoltaic devices, as well as a CZTS thin-film device (right). The absorber layers are labelled in white and thickness is shown to scale. Figure adapted from reference 62.

the terawatt scale due to the scarcity of Te and In and the relatively long energy payback time for crystalline Si due to the cost and energy intensive fabrication of Si wafers [143]. Models have even quantified such statements with a predicted In-constrained growth potential of power generation from CIGS PV technology of 20 GW per year in 2020 due to competing applications of In, such as in liquid crystal displays [40]. In order to significantly increase the contribution of solar power to global power consumption, it is therefore necessary to develop more economically viable earth-abundant materials for sustainable PV electricity generation. Furthermore, there must be considerable technological breakthroughs that would enable low-cost manufacturing of highly efficient devices with enough of a cost benefit to outweigh the initial cost outlay in optimizing the manufacturing process of the whole device as has been done for silicon over the past 60 years. For this purpose, there is a drive for solar absorber materials with more optimal properties, such as a direct and sunlight matched band gap (as in thin-film technologies such as CdTe and CIGS), but also for materials that are composed of only earth-abundant components.

## 1.2 The Role of Computational Modelling in Material Design

The discovery of new functional materials by experimental methods is largely hindered by high costs and time-consuming synthesis procedures [29]. However, with the rapid increase in computational processing power and the availability of large-scale supercomputers, we are entering a very exciting era in computational materials design. There are two main contributions that computational simulations could make towards the technological breakthroughs needed for the development of photovoltaic devices for economically-viable, large-scale solar energy generation. Firstly by predicting properties and screening for certain desirable properties for a solar absorber material, such as an optimal band gap and high carrier mobility, materials simulations are able to aid in the discovery of new materials for use in photovoltaic devices. Secondly, material simulations are able to provide valuable insight to improve understanding of known photovoltaic materials to enable the synthesis of better performing devices. So far in this study we have aimed to make both of these contributions to the field. Firstly, we perform simulations to understand the performance bottlenecks in the candidate earth-abundant, non-toxic solar absorber material Cu<sub>2</sub>ZnSnS<sub>4</sub>(CZTS) and we also study the optical properties of three candidate photovoltaic materials which have so far received little attention as solar materials but could provide another possible route for high-performance photovoltaic devices for cost-effective solar energy generation.

## 1.3 Overview of this Study

### 1.3.1 Promising Candidate Solar Absorber Materials

Refer to: CH 5 (other PV materials) + pg 187 (future of PV) [45]

As already discussed, to make solar energy generation on a large scale economically viable, it

must be possible to make devices with an LCOE that is comparable to fossil-fuel resources. Furthermore, the materials that make up the devices must also be sufficiently abundant such that there would be enough to make a substantial number of devices in the first place. For this reason there is a drive for photovoltaic materials that could be made using the low-cost methods associated with second-generation technology, but containing only earth-abundant components. Gauging the abundance of a given material is not as trivial a process as looking at crustal abundance as supply, demand, geographical distribution and extraction must all be considered. However, knowledge of solar cell technologies made from various different materials opens up the possibility of utilizing multiple different materials to collectively contribute to the global solar power capacity to enable larger-scale power generation from this renewable, low-carbon resource. Additionally by studying various different materials, the scientific community could eventually discover a select few that have the best properties to enable low-cost synthesis of highly efficient devices to eventually significantly reduce the LCOE of solar power.

Currently,  $\text{Cu}_2\text{ZnSnS}_4$  (CZTS) is one of the most studied candidate earth-abundant thin-film solar cell materials [143]. The potential of CZTS for photovoltaic applications was realised in 1988 by Ito and Nakazawa [60]. The band gap of the material has been predicted [151] and measured [114] to be 1.5 eV, which corresponds to a theoretical conversion efficiency limit of 28% as predicted by Shockley-Quieesser [117]. However, the current record device efficiency is 8.8% [125] and it is believed that this figure must be increased to at least 15% for the devices to be commercially viable [121]. PV devices composed of a CZTS absorber layer are hampered by low open circuit voltage ( $V_{OC}$ ) [121], which is believed to be due to the formation of secondary phases [10] and defects [23] in CZTS, although the exact origin of the low  $V_{OC}$  remains unknown. The first component of this study is therefore an attempt to determine possible origins of this deficit in CZTS.

A number of interesting PV phenomena have been observed in ferroelectric (FE) materials such as the bulk photovoltaic effect (BPE) and the anomalous photovoltaic effect (APE) [20]. Ferroelectric materials usually have a high dielectric constant (which was mentioned in section

1.1.3 as an important parameter for a photovoltaic material) and they possess a spontaneous electric polarization that can be switched between two or more states using an electric field [76]. The BPE was first recorded in 1956 in BaTiO<sub>3</sub> [27], where photovoltages were measured in un-doped single crystals [20]. The BPE effect is distinctly different from the typical PV effect in semiconductor p-n junctions as it is the polarization electric field that is the driving force for the photocurrent in FE-PV devices [148]. The APE was first observed in PbS films in 1946 [123] and has since been reported in polycrystalline CdTe, ZnTe, InP [63, 47, 133], where photovoltages output along the polarization direction can be significantly larger than the band gap of the material [148], which is usually the limit for a semiconductor PV material [20]. The Shockley-Queisser limit, which prevents any single p-n junction solar cell from converting more than 33.7% of the incident light into electricity, has not been predicted to apply for these photovoltaic phenomena. An upper limit for the theoretical power conversion efficiency (PCE) from this photovoltaic mechanism seems to still be an open question [95], although an ultimate maximum efficiency of any single-band gap absorber of 44% has been set by thermodynamic considerations [117].

The identification and understanding of such phenomena may open up the possibility of more efficient PV devices constructed from a number of different photoferroelectric materials. However, most of the commonly used ferroelectric materials such as LiNbO<sub>3</sub> and BaTiO<sub>3</sub> have band gaps larger than 3 eV and can therefore only absorb sunlight in the UV range to convert into electricity, which accounts for only around 3.5% of the solar spectrum [148], which is illustrated in figure 1.6. The optimal range for the band gap in order to absorb the majority of the solar spectrum under typical radiation conditions is between 1.06 eV and 1.50 eV [59]. Research efforts have also gone into adjusting the optical absorption of ferroelectric materials without influencing the ferroelectric properties of the material through chemical doping or alloying [148]. In Bi<sub>4</sub>Ti<sub>3</sub>O<sub>12</sub> (BiT) the optical band gap has been tuned in such a way, resulting in a decrease from 3.6 eV to 2.7 eV [26], although this is still considerably larger than the optimal range for a PV absorber material.

This then leads on to the second component of this study, which is an investigation of the optoelectronic properties of new candidate solar absorber materials that may also exhibit ferroelectricity, but have band gaps within the optimal range for the absorption of sunlight. In theory, these materials enable the possibility of exploiting novel photovoltaic phenomena such as the anomalous and bulk photovoltaic effects to overcome the Shockley-Quiescer efficiency limit without the need for such complicated device architectures as in third-generation tandem solar cells. Although the difference between the Shockley-Quiescer limit and the ultimate thermodynamic limit of a solar material is not enormous, it is also possible that ferroelectric materials have properties that enable more efficient devices to be made more easily, such as good screening of the effect of defects due to a high dielectric constant or enhanced electron-hole separation from ferroelectric domains resulting in reduced recombination and a higher performance solar cell with ‘low quality’ defective and nanostructured materials. Such technologies could provide one possible route for the technological breakthrough that could enable economically-viable, large-scale solar energy generation.

### 1.3.2 Investigating Possible Performance Bottlenecks of $\text{Cu}_2\text{ZnSnS}_4$ Devices

\*\* Check against Laurie’s April highlights (top two bullet points on disorder) + Susan Siebentritt’s: Why are kesterite solar cells not 20 percentage efficient?

The ground state crystal structure of CZTS ( $\text{Cu}_2\text{ZnSnS}_4$ ) is kesterite (space group  $I\bar{4}$ ). The conventional unit cell of CZTS is shown in figure 1.15, where each S is surrounded by two Cu, one Zn, and one Sn to satisfy local charge neutrality and the valence-octet rule. Kesterites meet two necessary conditions for highly efficient solar cells, which are a band gap that is both direct and relatively well-matched to the solar spectrum [59]. Over the last decade the power conversion efficiency of PV devices based on kesterite,  $\text{Cu}_2\text{ZnSn}(\text{S}_x\text{Se}_{1-x})_4$  (CZTSSe), compounds has improved greatly from around 5% in 2004 to 12.6% in 2013 [2]. However, this is still far from the record efficiencies of  $\text{Cu}(\text{In}_{1-y}\text{Ga}_y)\text{Se}_2$  (CIGSe) devices of >20%, where the materials have very

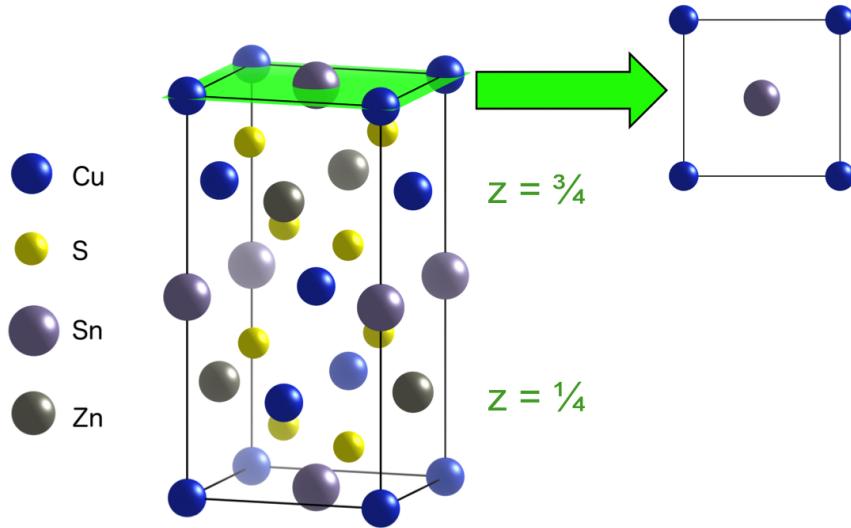


Figure 1.15: The conventional unit cell of CZTS (Cu<sub>2</sub>ZnSnS<sub>4</sub>) with the ground-state kesterite crystal structure (space group  $I\bar{4}$ ). The structure consists of alternating layers of Cu-Sn and Cu-Zn where Cu-Zn layers are at  $z=\frac{1}{4}$  and  $z=\frac{3}{4}$ .

similar band gaps to those of CZTSSe [18] and so should have the same theoretical efficiency limit as predicted by Shockley and Queisser [117]. Furthermore, the rate of improvement seems to have slowed considerably recently with the last improvement in efficiency being reported in 2014 and with only a 0.1% improvement [66]. A large number of possible explanations have been proposed to explain the current difference in efficiency between CZTSSe and CIGSe devices, many of these are illustrated in figure 1.16. The majority of studies converge towards the low open circuit voltage ( $V_{OC}$ ) relative to the band gap, i.e. the  $V_{OC}$  deficit, being the main limiting factor on device performance. As can be seen from the position of CZTSSe devices on the plot in figure 1.17, the open circuit voltages measured for these devices are considerably less than that of a CIGS device, which has a similar value for the band gap of the material.

As figure 1.16 shows, there are many different possible causes of the  $V_{OC}$  deficit in kesterite solar cells. Developing fabrication techniques to reduce the deficit is therefore an even greater challenge when the exact cause is not yet known. This is an area in which computational materials simulations should be able to provide valuable insight to help pinpoint the specific sources of the  $V_{OC}$  deficit in kesterite solar cells. The true power of simulation is the ability to take a

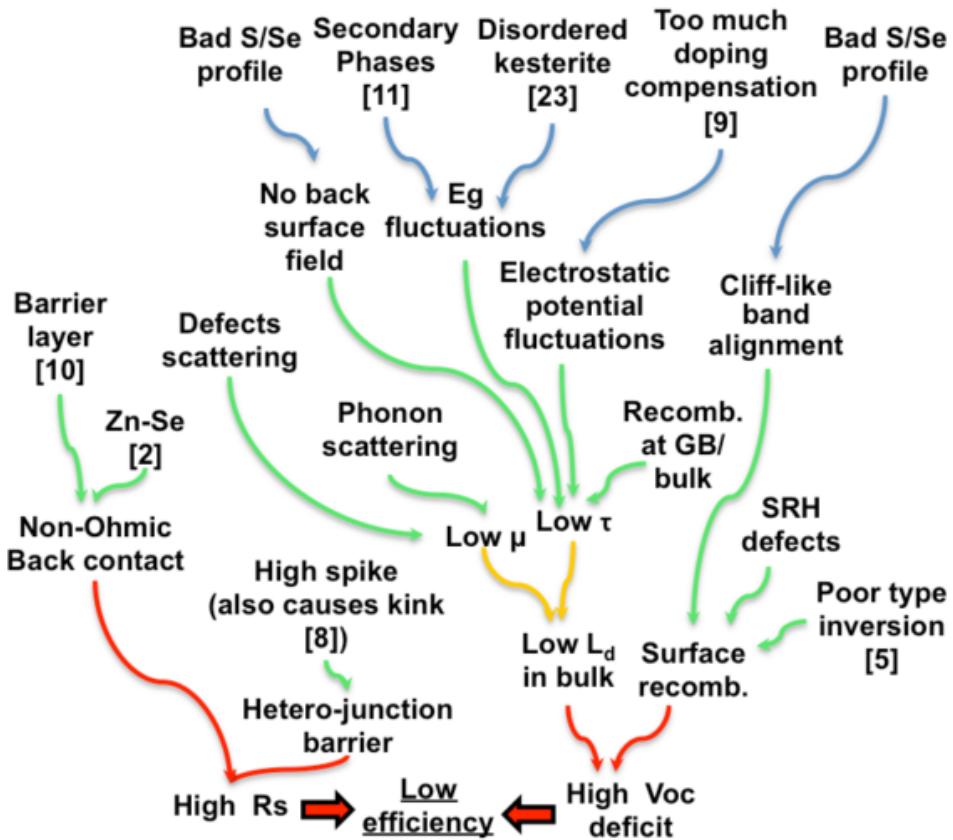


Figure 1.16: Mapping of the numerous possible mechanisms limiting the efficiency in kesterite devices and their possible causes.  $R_s$  is the series resistance between the absorber layer and back contact of the device and  $V_{OC}$  is the open circuit voltage across the absorber layer. Figure taken from 28.

perfect system and introduce various imperfections one at a time and then study the effect that particular imperfection could have on device performance. As opposed to in a real system in which there is a myriad of possible causes for each observation, as illustrated in figure 1.16. In our simulations we will start from the most simple system possible, before making any attempts to build up in complexity. Devices made from a compound of  $\text{Cu}_2\text{ZnSnS}_4$  and  $\text{Cu}_2\text{ZnSnSe}_4$ , i.e.  $\text{Cu}_2\text{ZnSn}(\text{S}_x\text{Se}_{1-x})_4$ , so far have given the highest performance devices, however in this study we are currently focusing on just the pure selenide material, CZTS. In addition to simplifying the system, figure 1.17 also indicates that the  $V_{OC}$  deficit is worse in purely CZTS devices and so potentially studying causes of the problem in this particular system could be more informative. Also although ultimately the aim is to make thin-film devices from CZTS, in which the material is likely to be highly polycrystalline with many grain boundaries, we are currently just focusing on the bulk material. We are doing this for two reasons. Firstly to improve the

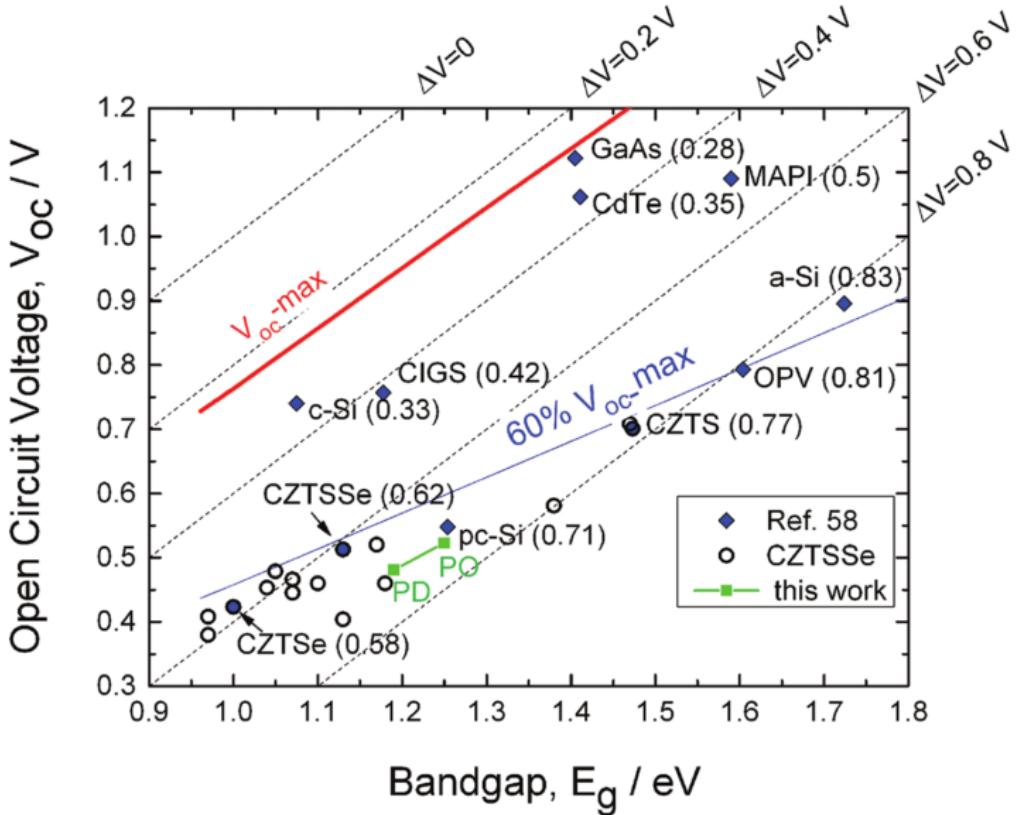


Figure 1.17:  $V_{OC}$  versus band gap of high performance CZTSSe devices ( $>9\%$  efficiency) indicated by circles with best devices based on other photovoltaic materials shown for comparison by diamond symbols: Methyl-ammonium lead iodide (MAPI), amorphous silicon (a-Si), organic photovoltaic films (OPV), crystalline silicon (c-Si) and polycrystalline silicon (pc-Si). The oblique lines give a constant  $V_{OC}$  deficit from 0.8 V to 0 V. The green points correspond to CZTSSe films that are partially ordered (PO) or partially disordered (PD) due to disorder amongst Cu and Zn. Figure take from reference 18.

understanding of the fundamental material properties before attempting to understand a more complex system to ensure we start from a solid foundation. Secondly, it has been proposed that the  $V_{OC}$  deficit in CZTSSe devices could actually be largely due to the natural bulk properties of the crystal [102]. For the purposes of our study therefore measurements performed on single crystals will be the most directly relatable to our findings, wherever the data is available.

In general, the main cause of  $V_{OC}$  deficit in a PV device is the recombination of photogenerated charge carriers in the bulk material or at surfaces [18]. Figure 1.18 shows photoluminescence (PL) spectroscopy measurements performed on CZTSSe thin films by Gokmen et al [46]. The emission spectra of semiconductors is discussed much more thoroughly in section 2.4.1 and a

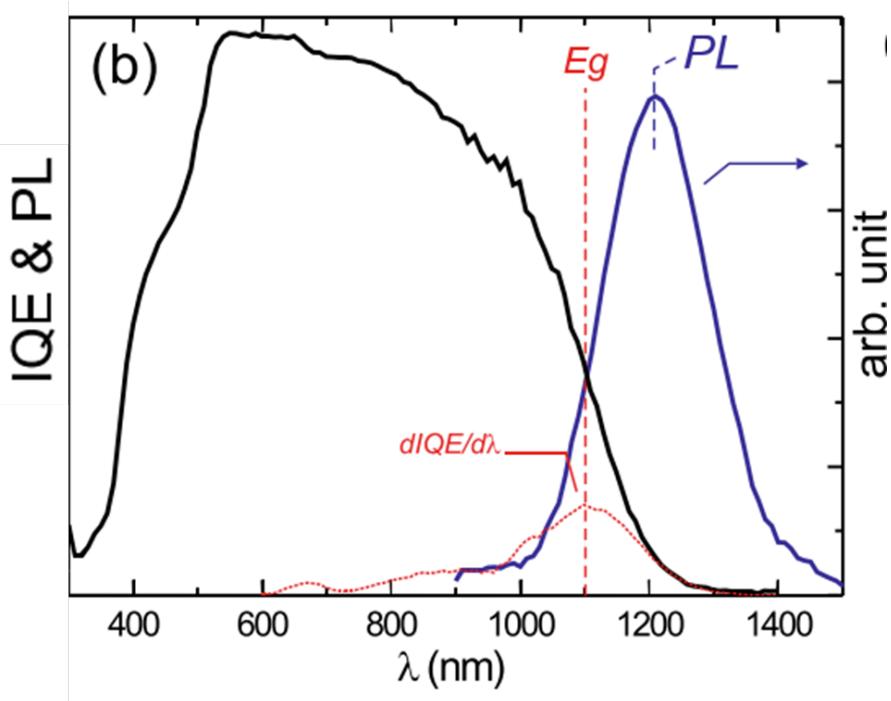


Figure 1.18: Internal quantum efficiency (IQE) and photoluminescence (PL) spectra of CZTSSe thin-films showing the shift of the PL peak to energies below the band gap of the material. Figure take from reference 46.

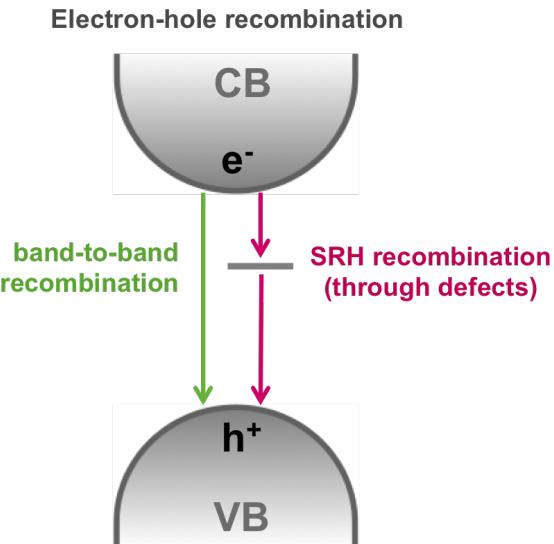


Figure 1.19: Illustration of Shockley-Read-Hall (SRH) electron-hole recombination due to energy states introduced into the band gap by defects.

review of various PL studies performed on kesterite thin films and crystals is given in section 2.4.3, but for current purposes the key observation to be made from figure 1.18 is that there is a shift in the PL peak to lower energies (red-shifting), below the value of the band gap obtained from internal quantum efficiency (IQE) measurements performed on the same thin films. It is

also noted in this study when comparing the PL spectra of CZTSSe films to that of CIGSSe films that the PL peak for CZTSSe thin films is broader and that the red-shifting was roughly twice as severe. This effect is referred to as ‘band-edge tailing’, where photons of energies less than the band gap of the material are emitted following photoexcitation and subsequent relaxation back to the ground state. This effect is known to be detrimental for device performance as emitted photons may then not have sufficient energy for subsequent photoexcitations in the absorber layer, the energy of the original photon may then not be converted into electricity if the photoexcited electron-hole pair recombine before the charge is collected [85]. Band tailing and the possible causes of this detrimental effect are discussed further in section 2.4.2, but for now it is worth briefly noting that possible causes are: Shockley-Read-Hall recombination due to defect-induced mid-gap states [118], as illustrated in figure 1.19, as well as fluctuations in electrostatic potential due to the presence of charged defects and fluctuations in the band gap of the material due to an inhomogeneous composition [46], which are both shown in figure 1.20.

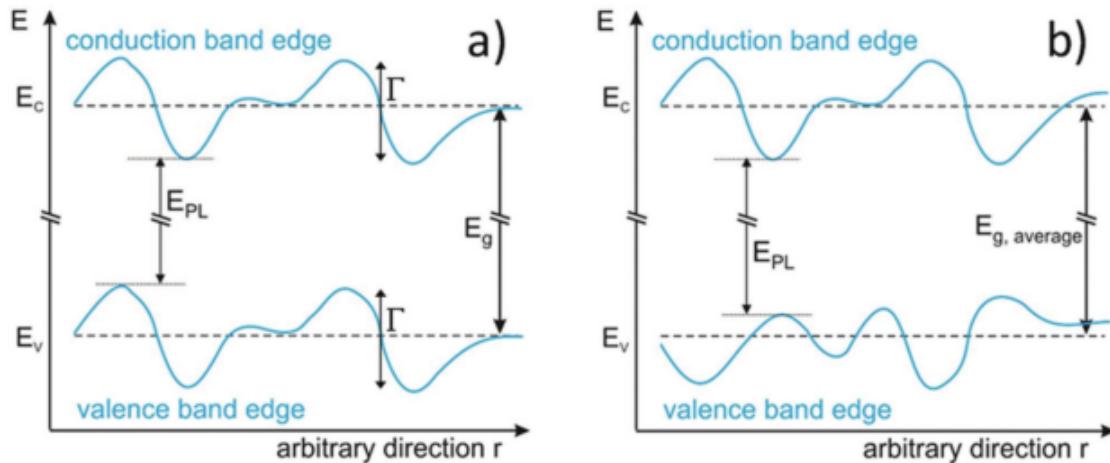


Figure 1.20: The effect of electrostatic potential fluctuations (a) and band gap fluctuations (b) on the electronic bands of a semiconductor. In both cases radiative transitions at energies below the (average) band gap are possible. The band gap in a is constant and not affected by local charged defects, while band edges in b can differ depending on e.g., long range composition variations. Figure taken from reference 18.

The extent of band tailing due to the additional energy levels introduced into the band gap of a material by particular intrinsic defects is dependent upon the concentration of those particular defects. The equilibrium defect concentration can be obtained directly from the defect forma-

tion energy [88], which is discussed further in section ???. For materials such as CZTSSe that are still at a fairly early stage of development, theoretical predictions of defect formation energies may be the only values available to help identify specific defects and their properties in real systems [68]. Theoretical predictions for the formation energies and depth of defect-induced energy levels for various intrinsic point defects and defect clusters in CZTS made by Chen et al [24] are shown in figures 1.21, 1.22, 1.23 and 1.24. Based on the predictions made by Chen et al, figure 1.22 shows that many of the intrinsic defects involving Sn would induce a mid-gap state, however figure 1.21 shows that the formation energy of those particular defects would all be expected to be high. It therefore would be expected that these defects are less likely to form and should be present in lower concentrations than other defects. Although other works have suggested that the formation of this defect could be more likely if it is forms part of a particular defect cluster [138, 18]. From the work by Chen on defect clusters, it is also expected that certain charge compensated defect clusters would have very low formation energies, in particular the  $[Cu_{Zn}^- + Zn_{Cu}^+]$  antisite defect pair, as shown in figure 1.23.

Disorder amongst Cu and Zn ions (or equivalently the formation of the  $[Cu_{Zn}^- + Zn_{Cu}^+]$  antisite defect pair) in CZTS has been proposed as one possible origin of the  $V_{OC}$  deficit in CZTS and consequently a number of experimental studies have been conducted to investigate this [113, 111, 36, 110]. Additionally it is worth noting that this substitutional disorder does not exist in the crystal structure of CIGSe due to the considerably larger chemical mismatch between Cu with In or Ga [18], whereas Cu and Zn are so similar that disorder between the two species can be difficult to detect experimentally. As Cu and Zn are neighbouring elements in the periodic table, the changes in the bonding between the two are subtle [82]. This results in a theoretical energy difference between the two structures of just 3 meV per atom [22] allowing for intermixing of the Cu and Zn cations in CZTS, which has been confirmed by neutron diffraction [111, 36] and also measured using near resonant raman scattering [113]. However, a recent work prepared samples with varying degrees of Cu-Zn disorder (by varying the cooling rate during synthesis, which had been shown in a previous study to have a considerable effect on Cu-Zn ordering in CZTS [113]) and in this work they showed that a reduction in Cu-Zn order resulted

in a reduction in both the band gap and  $V_{OC}$ , thereby not influencing the  $V_{OC}$  deficit relative to the band gap of the material [18].

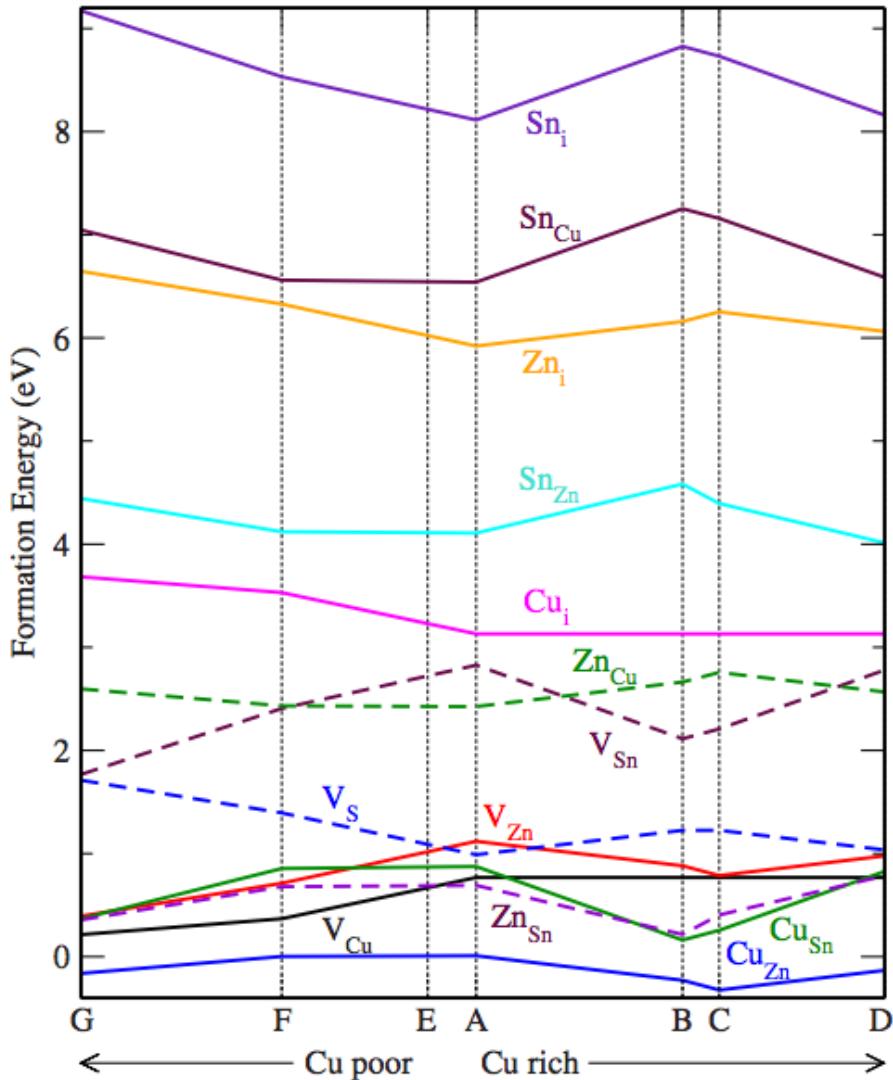


Figure 1.21: The formation energy of neutral intrinsic defects in  $\text{Cu}_2\text{ZnSnS}_4$  as a function of the chemical potential. Figure taken from reference 24.

In this work we begin three investigations to explore some of the possible explanations for the  $V_{OC}$  deficit in CZTS solar cells and to attempt to explain the PL spectra of CZTS shown in figure 1.18. As discussed above, intrinsic defects can introduce additional energy levels into the band gap of the material and energy states within the band gap are Shockley-Read-Hall recombination sites [118]. We re-investigate the formation energy of sulfur vacancies ( $V_S$ ) in CZTS. This is another possible deep donor defect in CZTS and it was proposed in a recent study using admittance spectroscopy measurements performed on CZTSSe, combined with electrical

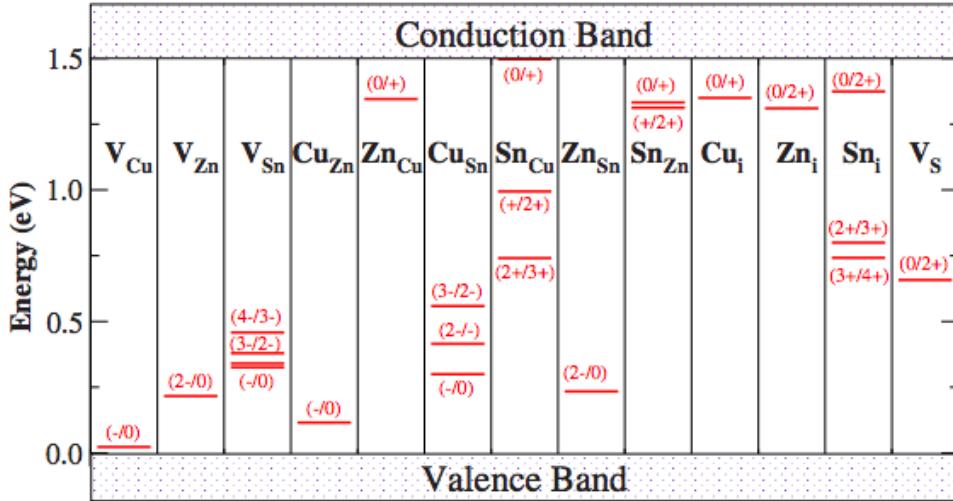


Figure 1.22: The transition-energy levels of intrinsic defects in the band gap of Cu<sub>2</sub>ZnSnS<sub>4</sub> where the GGA band gap has been corrected to the experimental value 1.5 eV, and the donor levels are shifted together with the conduction band minimum (CBM) level. Figure taken from reference 24.

modelling, that in addition to majority p-type defects in CZTSSe (giving the material its p-type conductivity), there may also been deep n-types defects [138]. V<sub>S</sub> in CZTS has been predicted to produce a mid-gap state in the band gap of the material [24], which could provide one explanation for the poor device performance. However in the same work this particular point defect was also predicted to have a high formation energy relative to other possible intrinsic defects, making it less likely to form. However, it is possible that the formation energy of this defect is reduced when considering the typical annealing conditions of CZTS in which S is in the gaseous phase. We therefore calculate the formation energy of a V<sub>S</sub> in CZTS as a function of the sulfur chemical potential, which has been calculated as a function of temperature and pressure in a previous study [61], making it possible for us to compare directly to experimental synthesis conditions.

Secondly, we examine possible causes of band gap broadening, which has been observed in electromodulation (?) measurements performed on CZTS crystals [? ]. We use materials modelling to determine the intrinsic band gap broadening to be expected even in perfect, bulk CZTS due to thermal lattice expansions. This contribution can then be subtracted from band

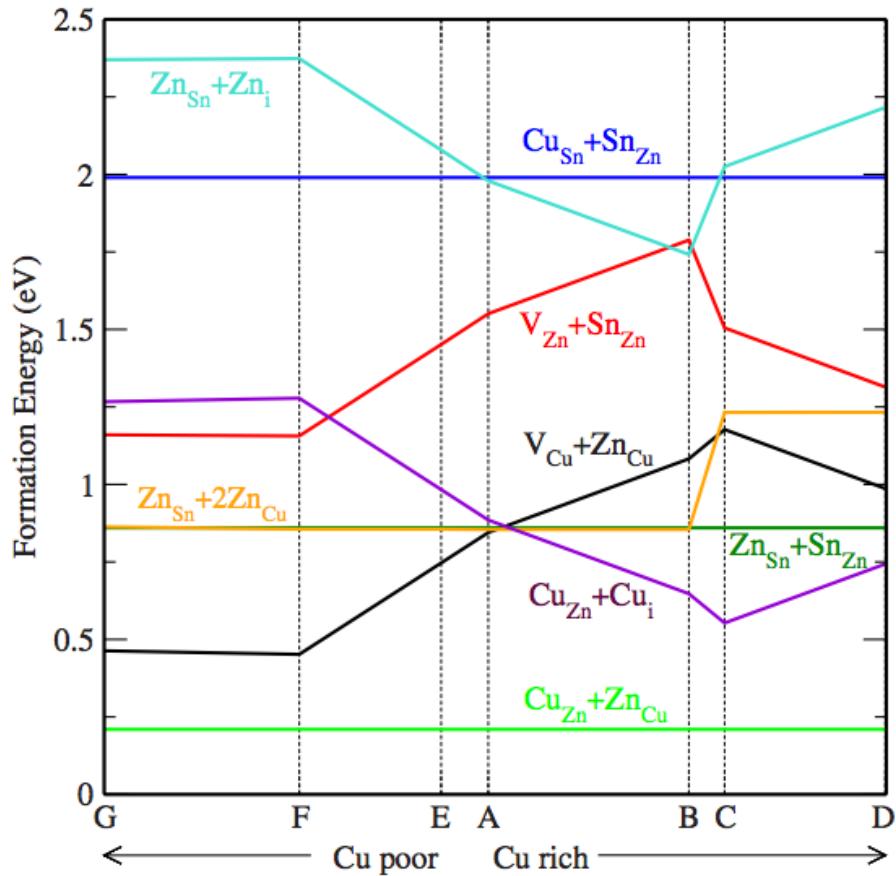


Figure 1.23: The formation energy of charge compensated defect complexes in  $\text{Cu}_2\text{ZnSnS}_4$  as a function of the chemical potential. Figure taken from reference 24.

gap broadening measured experimentally to determine how much of this effect is due to disorder and other factors. Lastly, we simulate thermodynamic substitution amongst Cu and Zn ions in CZTS and study the resulting changes in the distribution of electrostatic potential in the system in an attempt to extract the contribution of this particular type of disorder to the strong band tailing that has been observed in kesterite devices, which has been suggested to be due to fluctuations in electrostatic potential [46]. As discussed above, disorder amongst Cu and Zn ions has not only be predicted to be very likely based on energetics but has also been observed experimentally, it would therefore be important to know if this particular type of disorder is having a detrimental effect on device performance or to at least eliminate it from the list of many possible causes of the  $V_{OC}$  deficit.

\*\*Edit last paragraph once PVTEAM paper published so have more info + put eris study first to match order of results?\*\*

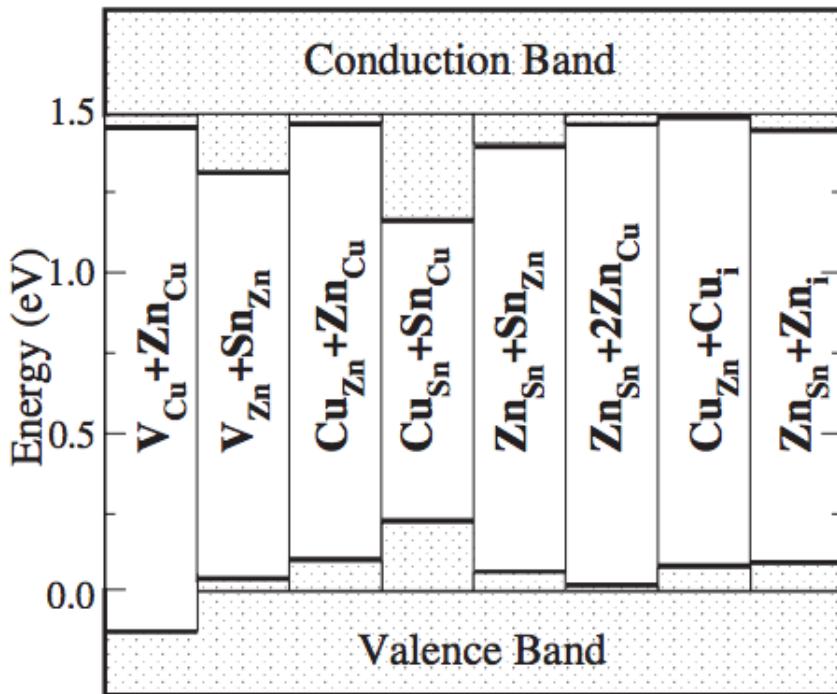


Figure 1.24: The conduction band minimum (CBM) and valence band maximum (VBM) levels in eV of  $Cu_2ZnSnS_4$  with different charge-compensated defect complexes relative to the host material at 0 eV and 1.5 eV respectively. Figure taken from reference 24.

Introduce PVTEAM collaboration here?

### 1.3.3 Predicting the Properties of New Candidate Solar Absorber Materials

The second part of this study involves using materials modelling to predict the optoelectronic properties of materials that could have the potential to be used to produce high performance PV devices, but until now have received little research interest for applications in PV. The central idea in selecting these candidate materials was to identify any that may be ferroelectric and so could exhibit some of the novel FE-PV phenomena discussed earlier but may also have a band gap within the optimal range for solar absorption. Photoferroelectric, or photoferroic, is the name given to materials that exhibit such properties. Using very simple screening criteria, we identified three candidate photoferroelectric solar absorber materials from a data set of over

200 naturally occurring minerals. A dark-coloured material suggests (but does not guarantee) that it absorbs light in the visible range. Ferroelectric materials are a subset of materials with polar crystal structures, therefore not all polar materials exhibit ferroelectricity. It is only polar materials that also possess a spontaneous electric dipole moment within the unit cell which can be inverted by the application of an external electric field that exhibit ferroelectricity [30]. Therefore, the conditions used to screen for candidate photoferroelectric materials shown in the Venn diagram in figure 1.25 are necessary conditions for photoferroelectricity, but cannot guarantee this property as a polar space group is a necessary but not sufficient condition for ferroelectricity. The three candidate photoferroelectric materials identified by our screening process were: enargite ( $\text{Cu}_3\text{AsS}_4$ ), stephanite ( $\text{Ag}_5\text{SbS}_4$ ) and bournonite ( $\text{PbCuSbS}_3$ ). All three minerals are sulfosalts, which are materials that contain two or more metals, semi-metals such as antimony and arsenic, and sulfur [17].

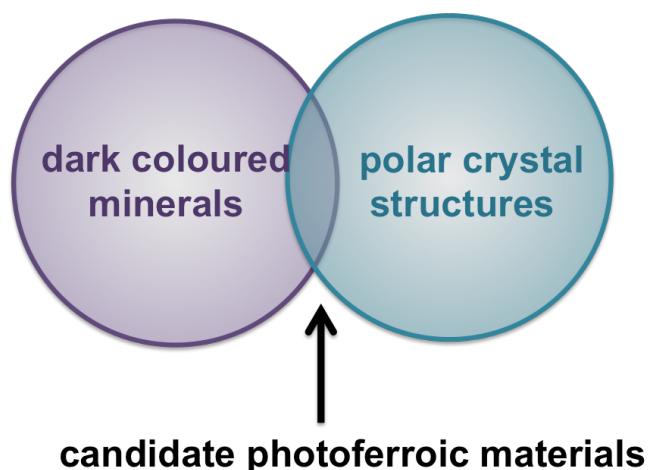


Figure 1.25: Venn diagram showing the necessary (but not sufficient) conditions for a material to exhibit photoferroelectricity, where the dark colour suggests absorption of light in the visible range and a polar crystal structure is a requirement (but does not serve as a guarantee) for a material to exhibit ferroelectricity.

Scientific research on sulfosalts has largely focussed on the thermodynamic properties and crystal structure of the materials, leaving knowledge of the optoelectronic properties of sulfosalts relevant for PV applications extremely scarce. The potential of sulfosalt minerals for PV applications however was highlighted by Dittrich et al in 2007 [31]. This work also provides an overview of thin film deposition methods that have been developed for sulfosalt layers and dis-

cusses a 1% efficient Sn-Sb-S sulfosalt thin film solar cell constructed by the authors. The thin film deposition methods discussed for other sulfosalt materials would also be particularly important for the eventual aim of constructing PV devices from these materials. The potential of the sulfosalt mineral enargite for PV applications has been suggested even earlier by Pauperté and Lincot in 1995 [97]. In addition to synthesis methods, another important consideration for the large-scale deployment of solar devices composed of the candidate materials is the price and abundance of the elemental components. Figure 1.26 shows a comparison of the price and abundance of some of the elemental components of the three candidate materials: Cu, Sb and S, to that of elements used in some current commercial thin film solar cell absorber materials such as CuIn(Ga)Se<sub>2</sub> (CIGS) and CdTe. The components of the candidate materials not included in the figure are As, Pb and Ag. Lead can be considered as the most abundant and universally diffused metal after iron. Although it is never found in the native state, its ores are very numerous [127]. 5,200,000 tonnes of lead was produced in 2012 [132], although its crustal abundance is considerably smaller than that of iron being around 10-14 ppm compared to approximately 60,000 ppm for iron [112]. Silver and arsenic are both fairly abundant metals. Silver often occurs in combination with lead, copper, iron, antimony and tellurium. Arsenic is also present in most ores of silver [127]. The crustal abundance of arsenic is approximately 1.5 ppm and that of silver is relatively low at approximately 0.070 ppm [112]. These values are however still larger than that of indium (0.049 ppm [112]), which is also in demand for the display industry [121].

The first candidate photoferroelectric material, enargite ( $\text{Cu}_3\text{AsS}_4$ ), is a mineral that corresponds to a semiconductor of type  $A_3^I B^V C_4^{II}$ , and is frequently found as an impurity in copper ores [134]. Minerals of the composition  $\text{Cu}_3(\text{As}, \text{Sb})\text{S}_4$  are known to occur in two polymorphs: tetragonal with sulfur in cubic close packing or orthorhombic with sulfur in hexagonal close packing. In both cases the coordination is tetrahedral for all atoms [119]. Enargite is the most common member of this group of minerals, its unit cell (as shown in figure 1.27a) has an orthorhombic crystal structure with space group  $Pmn2_1$  and chemical composition  $\text{Cu}_3\text{AsS}_4$  with a small percentage of Sb [79]. The main impurities in natural enargite are Sb and Fe, but

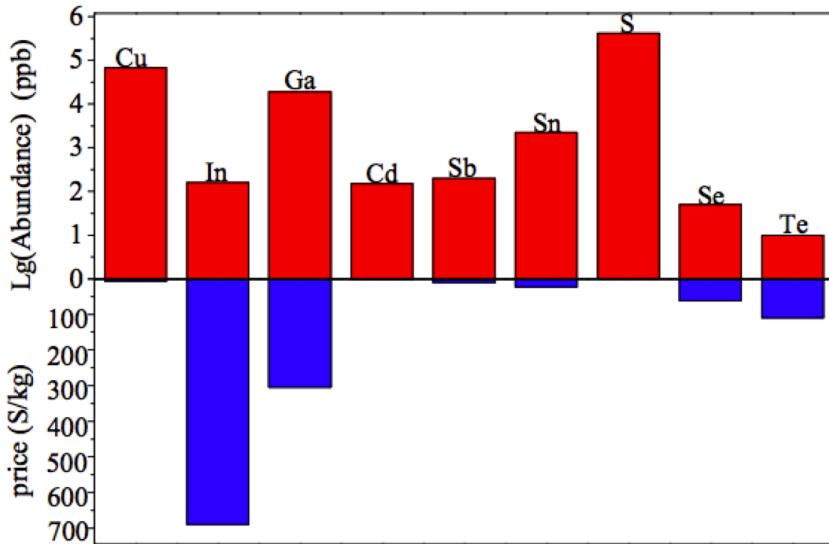


Figure 1.26: Comparison of element abundance and price between Cu, In, Ga, Cd, Sb, Sn, S, Se and Te. Figure taken from the supporting information of reference 144, where data was taken from the London Metal Exchange LME.

Pb and Ag are also known to be present to some extent [134]. Natural samples of enargite have been found to exhibit the electrical properties of a p-type doped semiconductor with a conductivity of 0.0014 S/m (from the stated value of approximately 7  $\Omega$  cm for the resistivity at 295 K) [97]. In the same work, two optical transitions were determined: an indirect one at 1.19 eV and a direct one at 1.44 eV. Although more recent studies have given a value of 1.28 eV for the band gap of enargite from measurements of temperature dependent resistivities, diffuse reflectance spectroscopy and photoacoustic spectroscopy [32]. A theoretical study using the first principles quasi-particle GW method based on wavefunctions generated from the hybrid functional HSE06 [52], has predicted a value of 1.32 eV for the band gap [145]. Although a number of different values have been reported for the band gap of enargite, all values stated fit within the optimal range of 1.06 eV to 1.50 eV [59] for a solar absorber material.

The unit cell of the second candidate photoferroelectric material, stephanite ( $\text{Ag}_5\text{SbS}_4$ ), also has an orthorhombic crystal structure but with space group  $Cmc2_1$ , and is shown in figure 1.27b. The structure is composed of columns of  $\text{SbS}_3$  pyramids extended along the z axis. The columns are located pairwise; in each column, pyramids occupied with antimony atoms

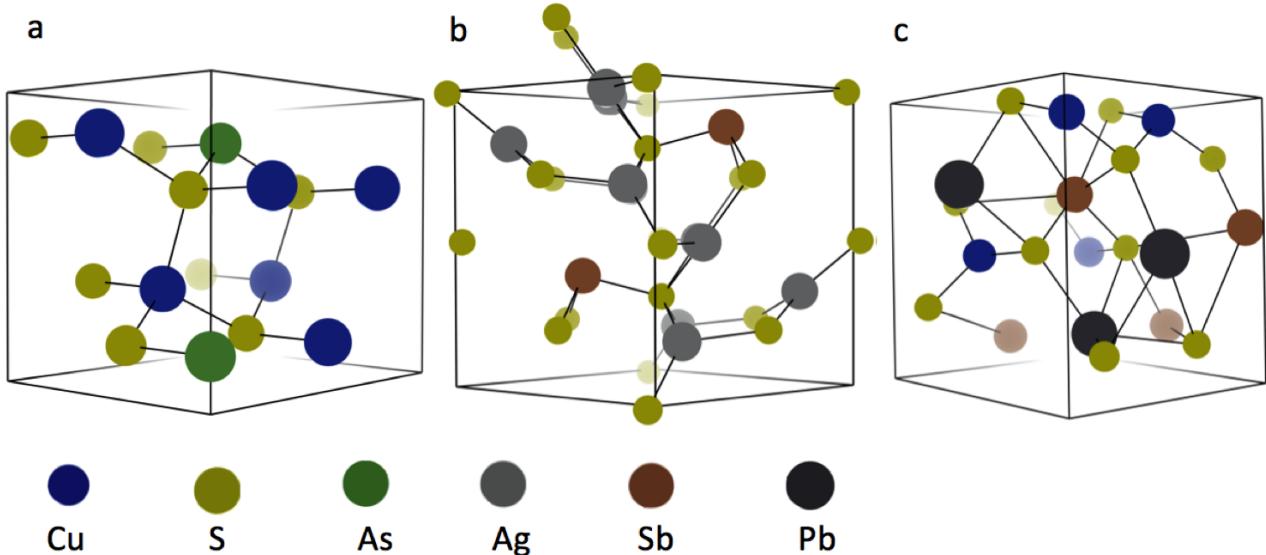


Figure 1.27: The 15 atom primitive unit cell of enargite ( $\text{Cu}_3\text{AsS}_4$ ) (a), 19 atom primitive unit cell of stephanite ( $\text{Ag}_5\text{SbS}_4$ ) (b) and 23 atom primitive unit cell of bournonite ( $\text{PbCuSbS}_3$ ) (c).

alternate with empty pyramids. The Sb-S distances in the pyramids are 2.48, 2.42, and 2.42 Å. Silver atoms are located in the tetrahedral coordination between  $\text{SbS}_3$  groups (at the centers of rhombic channels). Three types of  $\text{AgS}_4$  tetrahedra with different Ag-S distances can be identified. The distinctive feature of the structure is a large number of common edges of Ag tetrahedra [94]. It has been reported that stephanite has a band gap of 1.62 eV [32]. Otherwise, there is seemingly very little information available in the literature on the optical or electrical properties of stephanite apart from a work in 1973, given in reference 21, showing the electrical resistivity of a synthetic sample of stephanite as a function of temperature. The work measures a resistivity of approximately  $9 \Omega \text{ cm}$  for the stephanite sample at  $110^\circ\text{C}$ , which corresponds to a conductivity of 0.0011 S/m. There has also been some speculation in the literature on the possibility of ferroelectric behaviour in stephanite due to the presence of ferroelectric phases at very low temperatures in pyrargyrite ( $\text{Ag}_3\text{SbS}_3$ ), proustite ( $\text{Ag}_3\text{AsS}_3$ ) and stibnite ( $\text{Sb}_2\text{S}_3$ ), which are crystallographically related to stephanite [94]. The same study also notes that similar displacement structural changes occur in stephanite to those in proustite and pyrargyrite that are responsible for the ferroelectric properties of these materials.

Similarly, up until very recently, little information has been available on the optical or elec-

trical properties of the third candidate photoferroelectric material, bournonite ( $\text{PbCuSbS}_3$ ). Bournonite also has an orthorhombic crystal structure and the same space group as enargite,  $Pmn2_1$ , with measured values of 1.23 eV [32] and 1.31 eV [137] reported for the band gap. However, very recently this material has received increasing scientific interest for thermoelectric and rewriteable data storage applications due to a measured low thermal conductivity [33]. Consequently, works on the synthesis of bournonite are beginning to emerge such as that in reference 137. The low thermal conductivity of bournonite has been attributed to the distortive environment of the Pb and Sb atoms from the stereochemically active lone-pair  $s^2$  electrons [33]. In the same study they perform electronic structure calculations to predict the band structure of the material, however in the study they use only the generalized-gradient approximation (GGA) level of accuracy in density functional theory for their calculations, which is known to underestimate the band gap of a semiconducting material. They do however show that the inclusion of spin-orbit coupling (SOC) has a considerable impact on the calculated band gap of the material. In the study they predict a direct band gap of 0.686 eV before including SOC and two optical transitions when they do include SOC: a direct band gap of 0.445 eV and an indirect band gap of 0.385 eV. Different levels of accuracy in DFT electronic structure calculations and the impact of SOC on the optoelectronic properties of a material are discussed further in sections 3.1.1 and ?? respectively. A more recent study has made use of DFT+U methodology to avoid the underestimation of the band gap when calculating the optoelectronic properties of this material, where they predicted a band gap of 1.22 eV [124]. There was however no mention of SOC in the study, which was shown in the older study to influence the band structure of the material considerably, and the limitations of DFT+U methodology are discussed in section 3.1.1.

The key known experimentally derived properties of the three candidate materials that were described above are summarised in table 1.1. In this study we aim to use the highest level of theory possible to calculate as many of the properties relevant for a solar absorber material as possible, which were discussed in section 1.1.3, in order to determine if these materials are likely to perform well in this application. Although these materials were originally selected

Table 1.1: Summary of known key properties of the three candidate photoferroelectric materials from the literature.

Candidate	Empirical Formula	Space Group	Band Gap (eV)	Conductivity (S/m)
Enargite	$\text{Cu}_3\text{AsS}_4$	$Pmn2_1$	1.28 [32]	0.0014 [97] <sup>ii</sup>
Stephanite	$\text{Ag}_5\text{SbS}_4$	$Cmc2_1$	1.62 [32]	0.0011 [21] <sup>ii</sup>
Bournonite	$\text{PbCuSbS}_3$	$Pmn2_1$	1.23 [32], 1.31 [137]	-

<sup>i</sup> From resistivity of a natural sample measured at 295 K

<sup>ii</sup> From resistivity of a synthetic sample measured at 383 K

based on the possibility of exhibiting ferroelectricity, for now the study is just focused on the optoelectronic properties that are directly relevant for predicting the performance of these materials in a photovoltaic device. Firstly we use hybrid-DFT electronic structure calculations to optimize the crystal structure of a bulk system, starting from the highest quality X-Ray diffraction data available for the materials. From this we calculate the band structures of the materials to determine the size of the band gap and whether it is direct or indirect in nature as this would be a good indicator of how strongly the materials will absorb sunlight. We then go on to calculate the dielectric function and optical absorption coefficients of the materials...

# Chapter 2

## Background Theory

### 2.1 Models of Perfect Periodic Crystal Structures

Refer to: pg 28 29 35 [15]

Theoretical models of crystalline solids are based around the existence of translational symmetry in a crystal lattice such that the lattice can be constructed by periodically repeating a unit cell of atoms. The Bravais lattice specifies the periodic array in which the repeated units of the crystal are arranged. A crystal lattice can therefore be described by its underlying Bravais lattice and the arrangement of atoms, ions or molecules within a particular unit cell, i.e. the basis [4]. This principle is used in a number of ways during this study. Firstly, this process is performed on a finite scale to construct a 64 atom supercell of CZTS from the 8 atom primitive unit cell for use in density functional theory (DFT) calculations to predict defect formation energy. This process is discussed further in section 3.1.2. The principle is also used in all DFT calculations of solid state systems through the implementation of periodic boundary conditions to simulate an infinite, bulk system using only a finite unit cell.

Another important concept in the theoretical modelling of periodic structures is reciprocal space

and the reciprocal lattice. Converting to reciprocal space enables the description of periodic features with a longer-range periodicity than the unit cell in real space, such as the motion of electrons in a crystal and phonons. In the same way that any quantity that varies with time can be described as a sum of Fourier components in the frequency domain; the spatial properties of a crystal can be described as a sum of components in Fourier space, otherwise known as reciprocal space or  $k$ -space. The reciprocal lattice of a perfect single crystal is an infinite periodic 3D array of points whose spacings are inversely proportional to the distances between the planes in the lattice in real space. Vectors in real space have dimensions of length, whereas vectors in reciprocal space have dimensions of length $^{-1}$ . This can therefore be compared directly to the wavevector ( $k = \frac{2\pi}{\lambda}$ ) of an excitation such as a phonon or a moving electron and multiplication of each coordinate of the reciprocal lattice by  $\hbar$  converts reciprocal space into momentum space as for a quantised wave  $\mathbf{p} = \hbar\mathbf{k}$  [13].

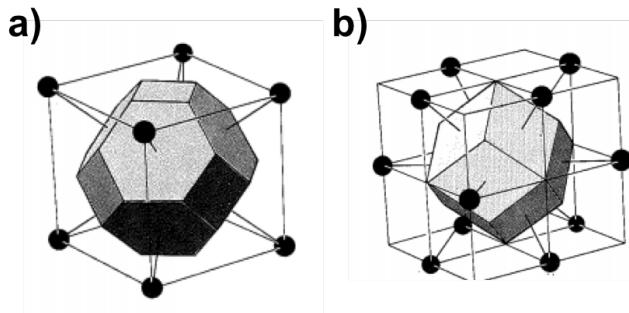


Figure 2.1: The Wigner-Seitz cell for the body-centred cubic Bravais lattice where there is a lattice point at its centre and on each vertex. The hexagonal faces bisect the lines joining the central point to the points on the vertices. The square faces bisect the lines joining the central point to the central points in each of the six neighbouring cubic cells. Figure taken from reference 4.

The Wigner-Seitz primitive cell is the most common choice of primitive cell with the full symmetry of the Bravais lattice. It represents the region of space around a lattice point that is closer to that point than to any other lattice point. For example, figure 2.1a shows the truncated octahedron that is the Wigner-Seitz cell for a body-centred cubic (bcc) lattice [4]. The first Brillouin zone is the Wigner-Seitz primitive cell of the reciprocal lattice. The reciprocal of the bcc lattice is face-centred cubic (fcc), therefore the first Brillouin zone of the bcc lattice is the fcc Wigner-Seitz primitive cell as shown in figure 2.1b [5]. As the full symmetry of the

reciprocal lattice is contained within the first Brillouin zone, it is only necessary to sample  $k$ -points within this single unit cell of the reciprocal lattice when calculating the electronic ground state of a periodic structure.

## 2.2 Band Theory & Band Structure of Semiconductors

Refer to: pg 18 [147], pg 105 112 128 131 137 [15], pg 111 + 119 [49]

\*\* Highlight link to PV and indication of PV performance from band structure + check against Nelson CH3

The band theory of solids provides a means to explain the difference in the electrical conductivity of conductors, semiconductors and insulators. Electrons bound to an atom have a number of possible discrete energy levels. When a large number of atoms are brought together to form a solid, it becomes impossible to assign individual electrons to individual atoms. Instead, the electrons are considered to be shared amongst the atomic nuclei. However, a consequence of this sharing would be a large number of electrons occupying the same energy state, which violates the Pauli Exclusion Principle. The original discrete energy levels therefore are broadened into bands. The new energy levels are so closely spaced that they are considered to be a quasi-continuous band of allowed energies. This is illustrated in figure 2.2. The series of bands of allowed energies in a semiconductor or insulator are separated by bands of forbidden energy, known as the band gap,  $E_g$ , of the material [149]. In the simplest model, the upper energy band (the conduction band) is separated from the lower energy band (the valence band) by a constant band gap, which was discussed in section 1.1.3 for the important role this optical property has in a solar absorber material. This is called the flat band model and is often shown in schematics of p-n junctions for PV devices, such as in figure 1.4. In real structures, the band architecture is more complicated than this simple model, like the band structures shown in figure 1.8 [126].

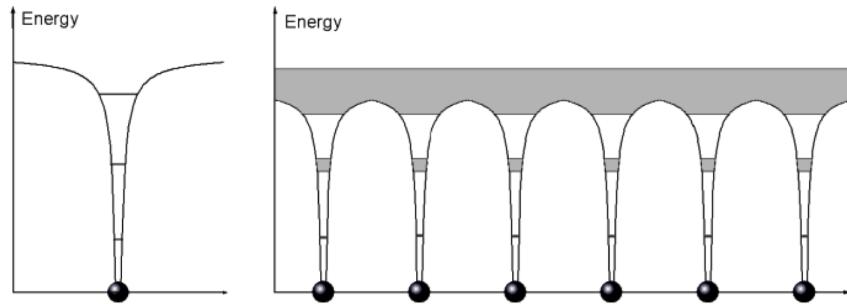


Figure 2.2: Electron energy levels of a single atom (left) and the formation of a quasi-continuous band of allowed energies in a solid crystal when many atoms are brought close together (right). Figure taken from 101.

The concept of the energy band model of a solid emerges from considering the behaviour of electrons in a periodic crystal lattice, but cannot be understood in terms of classical physics alone. Instead, the electron must be considered in terms of wave-mechanical terms as a wave propagating in a periodic structure with diffraction and interference effects [64]. In the band theory of solids, the energy of a single electron in a perfect crystal is described by the one-electron Schrödinger equation, shown in equation 2.1. The first term in equation 2.1 is the kinetic energy of the electron,  $V(\mathbf{r})$  is the effective non-zero periodic potential energy experienced by the electron in the crystal,  $\psi$  is the electron wavefunction and  $\epsilon$  is the eigenenergy of the electron. In band theory, it is assumed that for any electron, everything else in the crystal can be represented by the effective potential energy,  $V(\mathbf{r})$  [14].

$$\left[ \left( -\frac{\hbar^2}{2m} \right) \nabla^2 + V(\mathbf{r}) \right] \psi = \epsilon \psi \quad (2.1)$$

The spatial dependence of the potential experienced by an outer electron in a crystal for multi-electron systems was considered by Felix Bloch. He determined that the total potential is the sum of two parts. Firstly, the electrostatic potential due to the array of atomic cores. For a perfect lattice this should have the translational periodicity of the lattice. Secondly, the potential due to all other electrons. Bloch assumed that the charge density would have the same long-term average value in every unit cell of the crystal and therefore would be periodic. Bloch's theorem states that the wavefunction which satisfies equation 2.1 subject to a periodic

potential should be of the form shown in equation 2.2, where  $U_k(\mathbf{r})$  is some function (depending on the value of the wavevector,  $\mathbf{k}$ ) that also has the complete periodicity of the lattice and  $\mathbf{k}$  is confined to the first Brillouin zone [14].

$$\phi_k(\mathbf{r}) = U_k(\mathbf{r})e^{i\mathbf{k}\cdot\mathbf{r}} \quad (2.2)$$

$$\psi_k(\mathbf{r}) = \sum_k A_k \phi_k(\mathbf{r}) = \sum_k A_k U_k(\mathbf{r}) e^{i\mathbf{k}\cdot\mathbf{r}} \quad (2.3)$$

Due to the translational symmetry of a crystal lattice, an eigenfunction of the one-electron Schrödinger equation can be expressed as a sum of Bloch functions such as that shown in equation 2.2, as shown in equation 2.3. The one-electron wavefunctions therefore can be indexed by constants  $\mathbf{k}$ , which are the wave vectors of the plane waves forming the ‘backbone’ of the Bloch function. A plot of the electron eigenenergies from equation 2.1 versus  $\mathbf{k}$  is known as the electronic band structure of the crystal [147].

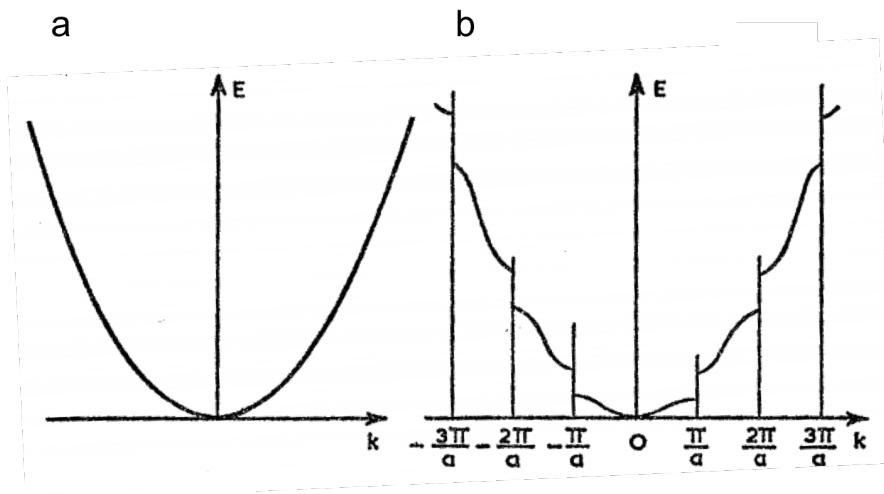


Figure 2.3: Energy-wave vector diagrams: (a) the free electron parabola, (b) modification due to a periodic crystal lattice. Figure taken from reference 64.

The introduction of a medium with a discrete structure, such as a crystal lattice, has a profound effect on the dispersion relation of the waves. The energy dispersion relation of a free electron and that in a periodic crystal lattice is shown in figure 2.3. A periodic medium does not completely suppress the propagation of waves, as would be expected in disordered or amorphous structures, but they do however introduce limiting frequencies and wavelengths for the

propagation, followed by cut-off regions. The lower limit of the wavelength is set by the lattice spacing,  $a$ , giving an upper limit of the wave vector,  $\mathbf{k}$ , of  $\frac{\pi}{a}$ . As figure 2.3 shows, the parabola of the free electron in modified in a periodic crystal by the introduction of discontinuities at values of  $\mathbf{k}$  corresponding to multiples of  $\frac{\pi}{a}$ . The appearance of such energy gaps implies that electrons in a periodic crystal may only have kinetic energies corresponding to certain bands, whilst being free to propagate in the lattice [65].

Each electron occupies a state of definite  $\mathbf{k}$ . Therefore, an infinite number of electrons within the solid would result in an infinite number of  $k$ -points. At each  $k$ -point, only a finite number of the available energy levels will be occupied. Therefore only a finite number of electrons need to be considered but at an infinite number of  $k$ -points. In practise, all of these  $k$ -points are not considered. Electron wavefunctions will be almost identical for values of  $\mathbf{k}$  that are sufficiently close, so the wavefunctions over a region of reciprocal space can be represented by considering the wavefunction at a single  $k$ -point. It is therefore sufficient to consider the electronic states at a finite number of  $k$ -points in order to determine the ground state energy of the solid. This approximation is illustrated in figure 2.4. Using Bloch's Theorem therefore has enabled the ground state energy to be determined by considering only the number of electrons in the unit cell at a finite number of  $k$ -points, which are chosen to sample the Brillouin zone appropriately. The choice here is a balance between more  $k$ -points for a more accurate representation of the Brillouin zone and fewer  $k$ -points to reduce the computational expense of the calculation [128].

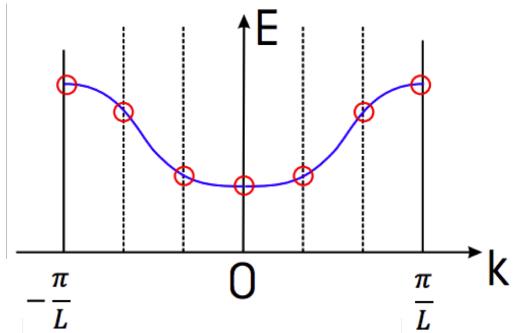


Figure 2.4: The energy dispersion relation for electrons moving in a crystal, illustrating how the function can be approximately represented by a finite number of  $k$ -points, which form an equally-spaced mesh. Figure adapted from reference 35.

A useful concept used to simplify the dynamics of an electron in a crystal lattice in the band theory of solids is that of effective mass, which was first mentioned in section 1.1.3 as a key material property for a solar absorber material. The effective mass is a convenient parameter which accounts for the influence of a periodic lattice on a free carrier, enabling an electron in a periodic crystal to be treated as though it were a free particle but with a different mass in calculations of charge transport. Values of effective mass in semiconductors usually vary between 0.01 and 1 times the mass of a free electron and it is determined by the curvature of the energy graph in  $k$ -vector space [65]. The effective mass is a parameter that can influence the efficiency of a solar cell, in particular, the effective mass of holes in the valence band and electrons in the conduction band (i.e. minority charge carriers) are of interest. The mobility of charge carriers is inversely proportional to the effective mass and the mobility of charge carriers in a PV material is important for efficient charge collection [9].

## 2.3 Vibrational Properties of Semiconductors

\*\* Look into Adam/ Jonathan's work on CZTS modes??

In section 1.1.3, both effective mass and dielectric function were discussed for the insight these properties can provide for the likely PV performance of a material due to the impact these properties can have on the mobility of charge carriers in that material. However these are certainly not the only features of a real material at finite temperatures that need to be considered to understand carrier mobility in a material. Even in a perfect crystal, atoms are involved in some sort of thermal motion about their idealized equilibrium positions. The simplest model to describe this motion is the Einstein model where each atom vibrates independently and as a simple harmonic oscillator in the potential well created by the force fields of its neighbouring atoms. The field can never be precisely a quadratic well with spherical symmetry, but on average the approximation is reasonable, especially when only a very crude picture of thermal vibrations is sufficient or at fairly high temperatures, when the assumption that atoms vibrate

independently of each other is more justified [? ]. In this model, the oscillations of the atoms can be expressed in terms of normal modes as they are independent of each other. Energies of these normal modes are then quantised, where a quantum of lattice vibration is referred to as a phonon [147].

The kesterite crystal structure of  $\text{Cu}_2\text{ZnSnS}_4$  is related to the zinc-blende-type crystal structure [? ], for which the features of phonon dispersion curves have been well studied and can be measured quite precisely by inelastic neutron scattering [147]. In the case of the zinc-blende-type lattice, there are two atoms per primitive unit cell which results in six phonon branches: three lower-energy acoustic branches and three optical curves. Acoustic phonons are coherent movements of atoms in a lattice out of their equilibrium positions, whereas optical phonons are out-of-phase movements of atoms in a lattice. Optical phonons can only occur in a lattice containing two or more atoms in the primitive unit cell and in ionic crystals optical modes are excited by radiation. Along directions of high symmetry these phonons can be classified as transverse or longitudinal depending on whether their displacements are perpendicular or parallel to the direction of the wavevector respectively. In a solid the long wavelength transverse acoustic (TA) phonons are shear sound waves, while the longitudinal acoustic (LA) phonons are compressional sound waves. The velocities of these sound waves are determined by shear and bulk elastic moduli respectively. As it is usually easier to shear than to compress a crystal, TA phonons typically travel with lower velocities than LA phonons. The atomic displacements from long wavelength acoustic phonons can correspond to a deformation of the crystal, this is referred to as deformation potential theorem. Such deformations will change the electronic energies at different points in the Brillouin zone. LA phonons always produce a change in the volume of the crystal, which affects all energy bands [147].

The interaction of charge carriers with phonons, often referred to as electron-phonon coupling, sets a fundamental limit on the mobility of charge carriers in a material in the absence of extrinsic scattering due to defects, impurities or interfaces [147, 141]. Thermal vibrations of the lattice atoms gives rise to a perturbation of the band edge [15], although the interaction of

charge carriers with phonons is currently still a subject of much debate [? ? 141]. Of all the various possible contributions to intrinsic band gap broadening from electron-phonon coupling, there is currently no clear picture of which mechanisms are active or the most dominant in determining the carrier mobility in a material [141]. A number of studies on non-polar inorganic semiconductors have examined the temperature dependence of the charge-carrier mobility [? ? ? ? ], where the carrier mobility,  $\mu$ , was found to scale with  $T^m$  where  $m$  has a value between -1.4 and -1.6. From theory, it is known that deformation potential scattering with acoustic phonons results in  $\mu \propto T^{-\frac{3}{2}}$ . Therefore several works in the literature suggest that electron-phonon coupling at room temperature is dominated by acoustic phonons [? ? ? ]. In our study, we will first be determining just the contribution from LA phonons due to the changes in lattice volume from to the thermal motion of the atoms in an attempt to gauge if the fundamental limit this places on carrier mobility is likely to be a key limiting factor for device performance. The carrier lifetime in CZTS has been measured to be considerably less than that of other technologies (e.g. MAPI)... \*\*FIND REF\*\* The methodology for this calculation will be discussed in section 3.3.

## 2.4 Electronic Properties of Defects in Semiconductors

Although the main framework for materials modelling of solid-state systems (as was outlined in section 2.1) is built around perfect, periodic systems; in reality absolutely perfect systems do not exist. There is an energy cost associated with the creation of a defect, but in many cases the free energy of a system can be lowered by the incorporation of a certain concentration of defects due to an increase in the configurational entropy of the system [6]. At this point it is worth distinguishing between different types of defects for the purpose of later discussions. Firstly, if a defect does not involve any atoms that are foreign to the host crystal, then the defect is called an intrinsic or native defect. Defects involving foreign atoms, or impurities, are referred to as extrinsic defects. Figure 2.5a and 2.5b show some examples of extrinsic and intrinsic defects. In our study on  $\text{Cu}_2\text{ZnSnS}_4$  as we are first interested in the fundamental material properties so we are currently only concerned with intrinsic impurities, although in real

systems impurities are often unintentionally present in the growth or processing environment. Defects are usually classified as point or line defects. Point defects usually involve isolated atoms in localized regions of a host crystal, whereas line defects involve rows of atoms, such as a dislocation defect. An example of a line defect is shown in figure 2.5a. Another possible type of defect is a defect complex, which is composed of a small number of point defects. Some examples of defect complexes in  $\text{Cu}_2\text{ZnSnS}_4$  were shown in figure 1.23. Defect complexes can be particularly interesting to study as there is some speculation in the literature that defects which are energetically less likely to form, could be more likely to form if they form a defect complex with defects that are more likely to form \*\*find ref\*\*. There are then a number of different possible point defects, such as: vacancies, interstitials and antisites. In the case of our study on defects in  $\text{Cu}_2\text{ZnSnS}_4$ , it is sulfur vacancies ( $V_S^0$ ,  $V_S^+$ ,  $V_S^{2+}$ ) and copper-on-zinc ( $Cu_{Zn}^-$ ) and zinc-on-copper ( $Zn_{Cu}^+$ ) antisites that are of interest, where  $Cu_{Zn}^-$  and  $Zn_{Cu}^+$  form the charge neutral defect complex  $[Cu_{Zn}^- + Zn_{Cu}^+]$ . The sulfur vacancy is an example of an electrically active defect. In this case the defect can contribute two free electrons to the host crystal and so is a donor or n-type defect. \*\*check\*\* The free electrons can then either be fairly localized on the defect site to form a small polaron, or extended across several sites to form a large polaron, or be completely delocalized across the system \*\*find ref\*\*.

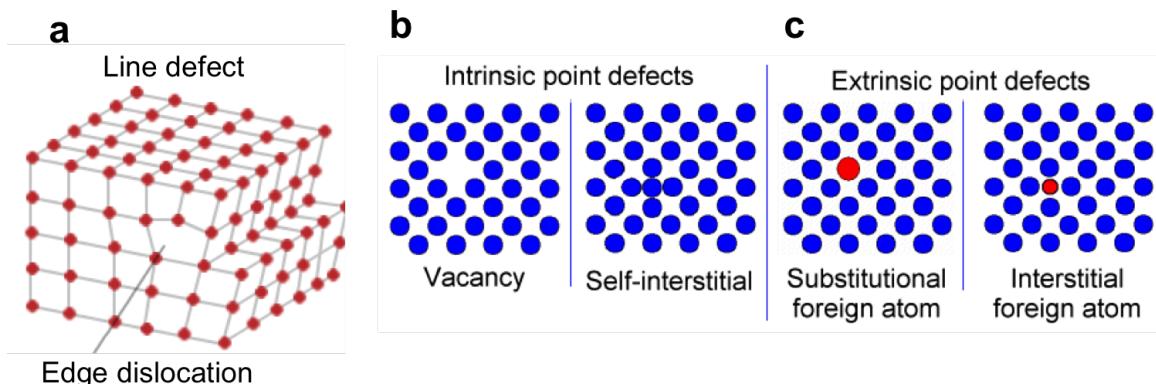


Figure 2.5: An example of a line defect (a) and both intrinsic (b) and extrinsic (c) point defects. Figures taken from references 37 and 98 respectively.

The electrical properties of semiconductors can be modified significantly by the incorporation of very small amounts of impurities or defects. It is often the case that less than one defect per

million of host atoms is sufficient to alter the properties of a semiconductor [147]. This sensitivity to defects is one of the reasons why semiconductors find many uses in device applications. For example, luminescence centres in wide-band-gap materials can be used to emit light at specific wavelengths or single-spin centres provided by defects can act as artificial atoms and serve as a qubit in a quantum information system [3]. In order to control the electrical properties of a material by introducing defects, typically processes must first be developed to produce a fairly defect-free material, before intentionally introducing particular defects [147]. However in the case of solar cell devices the presence of defects is typically detrimental. Various ways in which defects in the absorber material can impede solar cell performance are discussed further in section 2.4.2 and more general characteristics of defects in semiconductors are discussed in the next section.

### 2.4.1 Impact of Defects on the Band Structure & Optical Spectra

The energy band model, which was discussed in section 2.2, has been successful in explaining many aspects of the behaviour of solids and a large amount of experimental data collected has supported the theoretical predictions made using the model. Its main drawback however is that it assumes a perfect, or nearly perfect, crystal lattice. It applies well to single crystals and polycrystalline substances, but cannot be applied to materials that are amorphous or heavily disordered so that the structure deviates significantly from the periodicity of the crystal [64].

Some defects result in additional energy levels in between the valance-band maximum and conduction-band minimum, i.e. within the band gap of the material. Electrically active defects have at least one defect level in the band gap. This level then has an associated defect wavefunction, a state to which the electron is added to or removed when the charge state of the defect changes. If the defect level is positioned relative to the band edges such that the defect is likely to be thermally ionized at room temperature then the defect is conventionally referred to as a shallow level. Otherwise it is referred to as a deep level. Typically deep levels are thought to be the most detrimental to solar cell device performance, which will be discussed

further in section 2.4.2. Another way of defining a defect as ‘shallow’ or ‘deep’ is based on the degree of localization of the wavefunction. If a defect wavefunction is delocalized (on the order of many lattice constants) then the defect has the characteristics of a shallow defect. If the wavefunction is instead localized on the length scale of an atomic bond then this indicates a deep level defect [3].

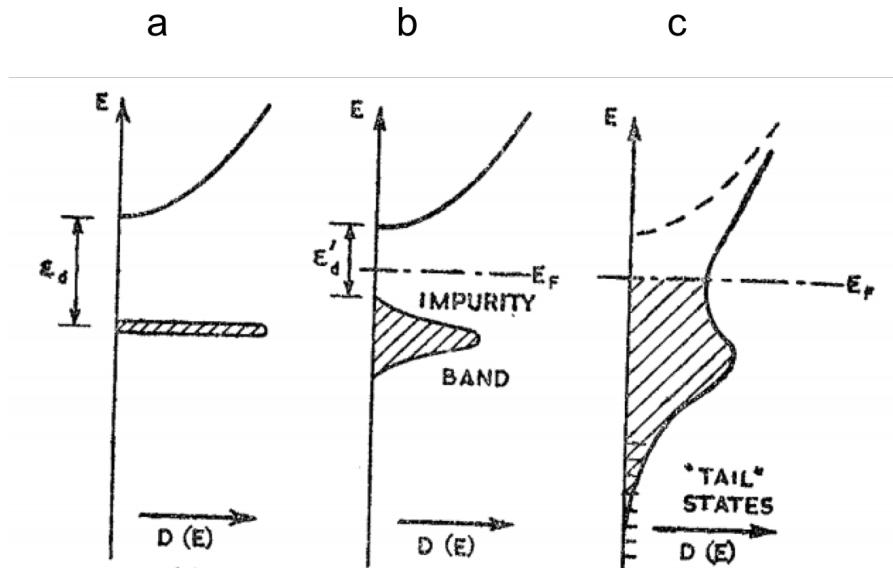


Figure 2.6: The influence of increased donor impurity density on the conduction band profile showing low (a), medium (b) and high (c) densities of impurities. Figure taken from reference 65.

Low concentrations of impurities and defects can be modelled by considering, for example, the introduction of distinct additional donor and acceptor energy levels within the band gap of a material and the scattering of electrons and holes in the solid. However, at higher defect concentration, these local levels interact to form a band. For high n-type doping, for example, the impurity band merges with the conduction band, causing a rigid shift of the conduction band towards the valence band [96]. The band profile can be modified with increasing donor density as shown in figure 2.6 to give rise to conductivity even at temperatures that are too low to produce excitation of carriers into the free conduction bands, called impurity band conduction [65]. In heavily-doped semiconductors it is possible to observe a phenomena called ‘band tailing’, where the valence and conduction bands are shifted towards each other resulting in a narrowing of the band gap, as shown in figure 2.7 [96]. The heavy-doping effects then result in

a different emitted spectrum which can be detected by techniques such as photoluminescence (PL) spectroscopy.

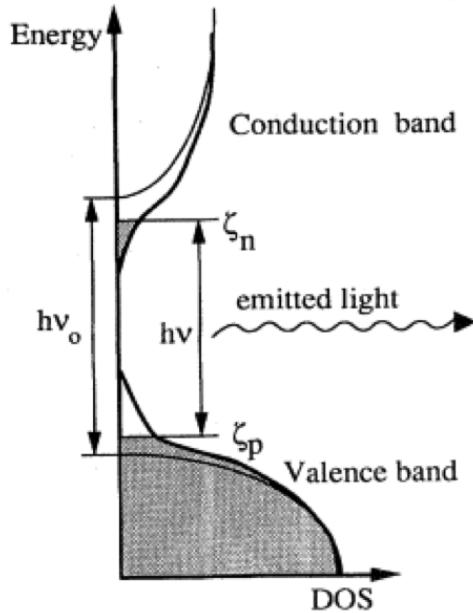


Figure 2.7: Schematic of the laser operation at  $T=0$  K in GaAs.  $\zeta_{n,p}$  are the quasi-Fermi level for electrons and holes respectively. The narrow line denotes the unperturbed DOS, while the heavy line depicts the DOS modified by heavy-doping effects. Both valence and conduction bands are shifted towards each other to give a narrowing of the band gap and the DOS is distorted, showing band tails. Heavy doping effects result in a different emitted spectrum. Figure taken from reference 96.

In a PL experiment, photons with energies larger than that of the band gap excite electrons from the valence band to the conduction band, as shown in figure 2.8a. In addition, electrons can be excited from or to defect levels, as shown in figure 2.8b. When the excited electrons transition to lower energy levels, they can emit light to conserve energy, resulting in a peak in the PL spectrum. In a photoluminescence excitation (PLE) experiment, the PL intensity is measured as a function of excitation photon energy. This gives an absorption profile for the defect. PL measurements are able to pick up optical signatures of defects even if they are only present at low concentrations with high resolution [3]. A review of some of the photoluminescence spectra for  $\text{Cu}_2\text{ZnSnS}_4$  in the literature and the implications for PV device performance is discussed in section 2.4.3. PL measurements alone however cannot be used to identify the character of a defect, this is an area where first-principles defect calculations (which are discussed in the

methodology section) can provide valuable insight [3].

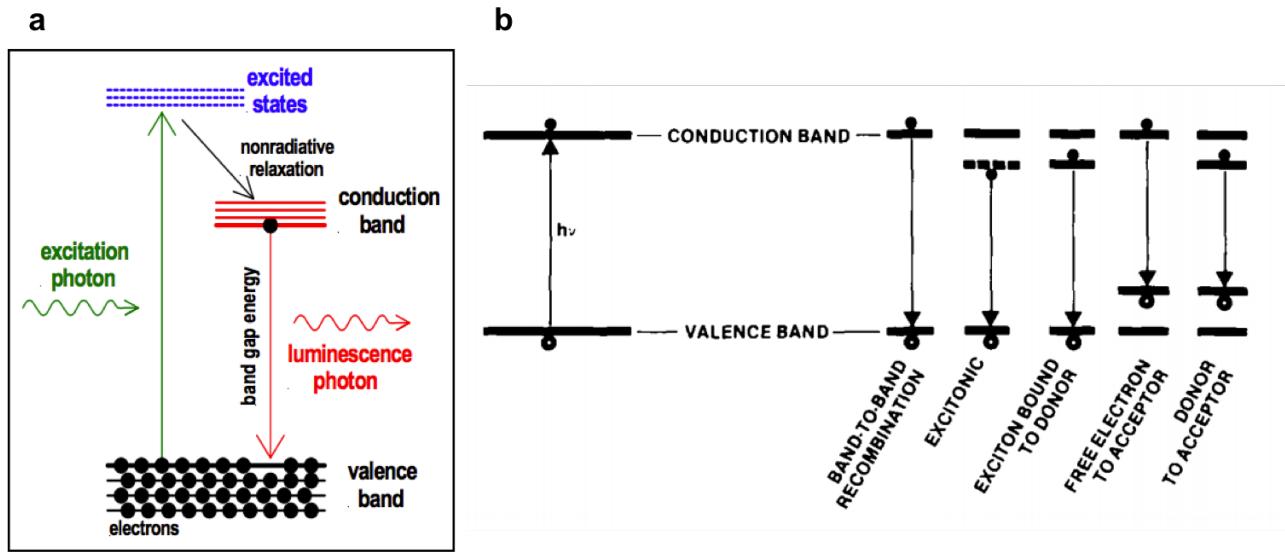


Figure 2.8: Basic optical transitions involved in a measurement during photoluminescence spectroscopy (a). Common emission transitions detected during photoluminescence measurements, including transitions involving defect levels (b). Figures taken from reference 1 and 96 respectively.

Observed band tailing can be caused by either spatial band gap variations or electrostatic potential fluctuations in the material [46]. In the case of the latter, it is the inhomogeneous distribution of ionized defects that cause the fluctuations. An ionized donor exerts an attractive force on conduction electrons and a repulsive force on valence holes. As the defects are distributed randomly, the local interaction varies depending on the crowding of the defects. In this case the energy gap between the valence band and conduction band is maintained, as shown in figure 2.9 and the states of each tail are spatially separated [96]. Defects can also result in fluctuations in the band gap of a material. For example, if an impurity atom is of a different size to the atoms of the host lattice, then this can result in a local mechanical strain, as shown in figure 2.10b which results in a deformation potential, such as that shown in figure 2.10c for an edge dislocation defect. Local strains can alter the separation of atoms in the crystal and, as figure 2.10a shows, the atomic separation within a crystal has a significant impact on the band structure.

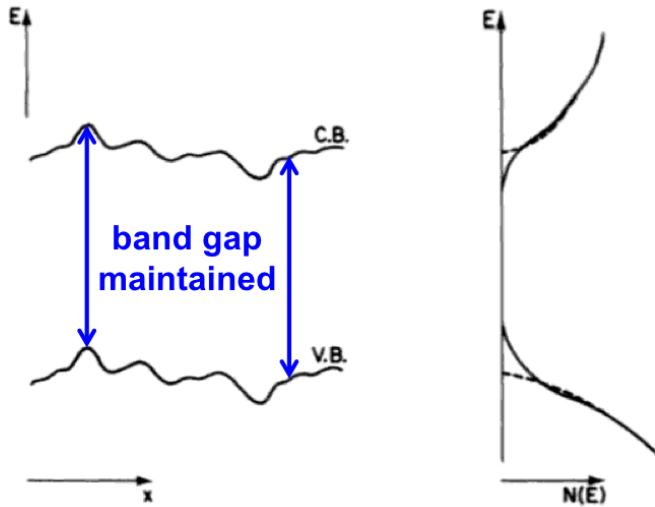


Figure 2.9: The perturbation of the band edges by Coulomb interaction with inhomogeneously distributed impurities (left), leading to the formation of tail states (right). Dashed lines show the distribution of states in the unperturbed case. Figure taken from reference 96.

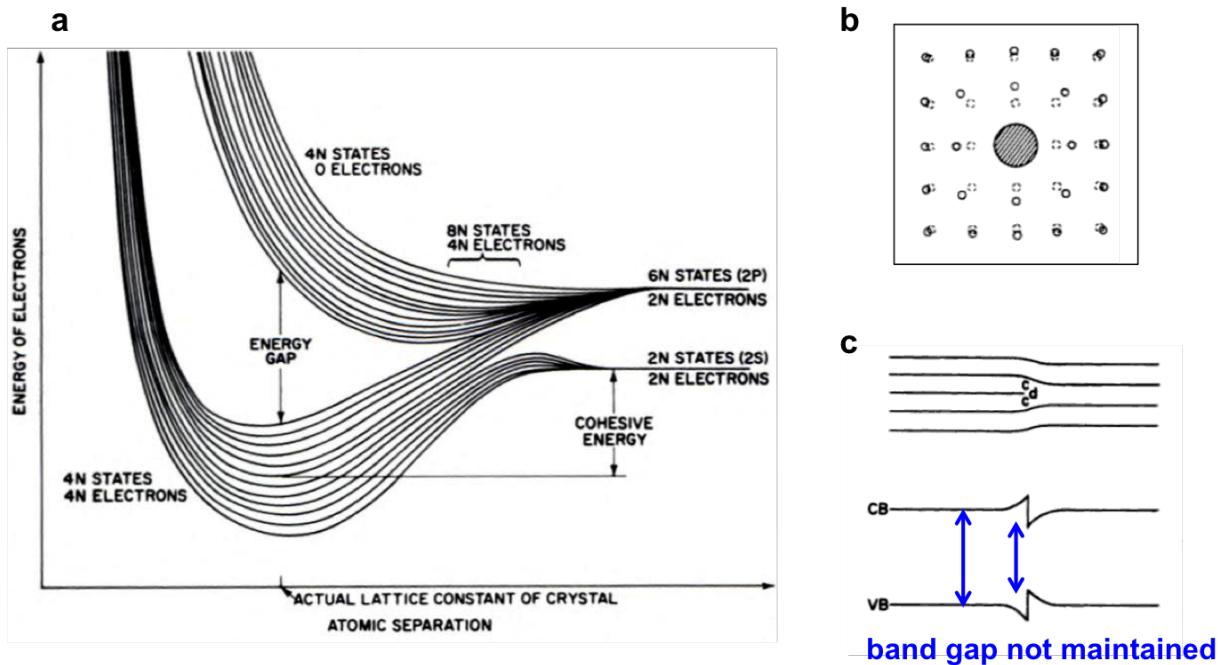


Figure 2.10: Energy banding of allowed levels in diamond as a function of spacing between atoms (a). Compressional strain induced in a crystal lattice by the incorporation of a large impurity atom (b). Deformation potential in the band structure due to compressional and dilatational strain from an edge dislocation defect (c). Figures taken from reference 96.

## 2.4.2 Impact of Defects and Disorder on Solar Cell Performance

As already discussed, even very low concentrations of defects in a semiconductor can have a significant impact on its optoelectronic properties and therefore heavily influence the perfor-

mance of an optoelectronic device composed of the material. As discussed in section 1.1.4, one of the main motivations behind developing thin-film PV technologies, where the absorber layer is considerably thinner than that of a conventional silicon wafer, was to reduce the demand on the quality and low-defect concentrations of the material to reduce the energy intensity and high costs associated with the fabrication of the high quality material. A large number of compound semiconductors with direct band gaps have been studied for use in solar cells and some, such as CdTe and CIGSSe, have been commercialized. However, as the number of elemental components in a compound semiconductor increases, so does the various types of defects and disorder that can be present in the material, some of which will have more detrimental effects on device performance than others.

Firstly, thin-films of solar absorber materials fabricated using low cost synthesis techniques will be highly polycrystalline, therefore the layer will contain many grain boundaries, which can heavily influence device performance. In the specific case of CuInSe<sub>2</sub>, the more polycrystalline material was found to produce higher-performing devices than its single crystalline counterpart [109, 105], but this has been attributed to the unique grain boundary physics of this material [99, 100]. Typically, grain boundaries are a sink for defects and therefore are more closely associated with the detrimental effect of defects on PV performance, such as Shockley-Read-Hall recombination which will be discussed further below. It can also be very challenging to synthesise a single phase of a multicomponent material as a large number of secondary phases will also exist which can unintentionally be produced. For CZTS, phase diagrams have been constructed that show only a very narrow region for single phase CZTS, where only an absolute deviation of 1-2% in the composition at most would still result in a single phase of the crystal [120]. A schematic showing various possible secondary phases that could be produced during the synthesis of CZTS is shown in figure 2.11. The formation of secondary phases can be problematic due to recombinations at interfaces between secondary phases but also because the different phases may have a different band gap. Some of which may be less than that of CZTS and so could hinder device performance. However in our study, we are primarily concerned with the properties of the bulk material, to determine if there are fundamental material properties that

will limit device performance.

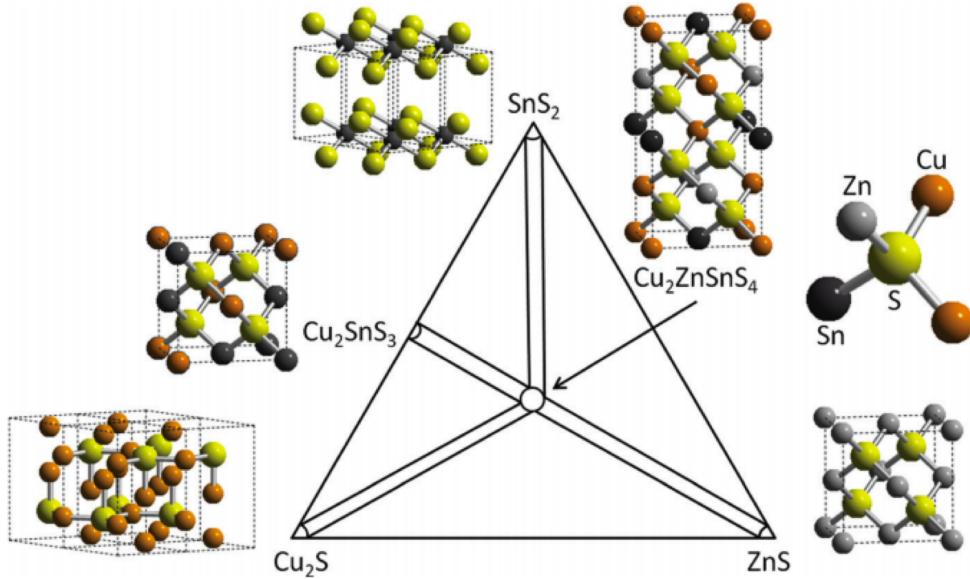


Figure 2.11: Schematic of the thin film  $\text{Cu}_2\text{S}$ - $\text{ZnS}$ - $\text{SnS}_2$  ternary phase diagram at 325°C deposition temperature. The crystal structures of CZTS and the observed secondary phases are also presented. Figure taken from reference 34.

Of bulk defects and disorder, defects that produce mid-gap states (i.e. deep defect levels) act as Shockley-Read-Hall recombination sites [118], which was illustrated in figure 1.19. This is regarded as the most important recombination process in real, non-perfect semiconductors. It is a form of non-radiative recombination where a charge carrier is trapped in the defect state before recombining with a charge carrier of opposite polarity. This type of recombination is known to be detrimental to device performance as essentially it results in energy input from sunlight not being converted into electricity [85]. In the case of  $\text{Cu}_2\text{ZnSnS}_4$ , for the most part predictions of defect formation energy and defect levels suggest that defects which would be expected to produce a deep defect level, also have a high formation energy so would be expected to be less likely to form [24].

For  $\text{Cu}_2\text{ZnSnS}_4$  a lot of attention in the literature has been paid to disorder amongst Cu and Zn cations with a large amount of experimental evidence for the presence of this disorder [110, 136, 81] and theoretical predictions for the low formation energy of the  $[\text{Cu}_{\text{Zn}}^- + \text{Zn}_{\text{Cu}}^+]$

[24]. During the synthesis of CZTS, temperatures above room temperature are used and it is possible for some of the thermal disorder associated with the system at higher temperatures to be ‘frozen in’ to the material as it cools to room temperature. Near resonant Raman spectroscopy has been used to examine thin films of CZTS prepared using different thermal treatments to determine if long post-annealing cooling times could produce films with a high level of order amongst Cu and Zn cations. However in this study, the authors postulate that achieving a very high level of order amongst Cu and Zn could require years [107]. This clearly wouldn’t be a practical treatment for a PV device and so it would seem that the presence of a fairly large amount of disorder amongst Cu and Zn, and hence  $Cu_{Zn}^-$  and  $Zn_{Cu}^+$  antisites, is inevitable in the material.

Although  $Cu_{Zn}^-$  and  $Zn_{Cu}^+$  antisite defects have been predicted to produce only shallow defect levels within the band gap of the material [24], their presence could be linked to band tailing in the material. Point defects in an otherwise perfect lattice can be regarded as missing lattice atoms, which are replaced by lattice defects. Therefore for every defect that creates one or more levels in the band gap of the material, the same number of levels that would have been created by the atoms in the host lattice are missing. Additionally, the lattice atoms surrounding the defect relax into shifted positions and also create states that could be shifted slightly into the band gap [15]. All of these states contribute to perturbations in the band edge, such as that shown in figure 2.7. Such a tail of band states into the band gap is often referred to as a Lifshitz tail [75], it can be observed experimentally and is most noticeable in heavily doped and amorphous semiconductors [15]. For disorder due to defects with a correlation length on the order of interatomic spacing, the absorption coefficient,  $\alpha_0$  (which was discussed as a key property for PV materials in section 1.1.3) shows an exponential decline. This effect is illustrated in figure 2.12. This dependence of the optical absorption is widely observed in disordered semiconductors [15] and is referred to as the Urbach tail [130]. Such tailing can be quantified by the Urbach energy, and it has recently been proposed that there is a direct link between the Urbach energy and open circuit voltage deficit in standard photovoltaic materials [18, 140].

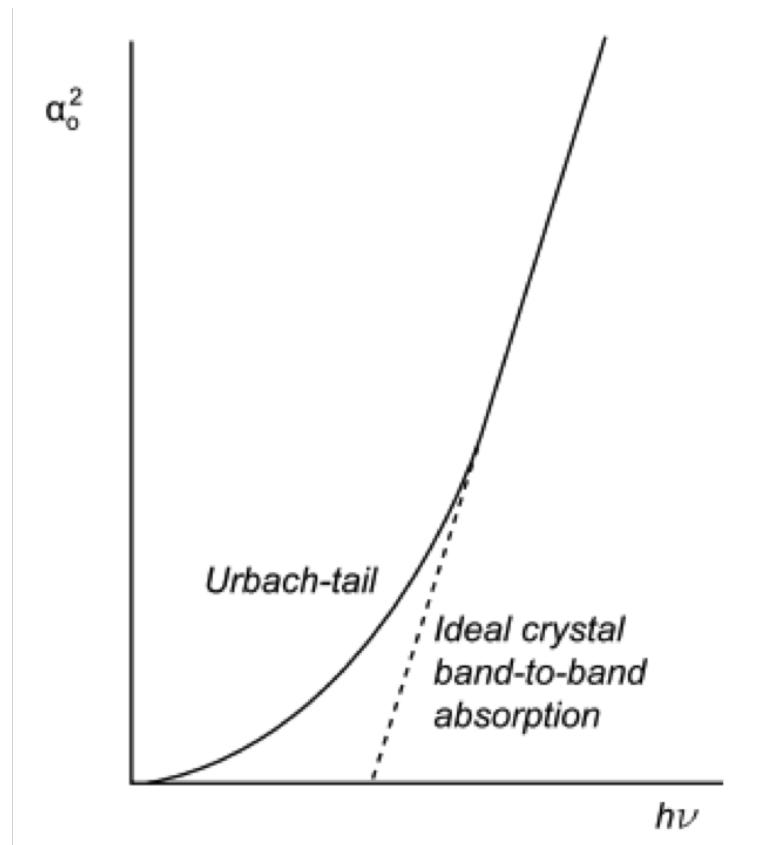


Figure 2.12: Optical absorption spectrum of a typical direct band gap semiconductor with the absorption coefficient,  $\alpha_0$ , proportional to the extended density of states in the Urbach tail. Figure taken from reference 15.

### 2.4.3 Photoluminescence Spectra of Cu<sub>2</sub>ZnSnS<sub>4</sub>

Photoluminescence (PL) spectroscopy is a popular method to inspect solar cell materials as it does not require a full functioning device and can be a powerful tool for probing defects in semiconductors. There are a large number of possible optical transitions that can be detected by PL measurements, some of which were illustrated in figure 2.8. For this reason, low-temperature PL can be a particularly powerful tool for probing defects as energy level occupancy is dependent upon temperature and so not all PL recombination will occur at the same temperature, allowing for the isolation of different types of recombination transitions [16]. There are also other variations in the set up of a PL measurement that can be altered to provide more information on the band structure and how it is altered by the presence of defects. Firstly the intensity of the laser can be increased to determine if states are localized (such as those introduced by defects) or extended states (such as the conduction and valence bands) by if it is possible to

saturate the states in the case of localized states such that an increase in laser intensity no longer increases the PL peak [42]. Secondly, time-resolved PL (TRPL) measurements can be used to differentiate between recombination mechanisms with different carrier lifetimes. Slower optical transitions usually involve carriers in localized states, whereas faster transitions usually involve delocalized states [42].

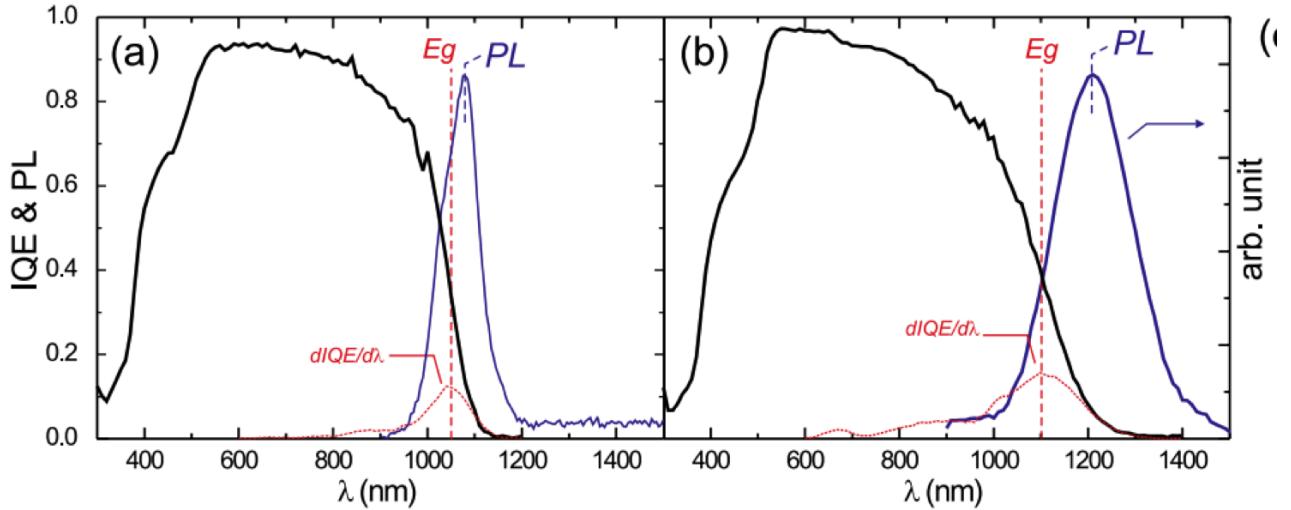


Figure 2.13: The internal quantum efficiency (IQE), band gap as determined from the IQE inflection point and the photoluminescence spectra of high performance devices with thin-film absorber layers of (a) CIGSSe ( $E_g = 1.19$  eV) and (b) CZTSSe ( $E_g = 1.13$  eV). Figure taken from reference 46.

Several PL studies have been performed on kesterite-structured samples of  $\text{Cu}_2\text{ZnSnS}_4$ ,  $\text{Cu}_2\text{ZnSnSe}_4$  and alloys of the two. PL measurements have been performed on both full devices and polycrystalline thin-films [46, 42, 41, 106, 84, 129] and single crystals [50, 73, 53]. In addition studies such as reference 50 compare the PL spectra for varying compositions of the sample, whereas in reference 46 measurements on both CIGSSe and CZTSSe thin films are performed in an attempt to account for the difference in the performance of these two technologies by comparing their defect-influenced PL emission spectra. Polycrystalline samples are more similar to those likely to be used in thin-film CZTS photovoltaic devices, however comparison between those measurements with single crystal measurements could enable the isolation of recombination at grain boundaries from those due to bulk defects. Also measurements performed on single crystals as close to perfectly stoichiometric  $\text{Cu}_2\text{ZnSnS}_4$  as possible are likely to be the most

directly relatable to our simulations on bulk systems. However one feature common to all of the PL spectra from studies on kesterite samples is clear evidence of defects and disorder from the observed band tailing. The PL spectra of kesterite samples usually features a much broader peak than that observed in CIGSSe samples, such as that shown in figure 2.13. The energy of the maximum PL peaks of kesterite samples is also usually considerably red-shifted compared to the energy of the band gap. These two features are usually attributed to band tailing caused by either spatial band gap variations or electrostatic potential fluctuations in the absorber material, which were discussed in section 2.4.1. Both effects lead to a non-zero density of states (DOS) within the band gap [18, 46]. Measurements performed in reference 46 found the tailing in CZTSSe to be roughly twice as severe as that observed in higher-performing CIGSSe devices.

However, there is some disagreement in the literature about the main recombination mechanisms that could explain the observed PL spectra. Of the measurements performed on single crystals, reference 73 perform measurements on near-stoichiometric CZTS crystals and report a free-to-bound transition between the conduction band and an acceptor level. In reference 53, donor-acceptor-pair (DAP) transitions are reported for large single grains of CZTS, whereas in reference 50 where measurements are performed on CZTS single-crystals of varying composition, they report PL measurements through spatially fluctuating band states as would be expected from either spatial band gap variations or electrostatic potential fluctuations from heavy defect compensation. Therefore in bulk monograins of CZTS PL band-to-impurity, DAP and spatially fluctuating band-type recombinations have all been reported and the exact sources, or rather associated defects, for these recombination mechanisms are not yet known [41].

For measurements performed on polycrystalline kesterite samples, some studies attribute the spectra to spatially fluctuating band tail states [106], whereas others suggest that recombination in CZTS is dominated by the distinct energy levels introduced by DAPs [129, 84]. In other studies, an explanation that is almost a combination of the two is proposed [42, 41]. These studies refer to a quasi-donor-acceptor-pair (QDAP) model, where the word ‘quasi’ is used to indicate a deviation from the classical DAP model for recombinations, such as that shown in

figure 2.8, due to interactions between defects. In reference 41 they note that distinguishing between DAP recombination and spatially fluctuating band tails caused by spatially varying densities of ionized donor and acceptor defects is particularly complicated as a high density of compensating DAPs is necessarily co-incident with spatial fluctuation in electrostatic potential. In the same work, they note that the dominance of donor and acceptor pairs on PL spectra is in agreement with theoretical predictions such as those by Chen et al shown in figure 1.23 [24] that antisite DAPs such as  $[Cu_{Zn}^- + Zn_{Cu}^+]$  should be abundant due to the low formation energy of the defect complex and also experimental observations of cation disorder by neutron diffraction, synchrotron radiation x-ray diffraction and aberration corrected scanning transmission electron microscopy respectively [110, 136, 81].

In this work we begin two studies on defects in  $Cu_2ZnSnS_4$ . Firstly, we will attempt to quantify the contribution to the observed band tailing in CZTS from disorder amongst copper and zinc cations, or equivalently, the presence of  $[Cu_{Zn}^- + Zn_{Cu}^+]$  antisite defect pairs. The methodology will be outlined in more detail in section 3.2, but the general approach will be to use Monte Carlo simulations that have been parameterised with first-principles calculations to determine the extent of Cu-Zn disorder in CZTS at various temperatures and to then study the distribution of electrostatic potential across the system from the inhomogeneous spatial arrangement of the charged antisite defects,  $Cu_{Zn}^-$  and  $Zn_{Cu}^+$ . Secondly we are re-examining the formation energy of sulfur vacancies as they have been predicted [24] to result in a mid gap state, but it is possible that the formation energy may have been overestimated when typical synthesis conditions are taken into account. This will be discussed much further in the methodology section, in particular in section 3.1.3.

# Chapter 3

## Methodology

### 3.1 Calculation of the Formation Energy of Defects in Cu<sub>2</sub>ZnSnS<sub>4</sub>

See Lany paper + Keith's posted paper + encyclopoedia of defects paper

As discussed in section 2.4.2, defects in a solar absorber material can heavily impact on the performance of a photovoltaic device composed of that material. In this study we perform first principles calculations of two types of defects in the solar absorber material Cu<sub>2</sub>ZnSnS<sub>4</sub>. We firstly performed calculations of the formation energy of the charge neutral Cu-on-Zn and Zn-on-Cu anti-site defect pair, [Cu<sub>Zn</sub><sup>-</sup>+Zn<sub>Cu</sub><sup>+</sup>], in order to parameterize our Monte Carlo simulations of thermodynamic Cu-Zn disorder, which will be discussed further in section 3.2. We also begin calculations of the formation energy of a sulfur vacancy in Cu<sub>2</sub>ZnSnS<sub>4</sub>. This defect can however take on three different charge states: V<sub>S</sub><sup>0</sup>, V<sub>S</sub><sup>+1</sup> and V<sub>S</sub><sup>+2</sup>, where electron occupancy varies from two to one to none respectively. We will then go on to calculate the formation energy as a function of the sulfur chemical potential to determine which charge state has the minimum formation energy at typical annealing conditions of Cu<sub>2</sub>ZnSnS<sub>4</sub>, in terms of temperature and pressure. This methodology is outlined in section 3.1.3. However, special correction techniques

must be applied when performing periodic calculations to simulate a bulk system with a finite unit cell when the unit cell possesses a net charge. This point is discussed in section 3.1.2.

[3]

### 3.1.1 Density Functional Theory & Hybrid Functionals

Density functional theory (DFT) has been referred to as the most powerful method for assessing the properties of defects in materials [3]. + refer to DFT in materials science paper?

The description of the electrons in a system requires the use of QM... outline of standard DFT...(explicitly introduce LDA and GGA)

- See Bechstedt book [11] + figures from Aron
- discuss band gap underestimation in standard DFT (GGA mentioned during intro, also discuss GGA+U and limitations)

DFT calculations typically yield reliable information about the atomic structure of defective systems, including relaxation of the host atoms. However the electronic structure has proved to be a greater challenge [3]. Traditional functionals such as the LDA and GGA used in standard DFT, which were outlined above, severely underestimate band gaps of semiconductors and insulators, which then leads to large uncertainties in the position of defect levels. This issue can be addressed by going beyond standard DFT, such as by making use of many-body perturbation theory, where the GW approach is typically used [56]. This method however is usually computationally expensive and difficult to implement self-consistently, so it is usually used to address the electronic structure only when used on top of atomic structures obtained from DFT [1, 25], which is often denoted as DFT@G0W0 \*\*CHECK\*\* [3].

Hybrid functionals are another powerful way to overcome the limitations of standard DFT, they mix ... screened... Hybrid functionals firstly have been round to produce band structures and band gaps in much better agreement with experiment, but also provide much more reliable description of charge localization, which is necessary to accurately model low symmetry defects or structures that give rise to polaron formation. Whereas standard DFT suffers from the self interaction error where ... In particular, the screened hybrid functional of Heyd, Scuseria, and Ernzerhof (HSE) [52] has proven reliable to predict formation energies and transition levels of native defects and impurities [3]

Brief outline of hybrid DFT...

### 3.1.2 The Supercell Method & Corrections for Charged Defects

see Aron's lectures + DFT in materials science paper [88] + Lany paper

Another important advance has been the ability to correct for errors that arise from the use of supercells to describe charged defects. While these supercells can typically be made large enough to minimize interactions between a neutral defect and its mirror images, the long range of the Coulomb interaction renders this essentially impossible in the case of charged defects. Explicit correction schemes are therefore essential, and a supercell-size correction scheme based on the rigorous treatment of electrostatics was described in Refs. 31 and 32. [3]

### 3.1.3 Defect Formation Energy & Equilibrium Concentration

Show formula for defect formation  $E$  as a function of electronic and atomic chemical potentials, discuss chemical potentials (especially  $S!$ ) and show Boltzmann expression for concentration.

## 3.2 Monte Carlo Simulation of Thermodynamic Disorder in $\text{Cu}_2\text{ZnSnS}_4$

### 3.2.1 Mapping the Crystal Structure of $\text{Cu}_2\text{ZnSnS}_4$ onto a Simple Lattice

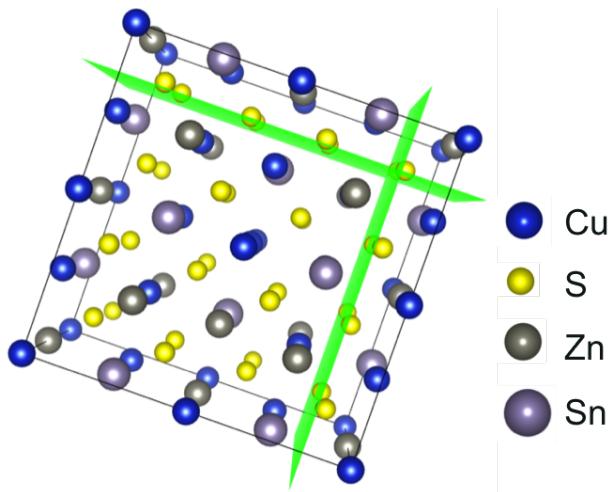


Figure 3.1: A supercell of the perfect  $\text{Cu}_2\text{ZnSnS}_4$  crystal lattice, which can be described by inter-penetrating face-centred cubic sub-lattices: one of metal cations and one of sulfur anions. Green planes are used as guides to the eye to show planes of S anions that form one of the two face-centred cubic sub-lattices.

In this study, we use a custom Monte Carlo code to simulate substitutional on-lattice disorder between Cu and Zn ions in  $\text{Cu}_2\text{ZnSnS}_4$  as a function of temperature. The crystal structure of  $\text{Cu}_2\text{ZnSnS}_4$  can be described by two inter-penetrating face-centred cubic (FCC) lattices: one of metal cations and one of sulfur anions, as shown in figure 3.1. We consider the sulfur sub-lattice to be stationary because any substitution between ions in the cation sub-lattice and sulfur anion sub-lattice would be energetically infeasible and any substitutions amongst the sulfur anions in that sub-lattice would be energetically equivalent. The sulfur sub-lattice is therefore neglected during the Monte Carlo simulations but incorporated later in calculations of lattice electrostatics. This then reduces the problem of mapping the  $\text{Cu}_2\text{ZnSnS}_4$  crystal structure onto a simple lattice to just one FCC cation lattice. We then map this onto a simple cubic (SC) lattice for our simulations by introducing empty lattice sites into the SC lattice, as shown in figure 3.2.

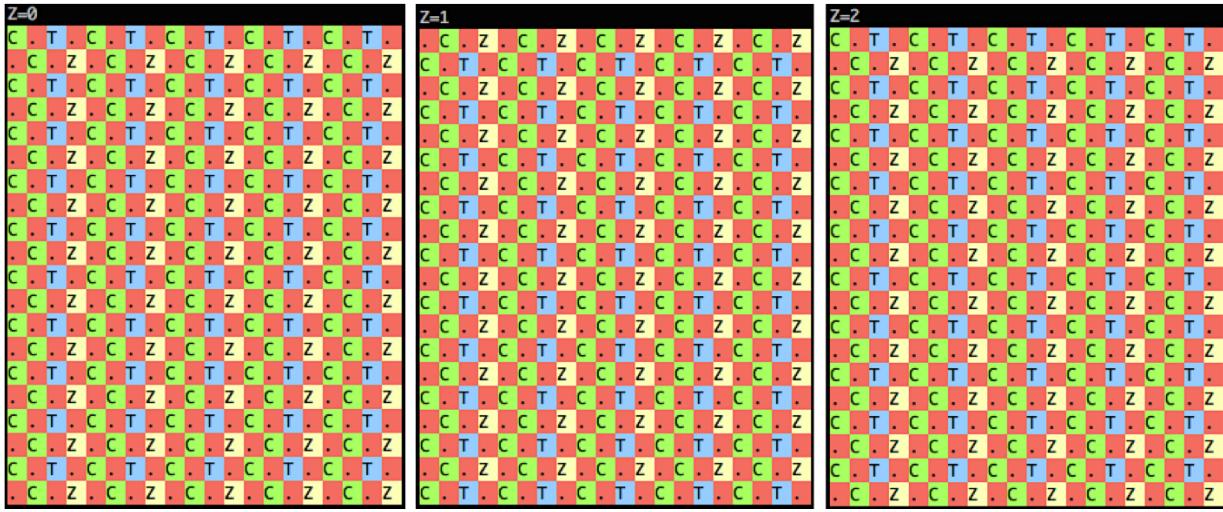


Figure 3.2: A two-dimensional (x-y) slice of a 20x20x20 cation sub-lattice of ordered  $\text{Cu}_2\text{ZnSnS}_4$ . Sulfur anions are neglected from the simulations and the face-centred cubic cation lattice is mapped onto a simple cubic lattice by including empty sites in the lattice. Alternating layers in the z-direction are displaced by one lattice unit in order to reproduce the correct kesterite structure. ‘C’, ‘Z’, ‘T’ and ‘.’ represent copper, zinc, tin and an empty site respectively.

For some of our simulations, we initialise the system as the perfectly ordered crystal structure of CZTS. Then for simulations where we want to start from a disordered system, we again take this perfectly ordered initial structure but ‘shuffle’ Cu and Zn ions. An initial configuration of a large SC lattice of perfectly ordered CZTS is generated by producing a supercell of a unit cell of the perfectly ordered structure, where this unit cell was determined by examining the geometry of CZTS one layer at a time in three dimensions. An example of this analysis is shown in figure 3.3. The smallest unit cell was found to be a 2x2x4 cell when including the gap sites. The crystal structure of  $\text{Cu}_2\text{ZnSnS}_4$  can also be described by alternating layers of Cu-Zn and Cu-Sn [110], as shown in figure 1.15. For the unit cells generated by eris, this corresponds to when the system is viewed along the y-axis and as we fix Sn ions in our simulations, we would expect this direction to always have this same repeating pattern when the system is perfectly ordered. We therefore intend to use order in this direction as one of our order parameters, which is discussed further in section 3.2.5. However, we will also check that our system crystallises in the same direction as we would expect it to by performing simulations from an initial randomized configuration until the ground state crystal structure is recovered at low temperatures. This process will be discussed in the results section.

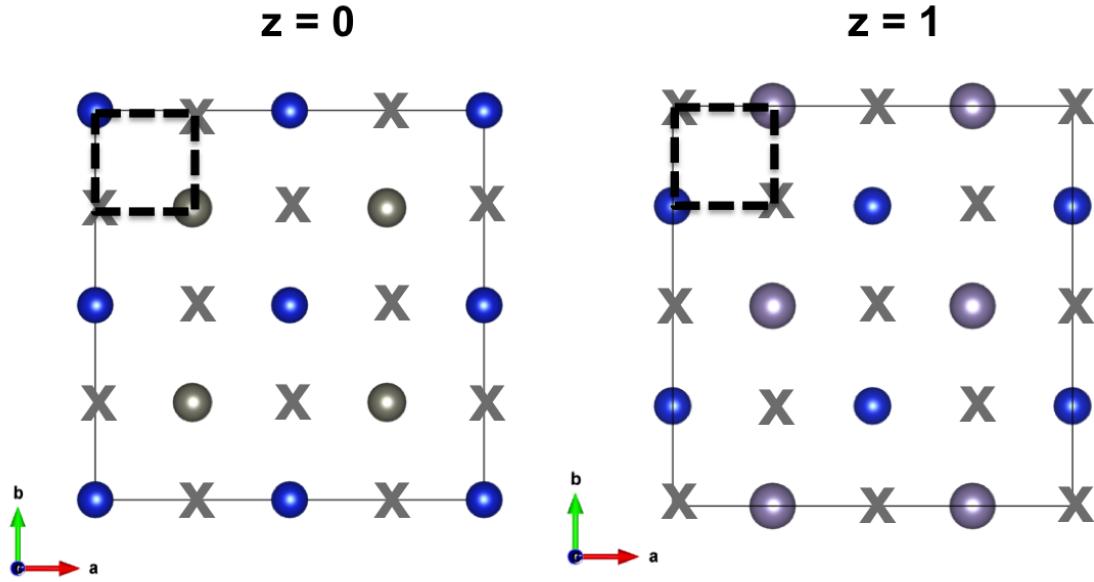


Figure 3.3: Some of the single layers of a CZTS supercell used to determine the minimum cation unit cell for constructing supercells in on-lattice Monte Carlo simulations. Here crosses are used to denote the empty sites used in to map a face-centred cubic lattice onto a simple cubic lattice.

During our simulation the separation between lattice sites is one lattice unit but this is rescaled for calculations of lattice electrostatics using our DFT-optimised lattice parameters of  $\frac{a}{2} = \frac{b}{2} = \frac{5.44}{2} \text{ \AA}$ . Where the lattice parameters are divided by 2 as empty sites are placed in between ions to map the FCC structure onto an SC lattice. Figure 3.4 shows flat representations of the crystal structure, with empty lattice sites marked out by crosses. Lattice parameter  $c$  for our model will then be approximated to  $2a$ , which is very close to the DFT-optimised value of  $10.86 \text{ \AA}$ .

### 3.2.2 Monte Carlo Simulation with the Metropolis Algorithm

The Monte Carlo method can be used to calculate thermodynamic information about a system of  $N$  interacting ions represented on a 3D lattice by using classical statistics, considering only two-body forces and assuming that the potential field of an ion is spherically symmetric. If we know the positions of the  $N$  interacting ions on the lattice then the potential energy of the system can be calculated using equation 3.1, where  $V$  is the Coulombic potential between two

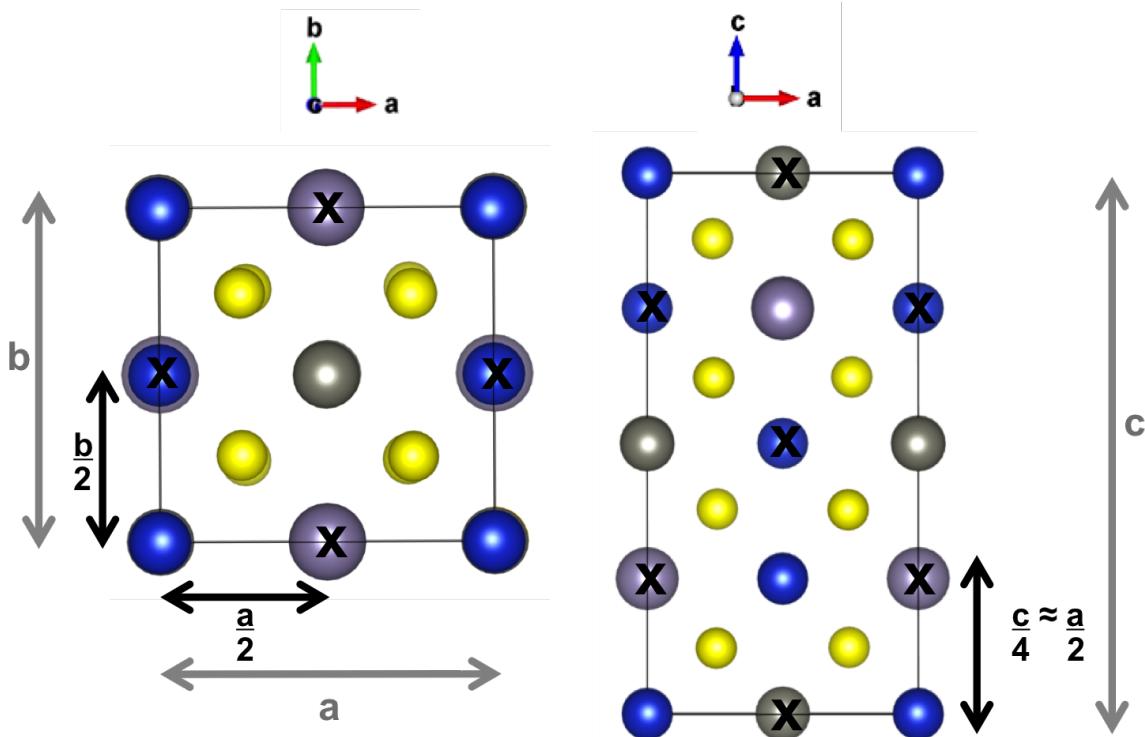


Figure 3.4: Visuals of the  $\text{Cu}_2\text{ZnSnS}_4$  crystal structure showing positions of empty sites (denoted by x's) used to map the face-centred cubic lattice of the cations onto a simple cubic lattice. Lattice parameters obtained from hybrid density functional theory geometry optimizations are  $a = b = 5.43770 \text{ \AA}$  and  $c = 10.85670 \text{ \AA}$ , and so  $c$  is approximately  $2a$ .

ions and  $d_{ij}$  is the minimum distance between ions i and j [83].

$$E = \frac{1}{2} \sum_{i=1}^N \sum_{j=1}^N V d_{ij} \quad (3.1)$$

To calculate the properties of the system, the canonical ensemble is used where the temperature, number of ions and volume are all constant. In this ensemble, the equilibrium value for any quantity of interest,  $B$ , is given by equation 3.2, where  $E_\alpha$  is the energy of the system when in state  $\alpha$  and  $p_\alpha$  is the probability of the system being in state  $\alpha$ .

$$\langle B \rangle = \frac{\sum_\alpha e^{-\frac{E_\alpha}{k_b T}} B_\alpha}{\sum_\alpha e^{-\frac{E_\alpha}{k_b T}}} = \frac{\sum_\alpha e^{-\frac{E_\alpha}{k_b T}} B_\alpha}{Q} = \sum_\alpha B_\alpha p_\alpha \quad (3.2)$$

$$p_\alpha = \frac{e^{-\frac{E_\alpha}{k_b T}}}{\sum_\alpha e^{-\frac{E_\alpha}{k_b T}}} = \frac{e^{-\frac{E_\alpha}{k_b T}}}{Q} \quad (3.3)$$

$Q$  in equation 3.2 is called the partition function. For most systems calculating the value of the partition function requires the summation over a large number of states. When applying the Monte Carlo method to a system of particles, the summation over discrete states for  $Q$  is replaced by a set of integrals. This is shown in equation 3.4 where  $U(\mathbf{r}^N)$  is the potential energy of the system which depends upon the position,  $\mathbf{r}$ , of the  $N$  interacting ions in the system and  $Z_{NVT}$  is the configurational integral [72].

$$\langle U \rangle = \frac{\int e^{-\frac{U(\mathbf{r}^N)}{k_b T}} U(\mathbf{r}^N) d\mathbf{r}^N}{\int e^{-\frac{U(\mathbf{r}^N)}{k_b T}} d\mathbf{r}^N} = \frac{\int e^{-\frac{U(\mathbf{r}^N)}{k_b T}} U(\mathbf{r}^N) d\mathbf{r}^N}{Z_{NVT}} \quad (3.4)$$

The configurational integral is over the three coordinates of each ion, as shown in equation 3.2.2. There are therefore  $3N$  coordinates that define all possible configurations of the system.

$$d\mathbf{r}^N = dx_1 dy_1 dz_1 dx_2 dy_2 dz_2 \dots dx_N dy_N dz_N \quad (3.5)$$

For a system containing several hundred ions this would be a several-hundred dimensional integral over the configuration space, which would be impractical to carry out by the usual numerical methods. The Monte Carlo method for many-dimensional integrals is used for this purpose [83]. It is conceptually easiest to think about this method for a one-dimensional integral. This method involves sampling a large number of random points within a region defined by the limits of the integral. The integrated function is then the fraction of points that fall below the curve of the function multiplied by the area of the sampled region. The value obtained becomes a better approximation to the actual value of the integral as the number of random numbers, called Monte Carlo steps (MCS), used to sample the integration region increases. [72].

The Standard Monte Carlo method for our system would involve placing each of the  $N$  ions at random positions in the lattice to define a random point in the  $3N$ -dimensional configuration space. The energy of the system would then be calculated using equation 3.1 and the configuration would then be weighted using  $e^{-\frac{U(\mathbf{r}^N)}{k_b T}}$  when obtaining the equilibrium value of  $U$ . However, many configurations are very improbable so performing this calculation for every

possible configuration would be inefficient and unnecessary to sufficiently evaluate the ensemble. The custom Monte Carlo code in this study makes use of the Metropolis modified Monte Carlo scheme [83]. In this implementation of the Monte Carlo method, instead of choosing configurations randomly and then weighting them, the Metropolis algorithm considers the relative probability of a system being in a new configuration,  $\beta$ , to that of being in the current configuration,  $\alpha$ . This is shown in equation 3.6, where  $E_\alpha$  is the energy of state  $\alpha$  and  $E_\beta$  is the energy of state  $\beta$ .

$$\frac{p_\beta}{p_\alpha} = \frac{e^{-\frac{E_\alpha}{k_B T}}}{Q} \frac{Q}{e^{-\frac{E_\beta}{k_B T}}} = e^{-\frac{E_\beta - E_\alpha}{k_B T}} \quad (3.6)$$

The relative probabilities of the two states are completely determined by the energy difference, such that if:

$$\Delta E = E_\beta - E_\alpha \leq 0 \text{ then } \frac{p_\beta}{p_\alpha} \geq 1 \quad (3.7)$$

and if

$$\Delta E = E_\beta - E_\alpha > 0 \text{ then } \frac{p_\beta}{p_\alpha} < 1 \quad (3.8)$$

The Metropolis algorithm creates a list of configurations through configuration space that has the correct probability distribution. This list is called a trajectory through configuration space. The approach involves making a trial move of the system to a new configuration, in the case of our study this would be a substitution between a Cu and a Zn ion. It is then decided if this new configuration should be added to the trajectory or not based on the probability of the new configuration relative to the current configuration. If the relative probability is  $\geq 1$ , as shown in equation 3.7, then the move is accepted and added to the trajectory. However, if the relative probability is  $< 1$  then the move will only be accepted if  $e^{-\frac{\Delta E}{k_B T}} \geq$  a random number generated between 0 and 1 [72].

### 3.2.3 Equilibration & Finite Size Effects

Our Monte Carlo model for Cu-Zn disorder is analogous to the Ising model of a magnet, descriptions of which can be found in many textbooks such as references 89 and 69. In the

case of an Ising model, the trial moves in the Metropolis algorithm are spin flips, whereas in our model the trial moves are swaps between Cu and Zn ions. In the case of the Ising model it is usually the average magnetization of the system or internal energy as a function of temperature that are the quantities of interest. In our system, it is the distribution of the electrostatic potential across the system that is of interest, as this can be related to the observed band tailing. We are also interested in the corresponding configuration of the ions (and extent of disorder) that results in such a distribution. In the case of the Ising model when, for example, determining the magnetization of a system at a given temperature, the simulation must be run for a suitably long time until the system has come to equilibrium at that temperature. This is referred to as the equilibration time and the point at which a system has attained equilibrium can be defined as being when the average probability of finding the system in any particular state  $\alpha$  is proportional to the Boltzmann weight of that state,  $e^{-\frac{E_\alpha}{k_b T}}$ . Once the system has equilibrated, the quantity of interest such as the magnetization must then be again measured over a suitably long time and averaged [89].

To gauge if a system has reached equilibrium, in the case of the Ising model, it is common practice to run the simulation for a large number of Monte Carlo steps (MCS) (where one MCS corresponds to attempting a trial spin-flip at all sites in the system once) and looking for how the value of a quantity of interest, such as the average magnetization across the system, changes with increasing number of MCS as the simulation progresses. Equilibration is often considered as the point at which the value of a quantity of interest, which initially changes by a large amount, eventually converges to fluctuating about a steady average value. An example of this is shown in figure 3.5a. This is dependent upon the principle that a system in equilibrium spends the overwhelming majority of its time in a small subset of states in which its properties take a narrow range of values [89]. In the case of our system, it is the distribution in electrostatic potential across the system that is of interest so we will look for a point after which the variance of the distribution of electrostatic potentials across the system has reached a steady value.

Provided the simulation is allowed to run for a sufficiently long time to reach this minimum configuration, the final configuration for a given system at a given temperature should always be the same, this point is illustrated in figure 3.5b. However, as this is a stochastic method,

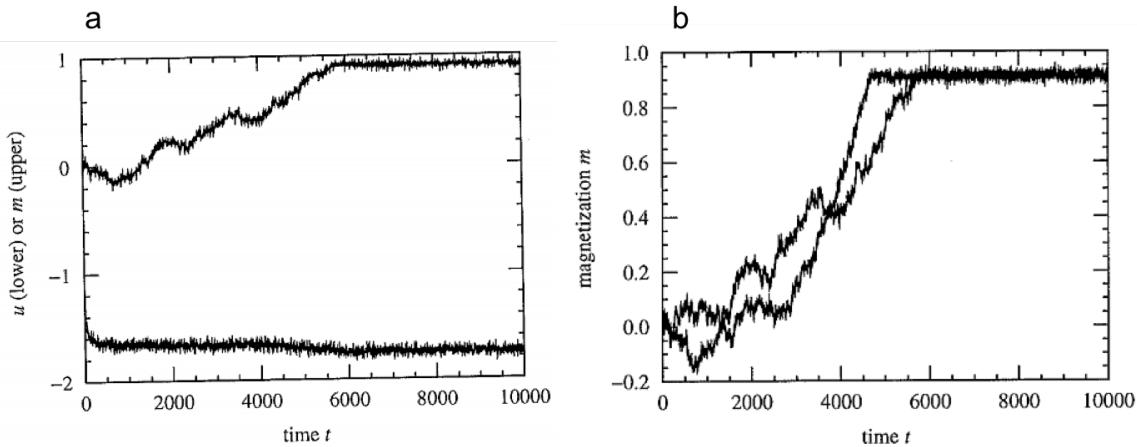


Figure 3.5: The magnetization (upper curve) and internal energy (lower curve) per site of a two-dimensional Ising model simulated using the Metropolis algorithm (a). Magnetization as a function of time for two different simulations (b). Time is measured in Monte Carlo steps per lattice site. Figures taken from 89.

making use of sampling many times with random numbers in order to determine the minimum energy configuration of the system, the trajectory to reach this final configuration will by nature be random and so we can draw no conclusions from configurations of the system until the final configuration at the particular temperature is reached. Even then we must consider the possibility of our system finding local minima instead of global minima, and therefore giving a false impression of having equilibrated. For this reason we perform multiple runs of the simulations, each seeded with different random numbers to ensure that the same final configurations, and associated equilibrium properties, are obtained.

As simulations are performed for finite lattices, in order to simulate a bulk system the edges or ‘boundaries’ of the system must be treated carefully. The boundaries can be effectively eliminated through the use of periodic boundary conditions (PBCs). In the case of an Ising model, this means that the first spin in a row interacts with the last spin in the row as if it were a nearest neighbour, and vice versa [69]. This principle is illustrated in figure 3.6. Although this procedure effectively eliminates boundary effects, the system is still characterized by the finite lattice size,  $L$ , which limits the correlation length to  $\frac{L}{2}$ . Resultant properties of the system may then differ for the bulk system than for the simulated system. We therefore perform simulations with increasing system size to look for any differences in the quantities of interest.

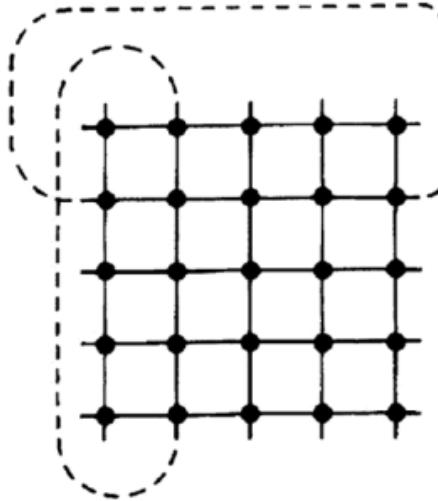


Figure 3.6: Typical periodic boundary conditions for the two-dimensional Ising model. Figure taken from 69.

### 3.2.4 Multi-Scale Approach with Density Functional Theory

$$E_{electrostatic} = \frac{q_1 q_2}{4\pi\epsilon_0\epsilon_r} e^2 \frac{1}{r} = q_1 q_2 I_{electrostatic} \quad (3.9)$$

Equation 3.9 can be used to calculate the electrostatic interaction between a pairs of ions, where  $q_1$  and  $q_2$  are the bare formal charges,  $r$  is the separation of the point charges and  $\epsilon_r$  is the bulk static relative dielectric constant. The interaction between all pairs of ions within the system are summed over when calculating the change in the energy of the system after performing a trial move in our Monte Carlo simulations. We separate out the parameter  $I_{electrostatic}$  in our simulations. The value is first calculated considering a purely classical, electrostatic case where only the bare formal charges on the ions are considered and the bulk dielectric constant of Cu<sub>2</sub>ZnSnS<sub>4</sub> is used. Using a value of 13.2 for  $\epsilon_r$  and 3.8 Å for  $r$ , which is the separation of nearest-neighbour Cu-Zn ions, gives a value of -0.284 eV for  $I_{electrostatic}$ . This treatment however only accounts for the Coulombic interaction between the point charges and neglects any changes in the electronic structure during defect formation. The screening effect of the electronic structure would be more significant for the microscopic dielectric constant than for the bulk, macroscopic dielectric constant. In this study therefore we scale the interaction energy,  $I_{interaction}$ , in the simulations by comparing the formation energy of a nearest-neighbour Cu-Zn anti-site defect pair calculated using the classical code GULP to that obtained using quantum

mechanical hybrid-density functional theory and the VASP code, where effects of the electronic structure are included in the calculation. We found that the defect formation energy obtained using VASP was approximately 1.5 times that obtained with GULP, we therefore scaled the interaction energy by the same amount and so  $I_{DFT} = 1.5 \times I_{electrostatic} = -0.425$  eV. Through doing this we aim to scale the macroscopic dielectric constant to be closer to the value of the microscopic dielectric constant.

### 3.2.5 Quantification of Disorder Using Radial Distribution Functions

- Brief overview of what an RDF is
- See new lab book and make figures to explain
- Reproducing GS: Cu-Zn RDF first peak to describe Cu Zn Cu layer, Cu-Sn RDF first peak to describe Cu Sn Cu layer nearest neighbours
- Using RDFs from initial, perfectly ordered system as a reference point: Cu-Sn and Cu-Zn perfectly overlayed, but expect to separate with disorder. First peak (near-neighbours) for Cu-Sn should remain same as Sn is fixed, but Cu-Zn first peak will change as will subsequent peaks for both.
- Need to normalize to recover coordination number for first peak?
- Increasing intensity of new nearest neighbour Cu-Cu and Zn-Zn peaks for disordered systems with increasing disorder

### 3.2.6 Band Tailing from the Distribution of Electrostatic Potential

May later move this to further work so methodology not necessary? + need to alter end of intro section on CZTS performance bottlenecks

### 3.3 Calculation of Intrinsic Band Gap Broadening in Cu<sub>2</sub>ZnSnS<sub>4</sub>

Discuss MAPI paper, calculating contribution to broadening from acoustic lattice vibrations, explicitly discuss calculations of elastic constant (bulk elastic moduli gives velocity of sound wave for LA, see Yu and Cardona pg 110) and deformation potential.

### 3.4 Calculation of Optoelectronic Properties of Candidate Solar Absorber Materials

- Hybrid geometry optimization with lattice fixed (but ions allowed to relax), starting from high quality XRD data and our own for stephanite performed by Prof Mark Weller (refer to original sources)
- Hybrid band structure calculations with FHI-aims
- Calculation of effective masses?

See MRes project2 write up + read up on SLME analysis and discuss this? Or discuss this just in further work?

# Chapter 4

## Performance Bottlenecks in $\text{Cu}_2\text{ZnSnS}_4$

### 4.1 Thermodynamic Disordering of Cu & Zn Ions in $\text{Cu}_2\text{ZnSnS}_4$

#### 4.1.1 Spatial Extent of Disorder Amongst Cu and Zn Cations

- Recovery of kesterite ground state at T=50k? (Cu-Zn and Cu-Sn layers, see lab book pg 2): visuals of structure in VESTA and RDF of Cu-Zn and Cu-Sn pairs
- Visuals of configs from eris and RDFs across T range

#### 4.1.2 Band Tailing due to Fluctuations in Electrostatic Potential

R plots for distributions of electrostatic potential of Sn

### 4.2 Formation Energy of Sulfur Vacancies

We investigate the formation energy of charge neutral sulfur vacancies ( $V_S^0$ ) as a function of the sulfur chemical potential, which itself is a function of temperature and pressure. We therefore

can assess the formation energy of the vacancy under typical annealing conditions. Work from Scragg et al showed that annealing out Cu and Zn disorder can be a very time consuming process, therefore for most practical purposes some disorder will be ‘frozen in’ after annealing. Typical annealing conditions for  $\text{Cu}_2\text{ZnSnS}_4$  are at ?? K and it has been shown that lower pressures are more optimal for the sulfide (whereas higher pressures are better for the selenide) \*\*cite Adam?\*\*. This is due to the allotropes of S?

On-going calculations are being performed for the charged sulfur vacancies ( $\text{V}_S^{+1}$  and  $\text{V}_S^{+2}$ ) so that the minimum energy defect, accounting for all possible charge states, across the temperature and pressure range can be determined.

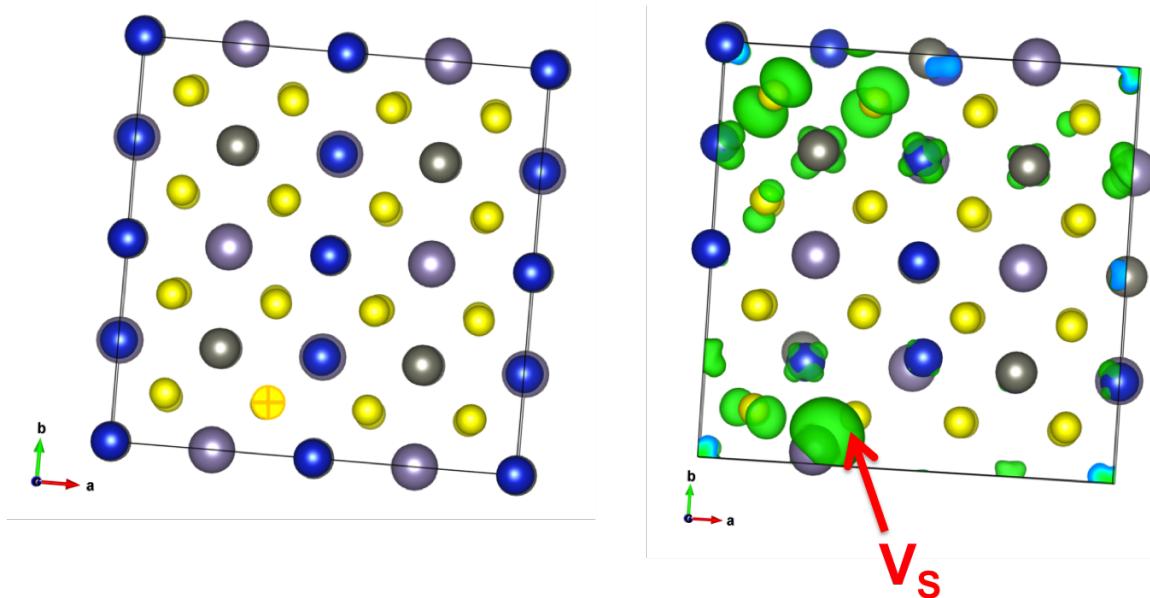


Figure 4.1: Perfect  $\text{Cu}_2\text{ZnSnS}_4$  supercell with S anion removed to form a sulfur vacancy ( $\text{V}_S$ ) indicated by a crosshair (left) and the calculated partial charge density of two excess electrons present for the charge neutral  $\text{V}_S$  (right).

## 4.3 Intrinsic Band Gap Broadening from Lattice Vibrations

For CZTS we find that the band gap decreases with temperature as a result of lattice dilation, which a trend observed in most typical semiconductors such as Si, Ge and GaAs. \*see slide show results\* – discuss deformation potential, elastic constant and band gap broadening as a function of T (fundamental intrinsic limit to charge-carrier mobilities) + discuss than we calculate just one contribution to the broadening currently to compare to expt to determine how much is intrinsic and how much is defect-related. Although we calculate only gamma-acoustic as opposed to LO? see MAPI paper eqn1

‘typical semiconductors such as Si, Ge and GaAs, for which the bandgap decreases with temperature as a result of lattice dilation<sup>26,37</sup>’ [141]

‘electronphonon coupling at room temperature is almost solely governed by deformation potential scattering with acoustic phonons, which is known<sup>18,25</sup> to theoretically result in  $m\bar{v}T^{3/2}$ ’ [141]

# **Chapter 5**

## **Optoelectronic Properties of Sulfosalt Materials**

### **5.1 Band Structures & Band Gaps**

### **5.2 Effective Masses**

N.B. In material properties section methodology for this calculation is referred to in the methodology section (may need to check if this gets cut out later)

# **Chapter 6**

## **Conclusions**

### **6.1 Performance Bottlenecks of Cu<sub>2</sub>ZnSnS<sub>4</sub> Solar Cells**

### **6.2 Potential of Sulfosalt Materials for Solar Cell Devices**

### **6.3 Future Work**

- Further work on S vacancies? (discuss defect formation E as a func of S chemical potential and charge corrections for charged defect states)
- More properties of sulfosalt materials (explicitly discuss SLME approach of predicting PV efficiency from dielectric function) + discuss calculations to predict FE?
- Many possible extensions with eris:
- Further investigations with eris? Cu-poor CZTS?
- Extend eris Hamiltonian to next nearest neighbour interactions (likely to be important for long ranged coulomb interactions)

- Simulate larger systems with eris - domain formation and band gap fluctuations?
- Next major project:
- Simulations to determine most likely surface terminations to inform exptl strategies for surface passivation?
- QM/MM surface defect simulations? - mention collaboration with PVTEAM?

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