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## DIPLOMARBEIT

# Modellierung der Formationsentropie der Leerstelle in Silizium

Ausgeführt am Institut für angewandte Physik der Technischen Universitat Wien in Zusammenarbeit mit Institut de Recherche et Développement sur l'Énergie Photovoltaïque (IRDEP) / Institut Photovoltaïque d'Île-de-France (IPVF)

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> > > Wien, am 28.10.2015



## MASTER THESIS

# Modeling of the Formation Entropy of the Silicon Vacancy

conducted at the Institute of Applied Physics at the Vienna University of Technology in collaboration with Institut de Recherche et Développement sur l'Énergie Photovoltaïque (IRDEP) / Institut Photovoltaïque d'Île-de-France (IPVF)

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October 28, 2015

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# Abstract

A large amount of the performance of a solar cell device is governed by point defects and impurities within the material. The computation of defect formation energies therefore allows the calculation of numerous macroscopic quantities such as diffusion coefficients, charge carrier or defect concentrations.

In the last decades, first-principle calculations have emerged as a powerful tool to compute formation enthalpies of point defects. However, it has been so far difficult to include temperature dependence within such calculations. An approach to solve this issue is the inclusion of temperature through the calculations of formation entropies. Until now large discrepancies for the value of the formation entropy can be found in the literature for systems as simple as the silicon vacancy. The interest of this work therefore lies in establishing and testing a methodology to compute formation entropies to reach the next level in accuracy for point defect calculations.

In this context, first principle density functional theory methods are used to study the energetics of various structural configurations of the silicon vacancy in charge states ranging from -2 to +2. The harmonic phonon frequencies and the vibrational formation entropy are calculated using the frozen phonon method. Moreover, the literature on different computational models used to calculate the formation entropy is reviewed.

For the silicon vacancy, three stable charge states (neutral, +2 and -2) are found that exhibit different symmetry configurations in their ground state structure. Moreover, the neutral silicon vacancy undergoes a Jahn-Teller distortion from a  $T_d$  to a  $D_{2d}$ symmetry configuration. For the neutral vacancy a formation entropy of  $-2 k_B$  is obtained for  $T_d$  and  $-3 k_B$  for  $D_{2d}$  at high temperatures. Extensive comparisons with several theoretical and experimental studies show that the conducted calculations are heavily impacted by finite size effects. Additionally, it is concluded that a high precision is required for real space projectors and sampling of the **k**-point and **q**point grid. Furthermore, it is found that different symmetry configurations trigger different formation entropies and that frequency regions contribute differently to the total formation entropy.

# Kurzfassung

Die Effizienz einer Solarzelle wird zu einem großen Anteil durch die im Halbleitermaterial vorkommenden Punktdefekte bestimmt. Die Berechnung der zur Defektbildung notwendigen Energie kann daher Aufschluss über makroskopische Größen wie Diffusionskoeffizienten, Ladungsträger und Defektkonzentrationen geben. Firstprinciple Methoden haben sich über die letzten Jahrzehnte als Standard für die Berechnung der Enthalpie der Defektbildung etabliert. Allerdings hat es sich bisher als schwierig herausgestellt Temperaturabhängigkeiten mit dieser Methode zu berücksichtigen.

Ein Ansatz zur Lösung dieses Problems ist das Miteinbeziehen der Berechnung der Defektbildungsentropien. Jedoch wurde bisher kein Konsens gefunden, wie diese zu berechnen seien. Selbst für einfache Systeme, wie für die Leerstelle in Silizium, werden verschiedenste Werte in der Literatur berechnet. Deshalb ist es von Interesse einen Formalismus zur Berechnung der Defektbildungsentropien, der die Bildung von Punktdefekten genauer beschreiben kann zu bestimmen und zu testen.

In diesem Zusammenhang wird die first-principle Dichte Funktional Theorie verwendet, um den elektronischen Grundzustand und die elektronische Grundstruktur der Leerstelle in Silizium für verschiedene Ladungszustände zu bestimmen. Die 'frozen phonon' Methode wird herangezogen, um die harmonischen Frequenzen der Phononen und die Defektbildungsentropie zu berechnen. Außerdem wird ein kurzer Überblick über die verschiedenen bereits entwickelten theoretischen Modelle gegeben.

Für die Leerstelle in Silizium werden drei stabile Ladungszustände gefunden (neutral,+2 und -2), die in ihrem Grundzustand verschiedenste Symmetriekonfigurationen einnehmen. Des Weiteren erweist es sich als energetisch günstig für die neutral geladenen Leerstelle ihre Symmetrie über den Jahn-Teller Effekt von  $T_d$  auf  $D_{2d}$  Symmetrie zu erniedrigen. Es ergeben sich eine Defektbildungsenropie von -2 k<sub>B</sub> für  $T_d$  und -3 k<sub>B</sub> für  $D_{2d}$  Symmetrie bei hohen Temperaturen.

Der Vergleich mit vielzähligen theoretischen und experimentellen Studien zeigt, dass im Allgemeinen Berechnungen stark von der endlichen Größe der verwendeten Simulationsbox abhängen. Außerdem wird klar, dass eine hohe Präzision für die Projektoren zwischen realem und reziprokem Raum und für die Integration über  $\mathbf{k}$ - und  $\mathbf{q}$ -Raum für akkurate Berechnungen unabdingbar ist. Schlussendlich wird erkannt, dass verschiedene Symmetriekonfigurationen zu unterschiedlichen Defektbildungsentropien führen und dass einzelne Frequenzdomäne unterschiedlich zur totalen Defektbildungsentropie beitragen.

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# 1 Introduction

The increasing consumption of non-renewable energy sources has been voted one of the top ten global issues to tackle in our lifetime by the United Nation's Global Action Forum forum in 2015 [1]. The development of affordable, inexhaustible and sustainable energy systems is therefore one of the most important challenges facing mankind today and in the near future.

In this context, solar energy has become an interesting technology to move towards renewable energy sources. It enjoys a glowing outlook due to falling solar energy costs and gains in efficiency.

In the following section, the chances of solar energy generation will be highlighted and the role of point defects and impurities will be introduced.

### 1.1 Why Solar Energy?

The sun has an impressive renewable energy potential: everyday a power of 1.362kW per m<sup>2</sup> reaches the Earth from the Sun ( $D_0 = 1.362$  kW per m<sup>2</sup> is called the solar constant [2]). Subsequently, one can deduce than an outstanding potential energy of approximately 23000 TW-years [3] reaches the Earth every year. In comparison, the world's primary energy supply in 2012 of electricity and fossil energy amounted to 18 TW-years (corresponding to 155 500 TWh of energy or 13371 Mtoe [4]).

But how do other energy sources stand in comparison? Figure 1 shows a comparison between the known reserves of finite fossil and nuclear resources and the yearly potential of renewable alternatives.



Figure 1: Energy spheres - The volume of each sphere represents on the left the total amount of energy recoverable per year from renewable sources and on the right the known finite reserves of non-renewables [3, 5, 6]

One can easily notice that the solar resource is orders of magnitude larger than all other reserves together. If one wants to meet the world's energy demand by using wind and biomass, the two sources would almost have to be pushed to the edge of their exploitable potential. On the other hand, only a small fraction of the sun's potential would be sufficient to meet the same requirements. Finite reserves like coal and uranium are still vastly endogenous, but far from limitless. Therefore, theoretically a big portion of the consumed energy per year could be supplied by solar energy. However, the world's current total primary energy consumption tells a different story.

In 2013, 82% of the worlds energy supply was derived from coal, oil and gas [4]. At the same time our global annual consumption of 18 TW-years rose at a rate of 2.3% [6]. According to the IEA Key World Energy Statistics [4], in 2012 the renewable energy share of the total primary energy supply made about 13% (see Figure 2). A large share of this amount was generated by traditional biomass and biofuel, whereas only 3.5% did come from modern renewable energies like hydro, wind, solar and biomass heat [7]. Within the global electricity generation renewables had a share of 22% in 2012 [8].



Figure 2: World total primary energy supply and the renewable energy share in 2012 [4,7]

Assuming the world's energy consumption continues to grow by two percent annually [6], fossil and nuclear reserves which today represent an energy source of 1700 TW-y [3], will be depleted around 2080 and the world will be dependent on alternative energy sources. Looking back at Figure 1 the importance of solar energy ultimately derives from the lingering long-term threat of climate change due to increased  $CO_2$  emissions. It is a technology that promises to sustain the world's long-term energy requirements while reducing  $CO_2$  emissions.

To get an estimate on what it would mean to meet the world's energy demand with current solar cell technologies, one can calculate the following. Under Standard Test Conditions (STC: AirMass = 1.5,  $T = 25^{\circ}$ C [9]) a radiation intensity of 1000 W strikes 1 m<sup>2</sup> of land on Earth. Considering an area that has 250 sun days per year and 8 hours of daylight, one obtains 2000 sun hours per year (e.g. Vienna's annual sun hours: 1930 h [10]). Current commercially available solar panels have an efficiency  $\eta$  of around 20%. All together this yields a power of 0.2 kW/m<sup>2</sup> and a capacity of 400 kWh per square meter for a solar panel. Using this capacity the surface of a solar panel necessary to power the whole world would be about 400 000 km<sup>2</sup> big. This is comparable to the size of Spain or 4 times the size of Austria or 1/18 of the size of the Sahara desert. However, solar technology still has to overcome the

obstacles of being integrated into a network of existing electricity systems on a large scale. One problem thereby is the intermittent supply of electricity of solar resources which are not continuously available and do not produce power at night.



Figure 3: Size of a solar panel to meet the world energy consumption would be  $400\ 000\ \text{km}^2$ , which is approximately 4-times the size of Austria

A commonly used term to economically compare different energy generation solutions is the levelized costs of electricity (LCOE). The LCOE [11] represent the netto value of the unit-cost of electricity over the lifetime of a power generation plant. The LCOE can be calculated as follows

$$LCOE = \frac{CAPEX + OPEX}{EP}$$
(1)

where CAPEX are the capital expenditure and investment costs, OPEX are the operations, maintenance and fuel costs and EP is the electricity production (in kWh). In the case of photovoltaic CAPEX are higher than for fossil energies, while one does not have to account for fuel cost when calculating OPEX. In Figure 4 the levelised costs of solar electricity are shown for different countries. On the contrary to its poor share in the total energy mix solar energy has very well become a competitive alternative to conventional energy sources in certain areas. Especially in sunny places or places where conventional electricity is expensive. To take some examples from Figure 4a in China, India and the US the LCOE can range around 100 USD/MWh.

In addition to the levelized costs of electricity, it is crucial to put into perspective the way prices are set. The competitiveness of solar energy depends on the cost and value of energy in the respective market where it is sold. Markets in China, the US or India may lead to various marginal costs of electricity depending on policies and regulations.

To compare the LCOE for PV to other energy reserves in Figure 4b the LCOE for different energy sources in Germany is shown. One can see that photovoltaic technologies are almost at the same level as conventional energy resources. Moreover, it is predicted that PV utility-scale power plants in Germany will drop below the average LCOE for all fossil fuel power plants by 2030 [12].



Figure 4: Levelised cost of Electricity (LCOE): (a) for solar electricity by region (USD/MWh), Source: Bloomberg New Energy Finance [13] and (b) LCOE of renewable energy technologies and conventional power plants of Germany in 2013, Source: Frauenhofer Institut for solar energy systems [12]

Generally, solar energy enjoys a glowing outlook due to falling energy costs and gains in efficiency in recent years. In 2013 PV power generation grew by 30% [6] and PV prices reported a drop of 50% - 70% per installed watt [14]. In fact during the last 40 years one could observe a very constant relationship between the cost and the deployment of solar panels. The Swanson law [15] states that with every doubling of production solar panel costs fall by 20%.

One obstacle PV technologies still have to overcome are their relatively low efficiencies of large scale solar panels. Although theoretically, only an hour of sun provides enough energy to power the world for a year, it is impossible to capture all energy due to limitations in efficiency. The efficiency  $\eta$  of an energy generating device is defined by

$$\eta = \frac{\text{Useful energy output}}{\text{Energy input}} \tag{2}$$

For example the efficiency of a solar cell is defined as the incident solar power from the sun  $P_{light}$  and the usable converted amount of electrical power  $P_m$ .

$$\eta_{solar} = \frac{P_m}{P_{light}} \tag{3}$$

According to the Carnot theorem [16] the maximum efficiency  $\eta_{Carnot}$  of a moving solar cell device is 85% and can be calculated by

$$\eta_{Carnot} = 1 - \frac{T_1}{T_2} \tag{4}$$

where  $T_1$  is the temperature of the solar cell and  $T_2$  the temperature of the sun. However, practical efficiencies today are still far from the theoretical limit of 85% due to reflectance inefficiency, charge carrier separation and conductive inefficiencies. Current commercially available large scale photovoltaic (PV) technologies have efficiencies of 16 - 20% on average. Record efficiency of a large scale solar cell panel is 25.6% (2014 Panasonic) and the record efficiency for a small scale solar cell obtained in the laboratory is 46% (2015 Frauenhofer ISE and Soitec [17]). It is known that the efficiency of a solar cell is highly influenced by the charge carrier lifetime properties to extract currents [18, 19]. The lifetime of the charge carriers is influenced by the defect structure of the material. Due to defects in the bulk material and on surfaces of a solar cell material its charge carrier lifetime and therefore its efficiency is altered by the presence of defects. It is therefore important to be able to control the formation of defects and impurities in the material.

### **1.2** The role of defects and impurities in solar cell materials

The efficiency of a solar cell device can be significantly altered by the introduction of point defects and impurities. Some defects can be beneficial and desired when they provide a free charge carrier of a certain type to the system leading to an increase in conductivity. On the other hand, their presence can be unintentional and harmful when they recombine with the charge carriers in the solar cell yielding lower device efficiencies.

In semiconductor devices, the intentional incorporation of impurities is called doping and can currently be regulated with high accuracy, especially in silicon. When exploiting semiconductor materials one needs to be able to control the formation of defects. However, the experimental investigation of point defects is typically difficult and can sometimes only be achieved by an ingenious combination of different techniques [20,21]. With the advent of numerical methods and powerful computers, theoretical modeling has emerged as a predictive tool to complement experiments.

A formalism based on the Gibbs free energy of forming a defect allows the calculation of point defect structures and concentrations. Currently, the energetics of point defects are mostly studied using first principle techniques. Due to the importance of this methodology several review papers have been published [22,23]. This methodology has been quite successful in calculating electric properties and formation enthalpies of native and impurity defects. However, those defect calculations are mostly conducted assuming 0 K for the temperature.

For several years, temperature dependent contributions to the formation energy were neglected because of their high computational effort. However, the formation of defects is triggered by temperature such as the defects encountered during thin film growth like annealing or evaporation.

especially during high temperature processing conditions like annealing or evaporation the concentration and formation of defects depend heavily on temperature. Several recent studies [24–26] claim that the formation entropy of a defect cannot be neglected and can add a term as high as 1.3 eV to the defect formation energy at elevated temperatures [27]. It is therefore thermodynamically necessary and correct to include the formation entropies, or in other words "without entropy to complement energy, thermodynamics would have the impact of one hand clapping" [28] . Consequently, the creation of a computational methodology to calculate the formation entropy is a crucial step to reach the next level in accuracy of point defect computation. The inclusion of formation entropies promises a better prediction of the experiment and a deeper insight on the formation of point defects. Furthermore, it will supply knowledge on how to create higher efficiency solar cells. In this work, at first a theoretical overview on the role of point defects and impurities in solids is given to supply the reader with a basic review on semiconductor physics. The reader will learn about the thermodynamic formalism that allows the investigation of physical properties of point defects, indicating how thermodynamic quantities like formation energy and entropy can be derived. Within Chapter 3 the computational approach to this formalism is explained by laying out the theoretical background on electronic ground state and phonon calculations. This is done by a description of density functional theory (DFT) and the frozen phonon method.

In Chapter 3.3, the literature on computational models for calculating the formation entropy is reviewed. Subsequently, phonon calculations on the silicon bulk material are conducted using DFT and the frozen phonon method. Afterwards, the methodology is tested by carrying out a systematic study of the formation entropy of the silicon vacancy in its different structural modifications.

Finally, in Chapter 7 an overview on the conducted research is given and results and findings are summarized.

# 2 Theory on Defects and Impurities in Solids

Semiconductors are useful for device applications because of the possibility to modify their electrical properties by incorporating impurities and defects. In fact, defects can have a huge impact on the electronic properties of semiconductors.

### 2.1 Energy Band structure

The behavior of the electrons in a solid can be described within the model of the electronic band structure. In a single, isolated atom electrons occupy discrete energy levels. In a crystal, atoms are not isolated anymore and their allowed energy levels are smeared out into energy bands. Those energy bands can be occupied by electrons. In between those bands lie energy states that electrons cannot occupy called energy band gaps. The highest energy band that is occupied by electrons is called the Valence Band Maximum (VBM). The conduction band (CB) quantifies the band of orbitals above the valence band (VB) that is high in energy and unoccupied. In between the CB and the VB lies an energy gap, the so-called band gap.

### 2.2 Semiconductors

Semiconductors are classified according to their conductivity intermediate between the conductivity of metals and insulators. Alternatively, semiconductors can be defined regarding their energy band gap  $E_g$  for electronic excitations. The bestknown semiconductor is probably silicon, whose band gap is about 1.1 eV large. Metals are materials with zero band gaps, while insulators are mostly known to have an energy gap larger than 3 eV [29]. It turns out that materials with large band gaps are difficult to obtain with a conductivity similar to the one of metals. In a semiconductor at T = 0 K the VB is filled with electrons and the CB states are unoccupied. For T > 0 K conduction can take place if electrons acquire enough energy to overcome the band gap, leaving a hole behind in the VB. In an intrinsic pure semiconductor the energy required by the electrons to do so is the energy gap  $E_g$ . Such properties do not exist in metals and thermal activation of electrons can be difficult in insulators.

#### Fermi-Level

The occupation of an energy state by a given particle is defined by the Fermi-Dirac statistics. In semiconductors, particles occupying those energy states can be electrons or holes, both are fermions. The Fermi-Dirac distribution f(E) gives the probability that an electronic state at energy E is occupied by an electron. Similarly, 1 - f(E) gives the probability of finding a hole at the energy E.

$$f(E) = \frac{1}{1 + exp((E - E_F)/k_B T)}$$
(5)

In equation (5),  $k_B$  is the Boltzmann constant, T is the Temperature and the Fermi-Level  $E_F$  is a chemical potential whose position depends on the electron and hole carrier concentrations n and p. In an intrinsic semiconductor the Fermi-Level lies in the vicinity of the middle of the band gap due to the same number of electrons and holes (n = p). If however the concentration of free holes p increases the Fermi-Level will shift towards the valence band maximum (VBM -  $E_V$ ). A higher electron concentration n in the system will lead to a shift of the Fermi-Level towards the conduction band minimum (CBM -  $E_C$ ).

#### Carrier concentration

At first the case of an intrinsic semiconductor is considered where no impurities are added to the material. In an intrinsic semiconductor the number of electrons n is equal to the number of holes p, the intrinsic concentration  $n_i$ ,

$$n = p = n_i \tag{6}$$

$$n = \int_{E_C}^{\infty} N_e(E) f(E) dE \tag{7}$$

The integral in (7) goes over the conduction band and  $N_e(E)$  is the total number of allowed energy states per unit energy per unit volume:

$$N_{e,h}(E) = 4\pi \left(\frac{2m_{e,h}}{h^2} E^{\frac{1}{2}}\right)$$
(8)

whereas  $m_{e,h}$  is the electron or hole mass. To obtain equation (8) the parabolic approximation is applied, assuming that energy states can be expressed by  $E = \frac{\hbar^2 k^2}{2m_{e,h}}$ . In the same manner, the number of holes p is calculated:

$$p = \int_{-\infty}^{E_V} N_h(E) \left[ 1 - f(E) \right] dE$$
(9)

For non-degenerate and intrinsic semiconductors the integrals in (8) and (9) can be approximated by Boltzmann Statistics [30], whereas  $N_C$  and  $N_V$  represent the effective density of state in the CBM and VBM.

$$n = N_C exp(E_F - E_C/k_B T) \tag{10}$$

$$p = N_V exp(E_V - E_F/k_BT) \tag{11}$$

This approximation applies for low doping concentrations and the Fermi-Levels lying several  $k_B T$  below the CBM. For an intrinsic semiconductor  $n_i$  equals

$$n_i^2 = N_C N_V exp(E_q/k_B T) \tag{12}$$

For degenerate semiconductors, equation (6) does not apply anymore and one should rely on the exact expressions (7) and (9).

#### Doping

In semiconductors, doping or native defects can modulate the electrical properties. The term doping refers to the intentional or unintentional incorporation of impurities and defects in the lattice. Dopants are called donors when they donate an electron to the system and render it n- type. If they accept an electron resulting in an extra hole in the system they are called acceptors and render the material p-type.  $N_D$  stands for the number of donor dopants and  $N_A$  for the number of acceptors.

#### Charge neutrality

However, not all impurities introduced into a material get ionized. For instance, the number of ionized donors  $N_D^+$  is given by

$$N_D^+ = \frac{N_D}{1 + g_D exp((E_F - E_D)/k_B T)}$$
(13)

and depends on the respective impurity energy level  $E_D$  and on  $g_D$  the ground state degeneracy factor. In a material, the charge neutrality equation must be valid.

$$p + N_D^+ = n + N_A^- \tag{14}$$

The charge neutrality equation (14) can be used to calculate the Fermi energy  $E_F$ . For example if one considers a donor impurity with the concentration  $N_D$ , at relatively high temperatures the number of electrons n is approximately equal to the number of ionized donors  $N_D^+$ .

$$n \approx N_D^+ \tag{15}$$

If one knows  $N_D$ ,  $E_D$ ,  $E_C$ ,  $N_D$  and T one can calculate  $E_F$  by comparing equation (10) for n with equation (13) for  $N_D^+$ .

### 2.3 Crystallographic defects

Before the probability of forming a defect and its effects on the electronic band structure is explained, a short overview on crystalline solids and the different crystallographic defects will be given. A crystalline solid is characterized by a periodic arrangement of atoms. The smallest subdivision which forms the entire crystal lattice when periodically arranged is called the primitive cell (for a more detailed explanation see 2.7).

A common classification is done regarding the dimension of the defects in point and line defects. Point defects are isolated atoms and can further fall into the following categories:

Vacancy: A vacancy is a missing atom A the periodic structure A – symbol  $V_A$ Interstitial: An interstitial empty site is occupied by atom A – symbol  $I_A$ Substitutional or antisite: A host atom A is replaced by Atom B – Symbol  $B_A$ 

A detail specific to semiconductors is that point defects are more complex as they can occur in different charge states that exhibit different symmetries [31].

Defects are called intrinsic or native, if they do not involve foreign atoms otherwise they are called extrinsic.

#### 2.4 Formation enthalpy of a defect

Before one turns to the calculation of the formation enthalpy of a defect, one should take a closer look at the inherit thermodynamics of the problem. The thermodynamic enthalpy H is commonly given by

$$H = U + pV \tag{16}$$

whereas U stands for the internal energy of the system, p stands for pressure and V for volume. The formation enthalpy for forming a defect  $\Delta H_f$  for constant pressure p and temperature T can be written as

$$\Delta H_f^{p,T} = \Delta U_f^{p,T} + p \Delta V_f^{p,T} \tag{17}$$

where  $\Delta V_f^{p,T}$  is the formation volume of the defect. The internal energy U consists of the static part the total energy at T = 0K  $E_{tot}$  and the term  $U_{vib}$  which is caused by lattice vibrations and accounts for temperature dependence and entropy contributions.

$$U = E_{tot} + U_{vib} \tag{18}$$

The next steps shortly outline the thermodynamic method that allows the calculation of the formation enthalpy  $\Delta H_f(D,q)$  of the defect D in its charge state q. Additionally, Figure 5 displays a visual illustration of the following equation:

$$\Delta H_{D,q}(E_F,\mu) = \underbrace{\left[E_{tot}(D,q) - E_{tot}(bulk)\right]}_{\mathbf{a}} + \underbrace{\sum_{i} n_i \mu_i}_{\mathbf{b}} + \underbrace{q(E_{VBM} + \Delta E_F)}_{\mathbf{c}} \tag{19}$$

a) Total energies The first term is the difference between the total energy  $E_{tot}(D,q)$  of the crystal containing the defect D in its charge state q and the total

energy of the perfect host crystal  $E_{tot}(bulk)$ . This difference gives the energy that is needed to form a defect. Those total energies can be obtained from electronic structure calculations based on Density Functional Theory (DFT) as explained in section 3.1.

b) Chemical potentials The number of atoms of type *i* that are involved in the defect D is defined by  $n_i$ . The second term takes into account the chemical potentials  $\mu_i = \mu_i^0 + \Delta \mu_i$  which reflect the growth conditions. Hereby,  $\mu_i^0$  is the bulk chemical potential of atoms of type *i* under standard thermodynamical conditions (STP: 273.15 K and p = 1 bar). The difference  $\Delta \mu_i$  of the chemical potential  $\mu_i$  and that of the elemental material  $\mu_i^0$  has an upper limit for growth conditions that are rich of atom *i*:  $\Delta \mu_i \leq 0$ .

The integer  $n_i$  can be  $n_i = +1$  if an atom is removed from the perfect host crystal (e.g.: vacancy) and  $n_i = -1$  if an atom is added to the perfect crystal (e.g.: interstitial defect).

This term b) can also be viewed as the energy of the reservoirs with which the atoms of the defect are being exchanged. The chemical potential  $\mu_i^0$  can be calculated by the computational method FERE (Fitted elemental-phase reference energies) [32].

c) Charge effects Similarly, in the third term the 'charge reservoir' is represented by its chemical potential, the Fermi Level  $E_F$ .  $E_F$  is conventionally defined with respect to the energy  $E_{VBM}$  of the VBM given by  $E_F = E_{VBM} + \Delta E_F$ . The charge state of a defect is indicated by q. If an electron is removed q = +1, if an electron is added q = -1 and for a neutral defect q = 0. The slope of the formation enthalpy is positive q > 0 for a donor defect and negative q < 0 for an acceptor defect, whereas q corresponds to the charge of the ionized defect. For a neutral defect  $\Delta H_f$  is not dependent on  $E_F$  and is represented as a horizontal line.



Figure 5: Illustration of the formalism used to calculate defect formation enthalpies

The concentration of impurity dopants in a material is related to the different terms of equation (19) and several reviews have been published explaining the factors limiting the doping of semiconductors [22, 33].

A high free carrier concentration will require a high dopant impurity. This is however

limited by the solubility of the material which defines how many incorporated impurities the material can sustain at thermodynamic equilibrium. One can enhance dopant solubility via control of the chemical potentials in equation (19).

Of course the amount of free charge carriers will also depend on how many dopants can actually be ionized, and therefore on the ionization energy.

Furthermore, Fermi-Level induced compensation effects can limit the doping as well. Equation (19) shows that for a donor defect q > 0 and the energy to form a donor defect increases with  $E_F$ . When a donor defect is introduced it adds electrons to the free-carrier charge reservoir whose energy is  $E_F$ . In the same way, acceptor defect formation energies decrease with increasing  $E_F$ . So when doping materials n-type the formation energy of native acceptors will decrease until they form spontaneously and take away electrons as free charge carriers.

#### 2.4.1 Defect formation enthalpy diagram

An example of a diagram for the defect formation enthalpy  $\Delta H_f$  with respect to the Fermi-Level  $E_F$  is shown in the following Figure 6 in the case of intrinsic and extrinsic point defects in ZnO. The Fermi Level is hereby referenced to the VBM. Visibly,  $\Delta H_f$  in Figure 6 is strongly Fermi-Level dependent as the defects are shown in their different charge states.



Figure 6: Defect formation enthalpies with respect to the Fermi energy  $E_F$  in ZnO obtained by ab-initio calculations taken from [34]

In the case of ZnO the formation enthalpy of donor defects is found to be lower indicating a native n-type conductivity. It is also shown that chlorine is a good candidate to dope the ZnO [34]. For a Fermi energy  $E_F$  from 1.5 eV to 3 eV the dominant donor is an antisite defect of a chlorine atom on an oxygen atom. The chlorine atom prefers the antisite defect  $Cl_O$  over the chlorine interstitial  $Cl_i$  due to its lower formation enthalpy.  $Cl_O$  acts as a n-type dopant as it remains ionized over the full range of the Fermi energy. This will lead to more free electrons being available to the system and a shift of the Fermi Level towards the CBM. However, the n-type doping of chlorine is limited by zinc vacancies  $V_{Zn}$ .

The stabilization of different charge states as a function of the Fermi level is called amphoterism. Depending on the location of the Fermi energy defects occur in different negative or positive charge states. For example, the chlorine interstitial defect Cl<sub>i</sub> can occur in four different charge states (q = -1, 1, 2 or 3) for different values of  $E_F$ .

#### 2.4.2 Transition Levels

Charged defects will occur in the energetically most favorable charge state regarding the position of the Fermi Level. The transition level between charge state  $q_1$  to  $q_2$ is the position of the Fermi-Level at which the formation enthalpy of the differently charged defect are the same  $\Delta_f H(D, q_1) = \Delta_f H(D, q_2)$ . The transition level  $\varepsilon(q_1/q_2)$ is then given as:

$$\varepsilon(q_1/q_2) = \frac{\Delta_f H(D, q_1) - \Delta_f H(D, q_1)}{q_2 - q_1}$$
(20)

A term often found in the literature are shallow and deep dopants. Deep dopants refer to impurity energy levels  $\varepsilon(q/q')$  that are located near the middle of the band gap. On the other hand the energy levels of shallow donors (acceptors) lie close to the CBM (VBM) and require little ionization energy to add free charge carriers to the system. In Figure 7 a deep donor transition level  $\varepsilon(+/0)$  and a deep acceptor level  $\varepsilon(0/-)$  are shown.



Figure 7: Defect formation enthalpy of a defect in three charge states with respect to the Fermi Level [22]

#### 2.5 Formation Gibbs free energy of a defect

Contrary to the formation enthalpy  $\Delta H_f$  the Gibbs free energy  $\Delta G_f$  of forming a defect considers full temperature and volume dependence. At temperatures T > 0 K the entropy of the system has an impact on the formation of a defect. The following expression gives the formation Gibbs free energy

$$\Delta G_f(T) = \Delta H_f(T) - T\Delta S_f(T) \tag{21}$$

Similarly, to the formation energy  $\Delta H_f$ , the formation entropy of a defect  $\Delta S_f$  is given by the difference between the entropy of the defective and the perfect cell

$$\Delta S_f = S(defect) - S(perfect) - \sum_i n_i \mu_i(T)$$
(22)

For a vacancy defect in an elemental material this can be simplified to

$$\Delta S_f = S(defect) - \left(\frac{N-1}{N}\right)S(perfect)$$
(23)

with N being the number of atoms in the perfect cell.

### 2.6 Formation Entropy of a defect

In thermodynamics, the entropy S is a measure of the disorder of a system. In the 1870s Ludwig Boltzmann defined entropy as

$$S = k_B \ln \Omega \tag{24}$$

with  $\Omega$  the number of distinct ways in which a system can be arranged and  $k_B$ the Boltzmann factor [28]. For a given macroscopic state,  $\Omega$  defines the number of different possible microstates for which the given macrostate can be obtained. The variables defining a macrostate are thermodynamic averages. Microstates are specified by the variables of each molecule of the system, their momentum and their position. If one defines  $p_i$  as the probability that the system is in the *i*-th microstate, the entropy can be written as

$$S = -k_B \sum_{i} p_i \ln p_i \tag{25}$$

By further assuming that the occupation of each microstate is equally probable resulting in  $p_i = 1/\Omega$ , one again obtains the Boltzmann equation (24).

A necessary step to calculate the entropy of a system to count all the possible microstates which give rise to the same macroscopic state. In practice this can be done by calculating the partition function Z of the system,

$$Z_i = \sum_{n}^{\infty} e^{-\beta E_i} \tag{26}$$

with  $\beta = 1/k_B T$  and the total energy E of the *i*-th microstate of the system. From calculating the Helmholtz free energy F one can further obtain the entropy by differentiating by T

$$F = -k_B ln Z \qquad S = -\frac{\partial F}{\partial T} \tag{27}$$

Often this problem can be simplified by separating the internal coordinates into configurational and dynamical ones leading to a configurational and a dynamical entropy.

#### 2.6.1 Configurational Entropy

Configurational entropy  $S_{conf}$  was to a huge amount understood by Gibbs [35]. The configurational degree of freedom is defined by the number of distinct ways  $\Omega_{conf}$  by which one can arrange *n* defects on *N* lattice spots.

$$\Omega_{conf} = \frac{(g_D N)!}{(g_D N - n)!n!} = \frac{(g_D N)^n}{n!}$$
(28)

The internal degree of freedom of the point defect is accounted with the degeneracy factor  $g_D$ . This factor takes into account the different states of a defect which have the same energy. The configurational entropy  $S_{conf}$  can be approximated by equation (24) and the Stirling approximation

$$S_{conf} = k_B [n \ln(g_D) + n \ln(n/N) + n]$$
(29)

Using the defect concentration c = n/N equation (29) can be written as

$$S_{conf}(c) = k_B[cln(g_D) - cln(c) + c]$$
(30)

With equation (21) and by applying the equilibrium condition  $\frac{\partial G}{\partial c} \equiv 0$  one can obtain the defect equilibrium concentration c for which G has a minimum.

$$\Delta G = c \Delta G_f - T S_{conf}(c) \tag{31}$$

$$c(T) = g_D exp\left(\frac{-\Delta G_f}{k_B T}\right) \tag{32}$$

#### 2.6.2 Vibrational Entropy

The vibrational entropy  $S_{vib}$  takes into account the different possible energy states M which m phonons can occupy.

$$\Omega_{vib} = \frac{(M+m)!}{M!m!} \tag{33}$$

Phonons are bosons and fill up energy states with an unlimited amount of particles. Phonons follow the Bose-Einstein distribution  $n(\epsilon_i)$  given by

$$n(\epsilon_i) = \frac{1}{e^{(\epsilon_i - \mu)/k_B T} - 1} \tag{34}$$

which gives us the expected number of particles in an energy state  $\epsilon_i$ , while  $\mu$  is the chemical potential,  $k_B$  is the Boltzmann constant, and T the absolute temperature.

As explained at the beginning of section 2.6 to determine  $S_{vib}$  one usually starts by calculating the partition function Z. For a single harmonic oscillator with the energy  $\epsilon_i = \hbar \omega_i$  the partition function is

$$Z_{i} = \sum_{n}^{\infty} e^{-(n+1/2)\epsilon_{i}/k_{B}T} = \frac{e^{-\epsilon_{i}/2k_{B}T}}{1 - e^{-\epsilon_{i}/k_{B}T}}$$
(35)

The extension to a solid with N atoms requires the consideration of 3N independent oscillators

$$Z_N = \prod_{i}^{3N} \frac{e^{-\epsilon_i/2k_B T}}{1 - e^{-\epsilon_i/k_B T}}$$
(36)

After calculating the vibrational free energy  $F_{vib}$  by using equation (27) one can then obtain the vibrational entropy  $S_{vib}$ .

$$S_{vib} = k_B \sum_{i}^{3N} \left[ -\ln\left(1 - exp\left(\frac{-\hbar\omega_i}{k_B T}\right)\right) + \frac{\frac{\hbar\omega_i}{k_B T}}{exp\left(\frac{-\hbar\omega_i}{k_B T}\right) - 1} \right]$$
(37)

To express  $S_{vib}$  using the phonon density of states (DOS)  $g(\omega)$  one considers  $3Ng(\omega)d\omega$  phonons in an interval  $d\omega$ , whereas  $n = n(\varepsilon_i)$  was defined in (34) and one gets

$$S_{vib} = -3k_B N \int_0^\infty g(\omega) \quad \left[ n \ln(n) - (1+n) \ln(1+n) \right] \quad d\omega \tag{38}$$

#### 2.6.3 Electronic Entropy

The electronic entropy  $S_{el}$  relates to the number of possible energy states N that m electrons can occupy. It is therefore dependent on the electronic density of states g(E) and the Fermi-Dirac distribution  $f(\epsilon_i)$ , as electrons are fermions. The Fermi-Dirac distribution  $f(\epsilon_i)$  is given by

$$f(\epsilon_i) = \frac{1}{e^{(\epsilon_i - \mu)/kT} + 1}$$
(39)

Then again, similarly to the vibrational entropy in equation (38) the electrical entropy yields

$$S_{el} = -k_B N \int_{-\infty}^{\infty} g(E) \quad [f \ln(f) + (1-f)\ln(1-f)] \quad dE$$
 (40)

Other contributions to the entropy can further be the magnetic entropy, polaronic entropy, etc.

#### 2.7 Crystal structure and Bloch Theorem

A crystalline solid is characterized by a well-structured periodic arrangement of atoms [30]. The smallest assembly of atoms that if periodically repeated can build up the whole crystal is called the primitive cell. Several semiconductors like silicon have a diamond crystal lattice structure. In silicon, the first four equidistant neighbors to an atom sit on the corners of a tetrahedron. In general, the three primitive basis vectors of the primitive cell  $\mathbf{a}$ ,  $\mathbf{b}$  and  $\mathbf{c}$  set up the crystal structure in direct space and the direct lattice sites can be defined by the direct lattice vector  $\mathbf{R}$ 

$$R = r\mathbf{a} + s\mathbf{b} + t\mathbf{c} \tag{41}$$

where r, s and t are integers. From the direct basis vectors a set of lattice vectors in reciprocal space  $\mathbf{a}^*$ ,  $\mathbf{b}^*$  and  $\mathbf{c}^*$  and the reciprocal lattice vector  $\mathbf{G}$  can be derived

$$\mathbf{a}^* = 2\pi \frac{\mathbf{b} \times \mathbf{c}}{\mathbf{a} \cdot \mathbf{b} \times \mathbf{c}} \quad \mathbf{b}^* = 2\pi \frac{\mathbf{c} \times \mathbf{a}}{\mathbf{a} \cdot \mathbf{b} \times \mathbf{c}} \quad \mathbf{c}^* = 2\pi \frac{\mathbf{a} \times \mathbf{b}}{\mathbf{a} \cdot \mathbf{b} \times \mathbf{c}}$$
(42)

$$\mathbf{G} = h\mathbf{a}^* + k\mathbf{b}^* + l\mathbf{c}^* \tag{43}$$

whereas h,k and l are integers. The reciprocal lattice represents the Fourier-Transformation of the direct lattice and an important resulting relationship is

$$\mathbf{G} \cdot \mathbf{R} = 2\pi n \tag{44}$$

where n is again an integer. Therefore each vector of the reciprocal lattice is normal to a set of planes in the direct lattice. The primitive cell in reciprocal space is represented by a Wigner-Seitz cell and is called the first Brillouin Zone or just Brillouin Zone (BZ).

#### The Bloch-Theorem

The band structure of a crystal is often obtained by solving the Schrödinger equation, simplified to a one electron-problem [36]

$$\left[-\frac{\hbar^2}{2m^*}\nabla^2 + V(\mathbf{r})\right]\psi(\mathbf{r},\mathbf{k}) = E(\mathbf{k})\psi(\mathbf{r},\mathbf{k})$$
(45)

whereas  $\psi(\mathbf{r}, \mathbf{k})$  is the wave function with  $\mathbf{r} \cdot \mathbf{k}$  being a multiple of  $2\pi$  and  $m^*$  the effective mass. An important theorem, the Bloch-Theorem, can be applied to

equation (45) when the effective potential V(r) is periodic in the real space. The solution of the wave functions is then given by

$$\psi(\mathbf{r}, \mathbf{k}) = e^{i\mathbf{r}\mathbf{k}} u_b(\mathbf{r}, \mathbf{k}) \tag{46}$$

where  $u_b(\mathbf{r}, \mathbf{k})$  is the cell periodic part of the wave function and b the band index. It can further be shown that the energy fulfills the relation  $E(\mathbf{k}) = E(\mathbf{k} + \mathbf{G})$ 

. Therefore for a given b, one only needs to consider **k**-vectors lying within the Brillouin Zone to define the energy uniquely. This will come in handy for theoretical calculations of the energy structure of materials using supercells. Within this method a crystal structure is described using a supercell which is a repeating unit cell of the crystal that contains several primitive cells.

#### 2.8 Experimental ways to probe defects

Identifying defects with experimental methods can be difficult and indirect, requiring a combination of different techniques [20,21]. Experiments can often only probe the consequence of a defect such as an electronic excitation and not the defect directly. It is therefore difficult to provide a complete picture of all defects and their influence on physical properties. Therefore, computational predictions have become a helpful tool as their reliability increases.

Experimentally, there are two quantities that are useful to measure when wanting to find out about the defects and impurities comprised in a material. On one hand one can look at the changing of the voltage which can be led back to a changing Fermi-Level. On the other hand one can take a look at the capacitance with regard to a change in temperature to learn about the transition energy.

When running computational calculations of semiconductor properties, it is important to consider the essential physical quantities which can be compared to the experiment. An important quantity is the defect and impurity concentration which can be obtained when calculating the formation Gibbs free energy using expression (32). Experimentally, the defect concentration can be determined using Secondary ion mass spectrometry (SIMS), Rutherford backscattering spectrometry (RBS) and specific heat measurements. Atomic and electronic structures are investigated by x-rays, scanning tunneling microscopy (STM) or scanning tunneling spectroscopy (STS). The theoretical obtained transition levels can be compared to the measurements of Deep-level transient spectroscopy (DLTS).

# 3 Theory on Computational models to calculate point defects in solids

In this chapter the thermodynamic formalism that allows the investigation of point defects will be explained. Within this formalism the Gibbs free energy of defect formation  $\Delta G_f$  can be calculated. We will start by outlining the different terms in equation (47) and computational models that are necessary to calculate the formation energy of a defect.

$$\Delta G_f(E_F, \mu, T) = \Delta H_f - T\Delta S_f =$$

$$= [E_{tot}(D, q) - E_{tot}(bulk)] + \sum_i n_i \mu_i + qE_F - T\Delta S_f \qquad (47)$$

$$1) \qquad 2) \qquad 3) \qquad 4)$$

- 1 Total energy  $E_{tot}$  $E_{tot}(D,q)$  and  $E_{tot}(bulk)$  calculated by Density Functional Theory (DFT) (Section 3.1)
- 2 Chemical potentials  $\mu_i$ FERE calculation method: Fitting procedure based on Density Functional Theory (DFT) total energy
- 3 Fermi energy  $E_F$ Resolution of the neutrality equation
- 4 Formation Entropy of a defect  $\Delta S_f$ 
  - (a) Configurational Contribution
  - (b) Electronic Contribution
  - (c) Vibrational Contribution: see section 3.2 and section 3.3

In equation (47) the Gibbs free energy of formation is dependent on the defect D and its charge state q. The number of atoms that are involved in the defect D is defined by  $n_i$ .

### 3.1 Total energy calculations using Density Functional Theory (DFT)

One of the most popular and successful quantum mechanical approaches to solve the Schrödinger equation for condensed matter is the Density functional theory (DFT). Due to its few computational effort and its high accuracy without the need for adjustable parameters, DFT has become the standard tool for electronic structure calculations. The next paragraph is therefore devoted to describing the theoretical background of this theory.

Let us first outline the quantum mechanics of the electronic structure of a crystal, which will lay the ground for computational methods and the formulation of density functional theory (DFT). A many body problem can be described by the many body time-independent, non relativistic Schrödinger equation.

$$\hat{H}\psi(\mathbf{r}_1,...,\mathbf{r}_N,\mathbf{R}_1,...,\mathbf{R}_L) = E\psi(\mathbf{r}_1,...,\mathbf{r}_N,\mathbf{R}_1,...,\mathbf{R}_L)$$
(48)

In this expression the 3N coordinates denote the position of the i-th electron while the 3L coordinates give the position of the l-th nucleus. The Hamiltonian in this equation can be split into several parts:

$$\hat{H} = T_{e} + V_{e,e} + V_{e,N} + T_{N} + V_{N,N} = = \sum_{i} \frac{p_{i}^{2}}{2m_{i}} - \frac{1}{2} \sum_{i,i'} \frac{e^{2}}{4\pi\varepsilon_{0}|\mathbf{r}_{i} - \mathbf{r}_{i'}|} + \frac{1}{2} \sum_{i,l} \frac{Z_{l}e^{2}}{4\pi\varepsilon_{0}|\mathbf{r}_{i} - \mathbf{R}_{l}|} + \sum_{l} \frac{P_{l}^{2}}{2M_{l}} - \frac{1}{2} \sum_{l,l'} \frac{Z_{l}Z_{l'}e^{2}}{4\pi\varepsilon_{0}|\mathbf{R}_{l} - \mathbf{R}_{l'}|}$$
(49)

 $T_e$  and  $T_N$  are the kinetic energy of electrons and nuclei.  $V_{e,e}$  is the potential for the repulsive electrostatic electron interaction,  $V_{e,N}$  the interaction potential between electrons and nuclei and  $V_{N,N}$  stand for the interaction potential between the nuclei. The electron and nucleus mass are  $m_i$  and  $M_l$  and e the electronic charge. The sum  $\sum_{i,i'}$  means that summation is only done over pairs that are not the same.

Equation (49) is difficult to solve because its solution is a function of 3N + 3L variables. If we were to calculate its solution by a numerical integration the required computational time would scale exponentially with the number of particles. It is here where the DFT method provides a viable alternative to the struggle of solving a many body problem.

Assuming that the kinetic energy of the much heavier and slower nuclei can be neglected  $T_N \approx 0$ , it allows the separation of the electronic and nuclear degrees of freedom.

$$\hat{H}_{elec} = T_e + V_{e,e} + V_{e,N} \quad \text{and} \quad \hat{H}_{nucl} = V_{N,N} \tag{50}$$

$$\hat{H}_{elec}\psi_{elec} = E_{elec}\psi_{elec} \tag{51}$$

For the many electron system with the Hamiltonian  $\hat{H}_{elec}$  under the influence of an external nuclear potential we consider the Hohenberg-Kohn formulation of DFT [37], which is based upon the following two theorems:

- Theorem 1 For any system consisting of electrons moving under the influence of an external potential, the external potential and therefore all ground state properties are a unique functional of the electron density  $n(\mathbf{r})$ .
- Theorem 2 The ground state energy can be obtained by solving a variational problem: the electron density  $n(\mathbf{r})$  that minimizes the total energy E is the exact ground state density.

According to Theorem 1 the total energy  $E_{elec}$  is a functional of the density of particles n(r), which is given by the expectation value of the density operator  $\hat{n}(\mathbf{r}) = \sum_{i=1,\dots,N} \delta(\mathbf{r} - \mathbf{r}_i)$ 

$$n(r) = \frac{\langle \Phi | \hat{n}(\mathbf{r}) | \Phi \rangle}{\langle \Phi | \Phi \rangle} = N \frac{\int d^3 r_2 \dots d^3 r_N |\Phi(\mathbf{r}, \mathbf{r}_2, \dots, \mathbf{r}_N)|^2}{\int d^3 r_1, \dots, d^3 r_N |\Phi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N)|^2}$$
(52)

Theorem 2 defines an energy functional  $E_{elec} = E[n]$  that is minimized by the ground state density  $n_0(\mathbf{r})$ , whereas n' is an arbitrary density.

$$E_{elec}[n] = T_e[n] + E_{e,e}[n] + E_{e,N}[n]$$
(53)

$$E[n] = \min\langle \psi[n] | T_e + E_{e,e} + E_{e,N} | \psi[n] \rangle$$
(54)

$$E[n_0] \le E[n'] \tag{55}$$

The Hohenberg-Kohn theorems do not provide a practical method to compute the ground state density. A scheme to minimize the energy functional (54) was introduced by Kohn and Sham [38] one year after the Hohenberg-Kohn theorems.

The Kohn-Sham formalism maps the full real potential of the interacting system onto a non-interacting system in which particles move under the single influence of a local potential  $V_{KS}$ . Using the  $V_{KS}$  potential greatly simplifies the calculation and still yields the same ground state as the interacting system. For example the kinetic energy could be determined exactly and easily for a non-interacting system. The groundstate wavefunctions  $\psi_{KS}$  can be described as the single determinant of single particle orbitals  $\phi_i(\mathbf{r}_i)$ :

$$\psi_{KS} = \frac{1}{\sqrt{N}} det(\phi_1(\mathbf{r}_1), \phi_2(\mathbf{r}_2), ..., \phi_N(\mathbf{r}_N)$$
(56)

They then rearranged equation (53) into four terms

$$E[n(\mathbf{r})] = T_S[n(\mathbf{r})] + E_H[n(\mathbf{r})] + E_{XC}[n(\mathbf{r})] + E_{e,N}[n(\mathbf{r})]$$
  
=  $T_S[n(\mathbf{r})] + \int n(\mathbf{r})[V_H(\mathbf{r}) + V_{XC}(\mathbf{r}) + V_{ext}(\mathbf{r})]d\mathbf{r}$  (57)

In equation (57) all terms except for the exchange relation potential  $E_{XC}[n]$  are known :  $T_S[n]$  refers to the kinetic energy of a non interacting electron gas with the density  $n(\mathbf{r})$ ,  $E_H[n]$  is the classic Hartree energy of electrons.

$$E_H[n(\mathbf{r})] = \frac{1}{2} \int \int \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}'$$
(58)

The non-interacting kinetic energy  $T_S$  which is part of  $E_{XC}$  is given by

$$T_S[n(\mathbf{r})] = -\frac{1}{2} \sum_{i}^{N} \int \phi_i(\mathbf{r}) \nabla^2 \phi_i(\mathbf{r}) d\mathbf{r}$$
(59)

The exchange relation potential  $E_{XC}[n]$  is the difference in energy between the exact and non-interacting system which can be recast as

$$E_{XC} = (T_e - T_S) + (E_{e,e} - E_H)$$
(60)

the difference of the kinetic energies and the non-classical contribution to the electron-electron interactions. The Kohn-Sham potential then becomes

$$V_{KS}(\mathbf{r}) = V_H(\mathbf{r}) + V_{XC}(\mathbf{r}) + V_{ext}(\mathbf{r})$$
(61)

The ground state density is now obtained by solving the single particle Schrödinger equations of the fictional Kohn-Sham system

$$\left[\frac{-h^2}{2m}\nabla^2 + V_{KS}(\mathbf{r})\right]\phi_i(\mathbf{r}) = \varepsilon_i\phi_i(\mathbf{r})$$
(62)

and constructing the density of the real and the fictional system KS.

$$n_{KS}(\mathbf{r}) = n(\mathbf{r}) = \sum_{i}^{N} |\phi_i(\mathbf{r})|^2$$
(63)

As  $V_{KS}$  is a function of  $n(\mathbf{r})$  the Kohn-Sham equations (61)-(63) have to be solved by a self consistent procedure:

- Thereby one starts with an estimate of  $n(\mathbf{r})$
- With this  $n(\mathbf{r})$ ,  $V_{KS}$  is calculated. Next the Kohn-Sham equation (62) is solved and  $\phi_i(\mathbf{r})$ 's are obtained.
- Then a new  $n(\mathbf{r})$  is calculated from (63) as well as the total energy E[n] from equation (57).
- Afterwards the loop starts anew as long as the convergence condition is not fulfilled.

The DFT method has been extensively used to describe defects in semiconductors [39–42]. However, its predictive power has been limited due to constrains in accuracy. When calculating the defect concentration with the help of the formation energy of the defect, an accuracy of 0.2 eV at 1000 K is necessary to have a minimum error of less than an order of magnitude.

The next challenge of DFT calculations is that the formalism proposed by Kohn and Sham does not provide a practical way to calculate the exchange and correlation energy  $E_{xc}$ . One practical method to obtain  $E_{xc}$  is the local density approximation (LDA) [43] which states that, for regions of a material where the charge density is slowly varying, the exchange and correlation energy at a given point can be considered the same as that for a locally uniform electron gas of the same charge density. In this case  $E_{xc}$  can be written as

$$E_{xc} = \int n(\mathbf{r})\varepsilon_{xc}(n)d\mathbf{r}$$
(64)

where n is the electronic density and  $\varepsilon_{xc}$  is the exchange-correlation energy per particle of a homogeneous electron gas of charge density  $n(\mathbf{r})$ . Another functional, the Generalized Gradient Approximation (GGA) [44] is also a local density approximation, but also takes into account the gradient of the density. Both approximations are effected by uncertainties due to a systematic underestimation of the band gap that is inherent to the DFT method. In practice, it has been difficult to obtain the right band gap using a local Kohn-Sham potential. Furthermore, it has been found difficult to find common electrostatic references for the systems with and without a defect.

Moreover, within DFT calculations a large number of parameters is involved which can make it difficult to reach convergence when treating systems with flat energy landscapes. Methods for correcting the band gap problem are LDA+U methods and several other methods have been proposed (see [22, 45]).

### **3.2** Phonon calculations

To calculate the vibrational entropy described in section 2.6.2, it is crucial to calculate the lattice dynamics of the crystal and therefore its phonon density of states  $g(\omega)$ , which enters expression (38).

Phonon frequencies can be calculated within the Born Oppenheimer approximation. In the context of this approximation the movement of the ionic core atoms and the electrons can be separated due to the much slower displacement of the ionic atoms compared to the electrons. The displacement out of equilibrium of an ion A can be described by  $u_A(t)$  with  $\omega$  being the angular frequency.

$$u_A(t) = u_A(0)e^{i\omega t} \tag{65}$$

The force acting on the displaced ion A can be written equivalent to Newton's 2nd law of motion:

$$F_A = M_A \frac{d^2 u_A}{dt^2} = -M_A \omega^2 u_A(t) \tag{66}$$

With the potential energy  $E_{pot}$  of the moving ion, the force  $F_A$  can also be given by

$$F_A^{\alpha} = -\frac{\partial E_{pot}}{\partial u_A^{\alpha}} \tag{67}$$

where  $\alpha$  indicates that the force  $F_A$  is 3-dimensional vector. Next, the Taylor expansion of the potential energy  $E_{pot}$  is made:

$$E_{pot} = \left[E_{pot}\right]_{0} + \sum_{A,\alpha} u_{A}^{\alpha} \left[\frac{\partial E_{pot}}{\partial u_{A}^{\alpha}}\right]_{0} + \frac{1}{2} \sum_{A,B,\alpha,\beta} u_{A}^{\alpha} u_{B}^{\beta} \left[\frac{\partial^{2} E_{pot}}{\partial u_{A}^{\alpha} \partial u_{B}^{\beta}}\right]_{0} + \dots$$
(68)

The zeroth order term is the potential energy at equilibrium position  $u_i(t) = u_i(0)$ for i = [1, ..., N]. The first order term is the force acting on all atoms at equilibrium and is therefore zero. The second order term can be compared to the potential energy of a spring  $E_{pot} = \frac{1}{2}kx^2$  with x being the displacement and k the coupling constant.

Ignoring terms of third order and higher is called the harmonic approximation. Within this approximation the displacements of the atoms from their average positions are assumed to be small and the interaction potential can be described by a spherically symmetric harmonic well. The potential energy can be given as

$$U_{harm} = E_{perf} + \frac{1}{2} \sum_{lA\alpha, l'B\beta} \Phi_{lA\alpha, l'B\beta} u_{lA\alpha} u_{lB\beta}$$
(69)

where  $\mathbf{u}_{lA}$  is the displacement of atom A in unit cell l and  $\alpha$  and  $\beta$  indicate that  $\mathbf{u}$  are 3-dimensional vectors.  $\Phi_{A\alpha,B\beta}$  is the force constant matrix and is given by

$$\Phi_{A\alpha,B\beta} = \frac{\partial F_{B\beta}}{\partial u_{A\alpha}} = \frac{\partial^2 E_{pot}}{\partial u_{A\alpha} \partial u_{B\beta}}$$
(70)

where  $F_{B\beta}$  are the calculated forces on atom B, due to a displacement  $u_{A\alpha}$  of atom A in direction  $\alpha$ . The inter atomic coupling constants give the so called Hessian matrix  $D_{A\alpha,B\beta}(\mathbf{q})$  which is the Fourier transformation of  $\Phi_{A\alpha,B\beta}$  at wave vector  $\mathbf{q}$ .

$$D_{AB}^{\alpha\beta}(\mathbf{q}) = \frac{1}{\sqrt{M_A M_B}} \sum_{l} \Phi_{lA\alpha,l'B\beta} \quad exp\left[i\mathbf{q} \cdot (\mathbf{R}_{l'} + \mathbf{v}_B - \mathbf{R}_l - \mathbf{v}_A)\right]$$
(71)

Herby,  $\mathbf{R}_l - \mathbf{v}_A$  represents the original position of atom A with mass  $M_A$  in the primitive cell l and the sum runs over all primitive cells in the crystal. If one knows the complete force constant matrix then  $D_{AB}^{\alpha\beta}(\mathbf{q})$ , the frequencies  $\omega_{\mathbf{q}A}$  can be calculated at any  $\mathbf{q}$ . For this the force acting on atom A can then be written using the Hessian matrix D and a diagonalisation of the matrix can be performed

$$F_A^{\alpha} = -M_A \omega^2 u_A^{\alpha}(t) = -\sum_{A,\alpha} D_{AB}^{\alpha\beta} u_A^{\alpha}$$
(72)

$$\sum_{A,\alpha} \left( D_{AB}^{\alpha\beta} - M_A \omega^2 \delta_{AB} \delta_{\alpha\beta} \right) u_A^{\alpha} = 0$$
(73)

When diagonalizing the matrix one can determine its eigenvalues  $\omega_i$  of band index i which determine the vibrational frequencies.

$$D(\mathbf{q})\mathbf{w}_{\mathbf{q}i} = \omega_i^2 \mathbf{w}_{\mathbf{q}i} \tag{74}$$

\* with  $\mathbf{w}_{\mathbf{q}i}$  being the eigenvectors. The total phonon density of states (DOS)  $g(\omega)$  is then obtained as sum of all states *i* and wave vectors  $\mathbf{q}$ 

$$g(\omega) = \sum_{i,\mathbf{q}} \delta(\omega - \omega_{i,\mathbf{q}}) \tag{75}$$

In practice, a Gaussian function is used to model the delta function.

#### 3.3 Method to calculate lattice dynamics in solids

Ab initio and DFT methods have been the dominant method to calculate defect formation energies at T = 0 K [46] and the calculation of the temperature dependent contributions have not been considered [39, 47]. However, nowadays differing opinions exist, if one can just neglect the temperature dependent entropy contributions due to the argument of similarity in compared structures of the perfect crystal and the crystal with defect [24, 40]. It is found that especially at higher temperatures during processes like defect migration and annealing processes entropy contributions play an important role.

An important part of finite temperature thermodynamics of crystals is the energy and entropy of vibrations. Calculating the vibrational entropy allows the calculation of defect concentrations, which is useful for the comparison with experiments [24]. Ab initio methods are often limited to the use of small supercells and small defective regions. Throughout the literature it is agreed that formation entropy is strongly dependent on supercell sizes. It has been largely investigated that the convergence for formation entropies starts at super cell sizes that are larger than 216 atoms [42, 48]. For larger super cells not only the computational cost increases, but also the diagonalisation of bigger matrices can be numerically problematic [49]. A verification that is often used is the comparison of scaling of calculations with different supercells [24,41]. Another drawback of the supercell approach are artificial periodic images of a defect caused by the periodic placement of the supercells and the resulting boundary conditions.

Several researchers addressed the problem of the optimal handling of large super cells or finite size corrections. Different methods were introduced and compared to meet the demand of high accuracy for vibrational entropy calculations.

Harmonic approximation A common approach is to study defects using harmonic approximations [41] or quasi harmonic approximations (QHA) [28]. Local harmonic approximations are frequently used [50–52], in which atoms are treated as harmonic oscillators, as described at the beginning of this section.

**Embedded Cluster** Another approach to overcome the shortcoming of periodic images of the defect are 'embedded cluster schemes' [24,53,54]. Within this method one divides the supercell into a sphere around the defect, the cluster, in which the lattice dynamics of the atoms are calculated. Outside of the clusters atoms are viewed as static. Hatcher et al [55] and several other studies [24,40] furthermore add long term corrections according to linear elasticity theory. To overcome the problem of inaccessibility of the formation entropy at constant volume experimentally it is often converted to the formation entropy at zero pressure [25,56].

**Empirical potentials** Simulations of large supercells (> 1000 atoms) are computationally too costly to be calculated by first principle methods. Empirical potentials are often used instead [52, 57, 58]. Within such models the cohesive energy of a system of particles is given by an interatomic potential.

Linear response method The Density Functional Perturbation Theory (DFPT) or linear response method [59] provides an analytical way of computing the second derivative of the total energy to calculate lattice dynamics.

**Frozen phonons** Another way to compute the formation entropy is the frozen phonon method [60]. In practice one calculates the forces between every atom in the crystal using DFT and the Hellman-Feynman theorem. The shortcomings of this method are the explicit displacement of one atom in a small supercell will lead to

forces in all the periodic images of the supercell. The frozen phonon method is usually computationally cheaper than the linear response method but requires a larger supercell.

# 4 Bulk Silicon calculations

The theory and formalism explained in Chapter 2 and 3 will now be applied to the calculation of the thermodynamical properties of silicon. As the formation entropy of a defect  $\Delta S_f$  is the difference of the entropy of the defective cell and the perfect cell (see section 2.6) one will start by treating the perfect system of bulk silicon. One will see later on, in comparison with Chapter 5, that the perfect and the defective cell have to be treated as different systems.

### 4.1 Ground state structure relaxation

Electronic structure calculations are performed using the Vienna Ab-initio Simulation Package (VASP) [61]. The VASP program uses density functional theory (DFT) to compute an approximate solution of the many-body Schroedinger equation (for an explanation of DFT see Section 3.1).

Furthermore, the Projected Augmented Wave formalism (PAW) [62, 63], as well as Local Density Approximation (LDA) [43] and Generalized Gradient Approximation (GGA) [44] functionals are used to determine ground state structures.

A short description of the most important input files of VASP will now be given. How each of the input files is set up and what they define will be explained while simultaneously determining the ground state structure, energy and lattice constant of bulk silicon.

### POSCAR

The POSCAR file contains all the information on the atomic positions. The input data contains the lattice constant in Angstrom, the number of atoms in the unit cell, the three lattice vectors defining the unit cell and we use direct fractional coordinates to determine the position of the atoms, i.e. coordinates expressed in the coordinate system of the primitive cell. In the case of silicon a face centered cubic (fcc) primitive cell was used containing 2 atoms. The calculations are started using the experimental value a = 5.431 Å [64] for the lattice constant. Table 1 shows the resulting lines for the POSCAR input file.

Si 5.430.00.50.50.50.00.50.50.50.02Direct 0.00.00.00.250.250.25

Table 1: Input file POSCAR for a 2 atom fcc primitive cell of bulk silicon

#### **KPOINTS**

When using density functional theory within the VASP code the evaluation of many properties, like densities or energies, requires an integration over **k** throughout the Brillouin Zone (BZ) [65] p. 89, 239). For example for a function  $f_i(\mathbf{k})$  the average value over the BZ  $\bar{f}$  is given by

$$\bar{f}_i(\mathbf{k}) = \frac{1}{\Omega} \int_{BZ} f_i(\mathbf{k}) d\mathbf{k}$$
(76)

where  $\Omega$  is the volume of the Brillouin Zone and *i* denotes the discrete band index.

To evaluate those integrals computationally one can use a weighted sum over special  $\mathbf{k}$ -points. This is called  $\mathbf{k}$ -point sampling of the Brillouin Zone.

$$\frac{1}{\Omega} \int_{BZ} \to \sum_{\mathbf{k}} \omega_{\mathbf{k}_i} \tag{77}$$

The widely used Monkhorst and Pack method [66] provides a formalism to set up the  $\mathbf{k}$ -point mesh and to assign the  $\mathbf{k}$ -points a weight. One wants to have many  $\mathbf{k}$ -points were the integrand varies rapidly and fewer when the integrand varies slowly.

Furthermore symmetry can be used to reduce the calculation. In a perfect crystal all independent information can be found from states whose  $\mathbf{k}$ -vectors lie in the irreducible Brillouin Zone (IBZ). The algorithm extracts the irreducible k-points. The input lines of the KPOINTS file include the number of intersections in each direction along the three reciprocal lattice vectors. One has to consider that longer axes in real space lead to shorter axes in reciprocal space. Meaning that larger supercell sizes lead to smaller Brillouin Zones which can be sampled by  $\mathbf{k}$ -point grids with fewer intersections while keeping the same accuracy.

For our primary convergence calculations Figure 8 shows a convergence of the total energy  $E_{TOT}$  with regard to the number of intersection in the reciprocal space. We find that the total energy of the fcc primitive cell of silicon is converging for a **k**-points mesh parameter of 8 intersections in each direction, see Figure 8.



Figure 8: Convergence of total energy  $E_{TOT}$  with respect to the number of intersections in each direction along the three reciprocal lattice vectors

### POTCAR

The POTCAR file includes information on the chemical identity of each atomic species mentioned in the POSCAR file. It provides information on the electronicionic interaction potential  $V_{e,N}$  in the Schroedinger equation (49). Because the exact ionic potential would be computationally to costly to use one takes advantage of the pseudopotential approximation ([65] p.204). Within this approximation the strong Coulomb potential of the nucleus is replaced by a smoother effective ionic potential which only acts on the valence electrons. The tightly bond core electrons are thereby screened out. The Projector Augmented Wave method (PAW) is used in our case to establish the basis set of the pseudopotentials.

#### INCAR

The central input file of our VASP calculation is called INCAR. Here one defines the size of the basis set for the wavefunctions, the numerics and the precision of the calculation. It is also here where one has to define, if a static calculation or a structural relaxation of the atomic positions should be performed.

# Define size of the basis set: ENCUT

The parameter ENCUT controls mostly the technical accuracy of the calculation. This parameter sets the size of the basis set of the wavefunctions. It is convenient to use plane waves because they are fast to compute and many elements can be interpreted in a free electron picture and one can apply periodic boundary conditions through the Bloch theorem.

After the Bloch theorem wave functions  $\psi_{\mathbf{k}}$  of wave vector  $\mathbf{k}$  of a single electron can

be written as

$$\psi_{\mathbf{k}}(r) = e^{i\mathbf{k}\mathbf{r}}u_{\mathbf{k}}(\mathbf{r}) \tag{78}$$

$$u_{\mathbf{k}}(\mathbf{r}) = u_{\mathbf{k}}(\mathbf{r} + \mathbf{T}) \tag{79}$$

where  $u_{\mathbf{k}}(\mathbf{r})$  is the cell periodic Bloch function and **T** is the translation vector of the cell periodicity. The part  $u_{\mathbf{k}}(\mathbf{r})$  can be written as a sum of plane waves which will be used as the basis functions for the wavefunctions.

$$u_{n,k}(r) = \frac{1}{\Omega^{1/2}} \sum_{G} C_{n,G,k} e^{i\mathbf{Gr}}, \qquad \psi_{\mathbf{k}}(r) = \frac{1}{\Omega^{1/2}} \sum_{G} C_{nGk} e^{i(\mathbf{G}+\mathbf{k})\mathbf{r}}$$
(80)

where n corresponds to different electron bands and **G** is the wave vector in reciprocal space. The variables form the basis.

The complete number of plane waves needed to describe exact potentials would exceed computational limits. The energy cut off radius (ENCUT) defines the size of the basis set  $\{C_n, \mathbf{G}, \mathbf{k}\}$ : by setting ENCUT to a specific value only plane waves are included which satisfy

$$\frac{\hbar^2}{2m_{elec}} \mid \mathbf{G} + \mathbf{k} \mid^2 < ENCUT \tag{81}$$



Figure 9: Convergence of total energy  $E_{TOT}$  with respect to the energy cut off radius (ENCUT)

One wants to describe the wave functions with the minimal number of basis functions as possible, which means a low ENCUT reduces computational time. At the same
time one wants to remain within the area where the size of the basis set is large enough to describe the interaction potential and the total energy correctly. For the bulk silicon calculations we obtain a convergence of total energy around an energy cut off radius of ENCUT=500 eV, see Figure 9. This energy represents a maximum number of 1056 plane-waves for the two atom primitive cell.

### # Parameters related to the Fermi Dirac occupation

ISMEAR defines which method is used to determine partial Fermi-Dirac occupancies and integration; e.g.: Gaussian smearing, Methfessel-Paxton [67] or tetrahedron method. SIGMA defines the temperature of the smearing. Moreover, the ISMEAR flag relates to the density of the **k**-point grid. The finer the **k**-point grid is the more one can afford to decrease the smearing. For our calculations we choose a Gaussian smearing with a width of SIGMA=0.05 eV.

### # Numerics and precision of calculation

For the precision of the electronic energy minimization we again converge the total energy with regards to the convergence criteria for the electronic minimization and find that an energy difference of EDIFF=1E-8 is precise enough. For the numerics and Fast Fourier Transformation we set the general parameter Precision= Accurate which will be explain later in 4.3 in greater detail. The evaluation of projection operators is done in real space by setting LREAL=Auto.

### # Structural relaxation

If one wants the ions to relax into their equilibrium positions to evaluate the volume of the relaxed structure one can set the following parameters in the INCAR file:

The ISIF parameter defines if one wants to relax the ions, change the cell shape and/or change the cell volume. NSW defines the number of allowed ionic relaxation steps and EDIFFG its convergence parameter. The structural relaxation stops when the remaining forces acting on all atoms F are smaller than the convergence condition F < EDIFFG. Furthermore, IBRION defines which algorithm should be used for the ionic iterations. This defines how the trajectory of the ions will be updated. One can choose between Molecular Dynamics, Conjugate Gradient, etc.

For the 2-atom silicon cell, the only degree of freedom to be relaxed is the lattice constant. Therefore a volume relaxation is conducted by changing the lattice constant. When using the GGA functional a lattice constant of 5.465 Å was obtained starting from the lattice constant of 5.431 Å obtained from the literature. Figure 10 displays the total energy plotted versus the volume. Using a LDA functional results in a lattice constant of 5.403Å. This systematic error of LDA to underestimate the volume and the error of GGA to systematically overestimate the volume is expected [68]. One can then conduct a structural relaxation by setting the following parameters to: ISIF = 7, IBRION = 2, NSW = 100, EDIFFG=5E-4 eV/Å.



Figure 10: Volume profile, Structural relaxation of 2-atom silicon supercell with a GGA functional

## 4.2 Phonon calculation of bulk silicon

The calculation of the phonon spectrum of a solid is a necessary step when evaluating physical quantities such as the vibrational entropy, specific heat or the phonon band structure. Phonon calculations of bulk silicon are carried out using the program PHON [69], which is based on the frozen phonon method [70,71].

Within this method, one displaces one atom and calculates the force fields acting on all other atoms using VASP. This is repeated for all atoms in the supercell to build up the interatomic force constant matrix (IFC), see section 3.2. Using the IFC Matrix one can set up the dynamical matrix at several **k**-points. However, it is not always necessary to displace all atoms in the super cell due to the existence of symmetry operations. On this account, the PHON code calculates the symmetry operations and positions of atoms that need to be displaced, respectively. After the complete force constant matrix has been calculated the vibrational phonon frequencies are obtained as the square root of the eigenvalues of the dynamical matrix.

The PHON program looks for three input files INPHON, POSCAR and FORCES. The POSCAR file is the same as the one discussed in the previous section. The FORCES file contains the force field acting on all atoms for each displacement. In the INPHON file one defines the input parameters and what calculations should be executed.

### 1. Supercell generation

When computing forces appearing on all atoms in a cell due to a displacement of a single atom, the interaction range is confined to the size of the used cell. Therefore one uses supercells which include several primitive cells. This way the complete knowledge of the force constant matrix is derived from the calculation of the dynamical matrix of the range of several primitive cells. Within the frozen phonon method one assumes a short-ranged decay of the force constant matrix within the size of the supercell.

Therefore supercells of different sizes are generated by using the relaxed face centered cubic (fcc) primitive Si-cell of 2 atoms obtained in the previous section. Created supercell sizes are shown in Table 2. The flag NDIM found in the INPHON file refers to how often the primitive cell is multiplied along the 3 lattice vectors. For example the 16 atom cell corresponds to a  $2 \times 2 \times 2$  **q**-point sampling for the construction of the dynamical matrix.

After the supercell generation the program generates a file DISP which contains all the displacements that need to be applied to calculate the force constant matrix with regards to the found symmetry operations.

The magnitude of the displacement is set to 0.04 Å. This is chosen due to the fact that larger displacements would not be within the harmonic approximation and smaller displacements would lead to small energy differences prone to error and numerical noises.

## 2. Calculating FORCES

Next, a calculation of the force fields is performed using VASP while looping over all displacements. For the different supercell sizes, different **k**-point grids are used to sample the irreducible Brillouin Zone, which shrinks as the supercell sizes gets larger. The decreasing number of **k**-points for larger supercell sizes can be seen in Table 2. It was found that, for phonon calculations, denser **k**-point grids are required compared to the ones obtained from the convergence test of total energy.

NDIM	KPOINTS	Atoms in cell
111	12 12 12	2
$2\ 2\ 2$	$6\ 6\ 6$	16
$3\ 3\ 3$	$4\ 4\ 4$	54
$4\ 4\ 4$	$3 \ 3 \ 3$	128
$6\ 6\ 6$	$2 \ 2 \ 2$	432
888	$1 \ 1 \ 1$	1024
$9 \ 9 \ 9$	111	1458

Table 2: Generation of different supercell sizes: NDIM is the dimension of the fcc primitive silicon cell, KPOINTS are the number of intersections along the reciprocal lattice vectors

For the fcc perfect silicon cell, we find that only one displacement is necessary due to the equivalence of all other atoms. 48 symmetry operations are found of which 24 involve fractionate translation. The corresponding FORCES file in eV/Å for the 16-atom super cell looks the following:

1		
$1\ 0.00517206$	0.00000000 -0	0.00000000
-0.02470500	-0.37442300	-0.37442300
0.00024700	0.02654000	0.02654000
0.01382000	-0.02431800	0.01266000
-0.01418100	0.01240600	-0.02435600
0.01382000	0.01266000	-0.02431800
-0.01418100	-0.02435600	0.01240600
-0.00013800	-0.00146700	-0.00146700
0.00006400	0.00359700	0.00359700
0.13364000	0.16515200	0.16515200
-0.11196900	0.14906900	0.14906900
0.00184900	0.03353400	0.03566500
-0.00005500	-0.00707000	-0.00722200
0.00184900	0.03566500	0.03353400
-0.00005500	-0.00722200	-0.00707000
-0.00726300	0.00007600	0.00007600
0.00725900	0.00015800	0.00015800

Table 3: Displacement of atom 1 and corresponding FORCES acting on 16-atom supercell

#### 4. Thermodynamical properties and Phonon DOS

The PHON code now uses the following formulas to calculate the phonon density of states  $g(\omega)$ .

$$F_{vib} = U_{vib} - TS_{vib} \quad S_{vib} = (U_{vib} - F_{vib})/T \tag{82}$$

$$F_{vib} = 3Nk_BT \int_0^\infty ln \Big[ 2sinh \frac{\hbar\omega}{2k_BT} \Big] g(\omega) d\omega$$
(83)

$$U_{vib} = \sum_{i=1}^{3N} \left\{ \frac{\hbar\omega_i}{exp(\hbar\omega_i/k_B T) - 1} \right\}$$
(84)

The result of the phonon spectrum of bulk silicon for different super cell sizes is displayed in Figure 11. By increasing the size of the supercell in real space, the Brillouin Zone in reciprocal space decreases. Therefore one increases the sampling of the reciprocal space by using larger supercell sizes. Moreover, by using larger supercell sizes one includes more information on how the displacement of one atom, within the force field calculation, is disturbing the rest of the atoms at longer range. For the 16-atom supercell one only considers the forces acting on the 15 other atoms in the supercell. Therefore on the cell boundaries of the supercell artificial interactions can take place that are then periodically repeated.

The  $\Gamma$ -centered Monkhorst and Pack point grid [66] is used to sample the Brillouin Zone. It was found that a **q**-point mesh of  $100 \times 100 \times 100$  is necessary for the sampling used for the integration of the phonon DOS to obtain smooth spectra.



Figure 11: Phonon density of states  $g(\omega)$  of bulk silicon for different super cell sizes

Figure 11 shows that the shape of the phonon DOS is already reproduced by supercell sizes of 54 and 128 atoms. However, only for supercell sizes of 432 atoms and higher the positions of the peaks match well and small features are being reproduced. This corresponds to a  $6 \times 6 \times 6$  **q**-point sampling for the construction of the dynamical matrix. Therefore we conclude that a computationally affordable and accurate calculation can be conducted using a supercell size of 432 atoms, which will be used in proceeding calculations.

For areas of low phonon density of states, where for example the phonon bands are degenerate, it was especially difficult to obtain smooth spectra. This can be explained by the fact that when looking at the Brillouin Zone high symmetry points are easily calculated, e.g.: the  $\Gamma$ -point at  $\mathbf{q} = (0, 0, 0)$  or the *L*-point at  $\mathbf{q} = (\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ which lies in the middle of the hexagonal faces of the BZ. Due to the periodic boundary conditions the perfect silicon cell will have degenerate eigenvalues at high symmetry points like  $\Gamma$  and *L*. All other points in the primitive Brillouin zone (BZ) will be folded back into those points.

Consequently, Figure 12a and 12b show the convergence of the entropy of bulk silicon for different size of supercells corresponding to a finer and finer **q**-point mesh. While the entropy obtained with the 16 atom super cell is still 0.1 k<sub>B</sub> per atom higher than expected, for super cell sizes beyond 128 atoms a good agreement with the experiments [72] can be found with variations smaller then 0.01 k<sub>B</sub>. This trend is emphasized in Figure 12b for a temperature of T = 800 K.



Figure 12: (a) Entropy S per atom as a function of temperature T for different supercell sizes and experimental data from KSNLAF2015 [72] and (b) Entropy S per atom at T = 800K as a function of 1/N, N being the number of atoms in the Supercell.

For a more precise comparison with experiments Figure 13 shows a good agreement for the phonon density of states. The experimental data was obtained by inelastic neutron scattering on silicon to measure the phonon density of states. Longitudinal and transversal acoustic and optical modes (LA,TA,LO,LT) are identified and the experimentally found peaks match well with the calculated phonon spectrum and the error made is less than 0.05 THz.



Figure 13: Comparison of phonon density of states with experimental data KSNLAF2015 [72] at T=100K and identification of acoustic and optical modes

## 4.3 Accuracy of phonon calculations

The critical parameter influencing the precision of the calculation will now be explained and analyzed further.

Firstly the accuracy of the calculation depends strongly on the accuracy of remaining forces acting on the atoms after the relaxation of the atomic positions [73]. It is important to start from a relaxed structure where almost zero forces are acting on the atoms. Therefore a stringent convergence condition for the remaining forces F being smaller than  $5 \times 10^{-4}$  is chosen. It is also noticed that due to a flat potential energy of silicon, it is difficult to converge the forces completely to zero.

Moreover, for the phonon calculation of silicon we find it crucial to use the LREAL-Tag with appropriate care. Within the Projected augmented wave method in the evaluation of  $H|\psi_n\rangle$  projection operators can be evaluated in real space or reciprocal space.

When setting LREAL=.FALSE. one evaluates the projection operators in reciprocal space and the number of operations scales with the size of the basis set. On the other hand, for LREAL=Default the projection-operators are evaluated in real space confined to spheres around each atom [61] and the necessary computation time does not scale with the size of the system. Therefore the VASP guide recommends for large supercell sizes to evaluate the projections operators in real space by setting LREAL=Auto.

However, we observe that phonon calculations using the real space projection are sensitive to aliasing errors. Those errors are called wrap around errors because high frequency components are aliased to low frequency components. They appear for an insufficiently meshed Fast Fourier Transformation grid (FFT-grid) when going from reciprocal to real space. If the Fourier grid does not contain all wave vectors up to  $2 \times G_{cut}$ 

$$\frac{\hbar^2}{2m_0} \mid G_{cut} \mid^2 = ENCUT \tag{85}$$

when evaluating the charge density, components are wrapped around from the other side of the box. In conclusion, computation time is cut in half by using LREAL=Auto, however one has to converge the precision parameters of the FFT-grid. Calculations where conducted using the real space projection and the precision parameters ROPT=5E-5 and PREC=Accurate. Figure 14 shows a flow chart on how to reach the right accuracy for the forces using real or reciprocal projection schemes which is taken from the VASP guideline [61].



Figure 14: Avoiding wrap around errors when calculating the FORCES using real or reciprocal projections schemes taken from [61]

Another parameter that needs to be adjusted with care is the smearing employed in the calculation of the phonon density of states. The DOSSMEAR parameter gives the width of the Gaussian function used to represent the delta function in expression 75.



Figure 15: Gaussian smearing DOSSMEAR of the  $\mathbf{q}$ -point grid for the phonon spectrum of bulk silicon

The phonon density of states depends on how many q-points are considered and the smearing used: a large smearing will speed up the calculation while leading to

an improper description of the phonon spectrum. Figure 15 shows the impact of different smearing parameters. Convergence of the spectrum could be observed for a smearing of 0.02 THz, 0.1 THz, 0.5 THz and 1 THz.

Other input parameters like the augmentation sphere of the basis set ENAUG, changing the starting point of the phonon displacement by LCENTRAL and EDIFF do not influence the calculation sizeably and are set to the following values: ENAUG=1200, LCENTRAL=False, EDIFF=1E-8 eV.

## 5 Silicon Vacancy

As mentioned in previous sections (2.6 and 4) the formation entropy of a point defect is a weighted difference between the entropy of the defective and the perfect system. For the defective system, the step for calculating the ground state structure is not as straightforward as for the perfect cell. It will be shown that different ground state structures are obtained when relaxing the atomic positions of differently charged defects. Furthermore the extent of the distortion of the defective lattice will be studied and the impact on the phonon spectra analyzed.

## 5.1 Ground state defect structure relaxation

When relaxing the atomic positions of the defect structure of the silicon vacancy, one encounters several interesting phenomena related to the electronic structure of silicon. To remain consistent, we set the same input parameters as used for the perfect cell with respect to  $\mathbf{k}$ -point grids, pseudopotentials and plane wave energy cut offs for the ground state relaxations.

Firstly, it is found to be difficult to converge to a ground state structure as silicon vacancy generally inherits a flat energy landscape [74]. For the structure of the defective cell there can be found no definitive agreement in the literature whether the relaxation of the first 4 neighboring atoms that are enclosing the vacancy are undergoing an outward or inward relaxation [75, 76]. However, several authors conclude that it is crucial to use supercell sizes of at least 216 atoms for ground state structure relaxations [75, 77] and that it is necessary to run calculations without any symmetry restriction [78] and to set high accuracy on the remaining forces acting on the atoms.

Secondly, differently charged defects may exist, exhibiting different symmetries. Within this study, charged defects from -2 to +2 are investigated. For an illustration of this distortion, the different symmetries are characterized by their first 4 neighboring atoms which form a tetrahedral structure around the vacancy. Figure 16 displays such tetrahedral structures with their characterizing length.

The different structures can be described by crystallographic point groups within the Schönflies notation  $C_{nd}$  [79]. The capital letter C stands for cyclic, D for dihedral and T for tetrahedral structures. The index n refers to the n-fold rotation axis of the group symmetry.  $T_d$  is a simple tetrahedral structure with the same length for all six edges.  $C_{2v}$  is a cyclic structure with the addition of 2 mirror planes that lie parallel to the axis of rotation making one edge shorter than the others five. This can be seen in Figure 16 where the bond length  $R_{13}$  between atom 1 and 3 gets shortened. Within the  $D_{2d}$  symmetry the lengths of two edges facing each others are reduced. Again one can compare with Figure 16 where the distances  $R_{12}$  and  $R_{34}$ get shorter. A  $D_{3d}$  structure reduces the lengths of 3 edges ending at the same atom.  $D_{2d} / D_{3d}$  has 2/3 mirror planes parallel to the *n*-fold axis. The  $D_{3d}$  structure has also been described as the "split"-vacancy [80] or "split"-interstitial [81]: one atom moves halfway into the direction of the vacancy site and places itself in the middle of an octahedral symmetry which is formed with the first 4 neighboring atoms and 2 second-nearest neighbors.



Figure 16: Defect symmetry structures in Schönflies notation: Displayed tetrahedra show the  $1^{st}$  four neighboring atoms around the vacancy and how the distance between them  $R_{xy}$  changes with regard to different symmetries.

As a next step we are interested in which ground state symmetry structures are formed depending on the charge state of the considered defect. For an illustration of different defect levels in the energy gap, Figure 17 shows the Watkins model [82] for the defect charge states of the silicon vacancy. The vertical lines represent the linear combination of atomic orbitals (LCAO) [83] as a quantum superposition of atomic orbitals. In this model the electron configurations of atoms are described as wave functions. When looking at the neutral silicon vacancy an "energy state" in the band gap is introduced (displayed in Figure 17 using the red arrows). It shows that going from  $T_d$  to a lower  $D_{2d}$  symmetry the so-called Jahn-Teller distortion is observed. The energy cost of the structural relaxation is counter balanced by a splitting of energy levels and lowering of electronic energy. This basically describes the effect of a non-linear molecule undergoing a geometrical distortion to obtain a lower energy state. This removes part of the symmetry of the molecule and the degeneracy of the electronic ground states. For the +2 charged defect the  $D_{2d}$ configuration is shown in the second column of Figure 17 using the black arrows. In the same way the  $C_{2v}$  defect levels for +1 is shown in the third column as well with the black arrows displaying a further removal of the degeneracy of energy states.



Figure 17: Model of the silicon vacancy for differently charged defects (and neutral defect - red arrows) by Watkins [82] demonstrating a Jahn-Teller distortion for the neutrally charged defect going from  $T_d$  to  $D_{2d}$  symmetry.

Table 4 displays the obtained symmetry structures for charged defects going from -2 to +2 together with their energies. The atomic positions are relaxed until the maximum forces acting on the atoms are within the criteria  $F < 5.10^{-5} \text{ eV/Å}$ . This ranges in the same area as previously published studies  $F < 2.10^{-4} \text{ eV/Å}$  [84] and  $F < 5.10^{-3} \text{ eV/Å}$  [80].

As mentioned in the introduction of this section we also found it important to set the flag ISYM to zero in order to find symmetry breaking relaxations and lift symmetry constrains. Moreover, the expected Jahn-Teller distortion for the neutral defect is only observed for supercell sizes of at least 216 atoms. This slow convergence could be traced back to the interaction between periodic images of the defect center and the underestimation of band gap by DFT [74].

Therefore, in Table 4 relaxed structures, bond lengths and ground state energies are given for the 432 atom cell. Furthermore, to obtain structures significantly differing from the  $T_d$ , it is required to perform an initial random displacement of the 1st neighboring atoms, so the system is able to escape the  $T_d$  symmetry local minimum. Moreover, it is important to start from a preconverged starting guess and to continuously restart calculations for structures that are not yet converging. It can also be helpful to change the algorithm employed for the relaxation. When the starting point is located far away from the ground state structure the more aggressive conjugate gradient algorithm (IBRION=2) is found helpful. Close to the ground state structure it is better to use a quasi-Newton algorithm (IBRION=1) to relax the atoms into their close ground state.

In column 2 of Table 4 one can see that the symmetry structures found within this study (marked with a  $\bullet$ ) for charged defects of -2,0 and +2 lie in reasonable agreement with previously found theoretical studies [77, 78, 80, 84]. For the -1,0,+1

and +2 the observed structures further agree with deep level transient spectroscopy (DLTS) and electron paramagnetic resonance (EPR) experiments of Watkins [85,86].

Table 4 also shows that the main discrepancies between previously published results occur for the defect charge states +1 and -1. The same states are also found to be the most problematic to relax. One can see that their different symmetry structures only lie several meV of energy apart. This can be traced back to the negative-U behavior of the isolated Si vacancy as it was firstly described in 1979 by Baraff [86] and later found experimentally for the +1 state by Watkins [87]. In fact, the charge states +1 and -1 are found not to be stable within the range of chemical potential defined by the Si band gap [77]. The structure of the -1 charged defect is especially drawn to remain in a metastable  $T_d$  state forming a 3-times degenerated defect level. Moreover, the stabilized structure does only come close to a  $C_{2v}$  symmetry remaining a difference of 0.05 Å between the length of two edges away from  $C_{2v}$ . One can improve the relaxation of those states by adding the degree of freedom for spin polarization (by setting the parameter ISPIN=2). This leads to the same total energies, but with a faster convergence of the calculations.

To check the accuracy of our results we conduct the same ground state relaxations also with an LDA functional. Using LDA, the same stable symmetries where found for -2,0,+1 and +2 charge states. Only for the -1 charge state the  $D_{3d}$  symmetry was found to have a 0.04 eV lower energy than  $C_{2v}$  which was also found by other previous studies [84].

The calculated formation enthalpy for the neutral  $D_{2d}$  symmetry of 3.67 eV lies close within the values obtained in recent studies [80,84]. Considering formula (32) from section 2.6 one can obtain a defect concentration of the neutral vacancy with  $D_{2d}$  symmetry of  $3.7 \cdot 10^6$  per cm<sup>3</sup> which is in rough agreement with experimental studies who found a vacancy concentration of  $10^5$  per cm<sup>3</sup> in silicon wafers [89].

In comparison with the schematic model of defect levels in Figure 17 the electronic density of states for the neutral defect is shown in Figure 18. One can see that defect levels are introduced in the band gap in reasonable agreement with the model proposed by Watkins [82]. The broad bands of the defect levels lie very close to the CB and the energy difference between the defect levels and the CB is small.

$f$ or $\Delta E[eV]$	References		3.66 [84], $3.52$ [80]	4.20 [80]										0.09 [88]		0.12 [78]	0.14 [78]	pround state structures
$\Delta H$	This work	0.00	3.67	3.86	0.00	0.15	0.33	0.00	0.01	0.01	0.00	0.01	0.03	0.17	0.00	0.20	0.33	laved Found
	$E_{tot}[eV]$	-2343.74	-2334.64	-2334.46	-2345.94	-2345.79	-2345.60	-2340.26	-2340.25	-2340.25	-2328.66	-2328.65	-2328.63	-2328.49	-2322.76	-2322.56	-2322.43	rev are disn
first neigbors $[Å]$	R34	3.87	3.04	3.52	3.85	3.12	2.74	3.49	3.68	3.30	2.87	3.04	2.68	3.39	2.66	2.72	3.26	n vacar
	R24	3.87	3.55	3.52	3.85	3.58	3.64	3.68	3.68	3.69	3.44	3.45	3.58	3.39	3.55	3.29	3.27	Silion
	R23	3.87	3.55	3.52	3.85	3.57	2.74	3.68	3.68	3.67	3.44	3.45	2.68	3.38	2.66	3.29	3.26	l charge
etween	R14	3.87	3.55	3.52	3.85	3.58	3.64	3.68	3.68	3.69	3.44	3.45	3.58	3.39	3.55	3.29	3.27	tral and
ance be	$\mathbf{R}13$	3.87	3.55	3.52	3.85	3.57	2.74	3.68	3.68	3.67	3.44	3.45	2.68	3.38	2.66	3.29	3.26	the neur
$\operatorname{Dist}_6$	R12	3.87	3.04	3.52	3.85	3.14	3.64	3.49	3.68	3.63	3.37	3.11	3.58	3.39	3.55	3.37	3.27	ires of t
	Symmetry	Perfect	$D_{2d} \bullet, [77, 78, 80, 84]$	$T_d$	$T_d \bullet, [77, 78, 80, 84]$	$\sim D_{2d}$	$D_{3d}$	$D_{2d} \bullet, [77, 80, 84]$	$T_d$ [78]	$\sim C_{2v}$	$\sim C_{2v} \bullet, [78, 80]$	$\sim D_{2d}$ [77]	$D_{3d} [84]$	$\sim T_d$	$D_{3d} \bullet, [77, 78, 80, 84]$	$\sim C_{2v}$	$\sim T_d$	bund stable defect structu
	Charge	0	0	0	+2	+2	+2	+	+1	+1		-	-	-	-2	-2	-2	Table 4. Fa

within this study are marked with a bullet  $\bullet$  and other authors are referenced.

Symmetry-labels are given in Schönflies notation and distances R between the ions neighboring the vacancy for the 432 atom cell are given in  $\mathbb{A}$ . Furthermore total energies  $E_{tot}$ , energy differences  $\Delta E$  and for the neutral vacancy the formation enthalpies  $\Delta H_f$ are displayed.



Figure 18: Electron density of states shows states within the band gap for the defective cell

## 5.2 Distortion of the lattice

Particular interest lies in evaluating the amount of disorder a certain symmetry creates in the system, as it is loosely related to the entropy of the system. A generally interesting aspect is therefore the distortion of the lattice compared to the perfect crystal with regard to different symmetries and charge states (i.e. change of atomic positions.

For the neutral vacancy larger displacements are found for  $D_{2d}$  compared to  $T_d$  symmetry in agreement with lower number of symmetries of  $T_d$  with regards to  $D_{2d}$ . In Figure 20, snapshots of the four different symmetries are shown. In all four cases the first four atoms neighboring the vacancy are the most disturbed. For  $T_d$  symmetry the first for neighbors get displaced by 0.19 Å, for  $D_{2d}$  symmetry 0.42 Å, for  $C_{2v}$  symmetry 0.51 Å and for  $D_{3d}$  symmetry the split atom gets displaced 1.17 Å. However, depending on the local symmetry of the defect, the distortion of the lattice can extend to several successive shells.



Figure 19: Distortion of the lattice induced by the neutral defect. The size of the sphere is proportional to the displacement of one atom out of the perfect structure  $\Delta r$ :

Pink •  $\Delta r > 0.1$  Å, Cyan • 0.1 Å>  $\Delta r > 0.05$  Å, Blue • 0.05 Å>  $\Delta r > 0.01$  Å, Black •  $\Delta r < 0.01$  Å

Also the shape of distortion can differ as can be seen in Figure 20. For the  $T_d$  and  $D_{2d}$  symmetry the distortion spreads in form of a sphere around the vacancy site. The 1st four neighbors experience the same magnitude of displacement, for both cases separately. The  $C_{2v}$  and the  $D_{3d}$  tetrahedra display a less spherical symmetry. The distortion of the  $D_{3d}$  symmetry stretches out along the  $\{110\}$  axis and the split vacancy atom is the most displaced. However, in this case one has to consider that the fcc shape of the used supercell may magnify the shape of the  $D_{3d}$  distortion. For the  $C_{2v}$  symmetry the two neighboring atoms coming closer together are the most disturbed.



Figure 20: Distortion of the lattice induced by the vacancy. The size of the sphere is proportional to the displacement of one atom out of the perfect structure  $\Delta r$ : Pink •  $\Delta r > 0.1$  Å, Cyan • 0.1 Å>  $\Delta r > 0.05$  Å, Blue • 0.05 Å>  $\Delta r > 0.01$  Å, Black •  $\Delta r < 0.01$  Å

To further analyze the distortion of different symmetries in Figure 21 the displacement of the atoms out of their perfect position is plotted against how far they lie away from the vacancy. The length of the displacement  $\Delta r$  for all shown symmetries  $D_{2d}$ ,  $T_d$  and  $D_{3d}$  falls down to a certain value about 10 Å away from the vacancy site and fluctuates around that value while never going completely to zero. This shows that there is a small but long range interaction of the defect with atoms at the edge of the used supercell. In comparison, in the 16-atom supercell an atom at the edge of the supercell is only 5.47 Å away from the vacancy, in the 54-atoms cell 8.20 Å and 10.94 Å in the 128-atom supercell. This means that a 16, 54 or 128-atom supercell would be too small to capture the greatest amount of the distortion and will lead to periodic interactions of the forces at the cell borders. For a supercell of 432 atoms the atoms at the border are already 16.41 Å away from the defect and do not feel the largest extent of the distortion anymore. It is also interesting to consider the relation between defect symmetry and distortion of the lattice. One can clearly notice that the extent of the distortion is dependent on the symmetry and not on the charge state of the defect. One can see that  $T_d$ symmetry experiences smaller displacements.



Figure 21: Displacement of atomic position as a function of the distance from the vacancy for  $D_{2d}$ ,  $T_d$  and  $D_{3d}$  structures for the 432-atom supercell.

Subsequently, the distortion of the lattice leads to different lattice vibrations for each system and the question arises what the impact on the phonon density of states  $g(\omega)$  will be. In fact, the observed defect structures for different charge states have to be treated as different systems for which phonon calculations have to be conducted separately.

### 5.3 **Phonon calculations**

In the same way as described in section 5 for bulk silicon, the phonon density of states are now computed for the defective supercell by calculating the force fields acting on the atoms using VASP. At variance with the perfect silicon supercell more atoms need to be displaced in the case of the defective supercell to compute the phonon density of states.

At first, we focus on the neutral  $T_d$  defect. For the  $T_d$  symmetry, the PHON code finds 24 remaining symmetry operations and 88 atoms out of 432 have to be displaced to calculate the phonon density of states. This is highlighted here because the number of calculations is related to the necessary computational time.

The obtained phonon density of states for the neutral vacancy with  $T_d$  symmetry can be seen in Figure 22. At first, one can notice that the phonon density of states of the 432-atom supercell containing a single defect only change cosmetically in the low frequency range while larger changes are observed in the optical range. However, a lowering of the maximum frequencies is observed. The transverse acoustic (TA) peak at 4.1 THz and the peak of the optical modes (LA/LO) around 14 THz are reduced by approximately  $0.5 \text{ THz}^{-1}$ . This relates to lower energies, forces and less stringent spring constants acting between the atoms and generally speaking a softening of the interaction. In general, a shift to higher frequencies of the whole optical part of the DOS is observed.

Visibly, the phonon density of states does change less for the acoustical modes. The change for the optical part of the phonon spectrum can be explained by the alteration of local optical modes around the vacancy.

For the defective supercells a **q**-point grid of  $40 \times 40 \times 40$  is found to be fine enough for the sampling used for the phonon DOS in order to obtain smooth density of states. Although, the same parameters for the Gaussian smearing are used (DOSSMEAR=0.02 THz and DOSSTEP=0.1 THz) less **q**-points are required to sample the BZ of the defective supercell. Somehow, by introducing a defect, distortion of the lattice plays the role of an artificial smearing. For the defective supercell the degeneracy of some states is removed which speed up the sampling of the DOS.



Figure 22: Phonon density of states  $g(\omega)$  for the perfect and the neutral  $T_d$  vacancy and the used **q**-point grids (supercell size 432 atoms)

A further observation is made for the imaginary part of the phonon spectrum. During the phonon calculation low imaginary frequencies  $\omega^2 < 0$  are found, which are not included in Figure 22 because they are too low in density to be seen. The observation of those imaginary frequencies has been found by other studies before [90] and can be traced back to the shallow nature of the energy landscape of the silicon vacancy, to the use of the constant volume formalism or to the difficulties of obtaining the correct ground state structure, which can all lead to imaginary frequencies. The imaginary frequencies make up less than 0.004% of the phonon DOS. Only for the neutral  $T_d$  vacancy the negative frequencies make up 0.016% of the phonon DOS. This can be explained by the  $T_d$  symmetry being dynamically unstable and by  $T_d$  not being the symmetry structure of the lowest energy for the neutral vacancy.

When trying to disturb only clusters of the first second and third neighboring shells around the vacancy and leaving all the other atoms in their perfect position, it is not possible to increase the number of found symmetry operations to decrease computational time. On the contrary, when only disturbing the first four neighboring atoms less symmetry relations are found than when including all atoms. This can be due to the distortion of the lattice going beyond the first three successive shells around the vacancy. Furthermore it can be problematic to conduct phonon calculations on non-relaxed structures where the forces acting on some atoms are not zero.

For other ground state structures and different charge states the amount of symmetry operations that can describe the relaxed structures is reduced and more displacement for the phonon calculations are needed. For the 432-atom supercell  $T_d$  structures required 88-187 displacements and  $D_{2d}$  205-418 displacements. For the  $D_{3d}$  structure of the -2 charged defect, 6 symmetry operations result in 251 displacements. The  $T_d$  structure of the +2 charged defect requires 128 displacements corresponding to 11 found symmetry operations.

The corresponding phonon spectra can be found in Figure 23. Again, in the low frequency the phonon DOS only changes cosmetically while larger changes are observed in the optical range. However, for the neutral  $D_{2d}$  and the +2 charged vacancy small wiggles can be observed in the low frequency range between 0 and 4 THz. Moreover, the lowering of the maximum frequencies is observed for all charge states and is the largest for the -2 charged vacancy.



Figure 23: Phonon density of states  $g(\omega)$  for the differently charged vacancies for a  $40 \times 40 \times 40$  **q**-point grid

## 5.4 Finite size effects

When conducting phonon calculations for different supercell sizes, again finite size effect are observed. Those will now be analyzed for the  $T_d$  structure of the neutral vacancy. The phonon density of states for different initial supercell sizes in Figure 24 clearly exhibits this effect. In fact, the different supercell sizes stand for different concentrations of defects as the different cells contain one point defect in 54, 128, 432 or 1024 atoms. To still describe the **q**-point sampling of the Brillouin Zone correctly when calculating the phonon DOS the following procedure is applied: for the concentration of one defect in 54 and in 128 atoms supercells of 432 and 1024 atoms are used. A supercell of 54-atoms containing the defect is multiplied twice in x-,y- and z-direction to obtain a supercell of 432 atoms containing 8 defects. The supercell of 128 atoms containing one defect is multiplied twice in x-,y- and z-direction to obtain a supercell of 1024 atoms containing 8 defects.

One observes that for supercell sizes of 54 and 128 atoms, the phonon DOS displays fluctuations. A 54-atom supercell translates to a  $3 \times 3 \times 3$  **q**-point sampling of the dynamical matrix, and the 128-atom supercell translates to a  $4 \times 4 \times 4$  **q**-point sampling. The interaction range within those supercell sizes of the supercell may be to small to include enough information for the force constant matrix. Periodic interaction of the forces at the cell boundaries may also lead to poor description of the phonon DOS. For 432 and 1024 atoms, a tendency towards the same phonon DOS can be seen displaying peaks at the same position and height as the phonon DOS of the perfect cell. For the 54-atom supercell large perturbation are observed especially in the low frequency region which is difficult to model due to low phonon DOS. Around 13 THz a peak is observed for 54 and 128 atoms which vanishes for larger supercell sizes. In general, a shift to larger frequencies and therefore energies can be observed when going to larger supercell sizes.



Figure 24: Size Effects  $T_d$  symmetry for a **q**-points grid of  $40 \times 40 \times 40$ 

## 6 Formation entropy of the silicon vacancy

A wide range of values can be found in the literature for the formation entropy of the silicon vacancy  $\Delta S_f(T)$ , see Figure 25. The following calculations focus on the vibrational formation entropy, as standard methods have been developed to calculate the configurational and the electrical entropy (see section 2.6 and [22, 26]).



Figure 25: Formation Entropies for the Si vacancy from literature, References are marked with the first letter of the authors last names and the year the paper was published: SS0Y15 [91], MN03 [90], MB93 [92], CA93 [93], RF07 [94], DMK86 [95], BSCLAP93 [96], LA82 [97]

Large discrepancies for  $\Delta S_f$  ranging from -4 k<sub>B</sub> to 11 k<sub>B</sub> at high temperature have been found within theoretical [90–94, 96] and experimental studies [95, 97]. Furthermore, the peculiarity of the silicon vacancy exhibiting different symmetry structures is not mentioned by all listed references. While some theoretical studies [90, 91] obtain a  $D_{2d}$  structure for the neutral vacancy, others do not give precisions about the different defect structures considered [92–94]. Within experimental investigations, vacancies, interstitials and maybe other defects coexist at high temperatures and their measurement with positron annihilation becomes difficult due to small defect concentrations [95]. Nevertheless, first-principle calculations can serve as a predictive tool to support experiments and will now be used for the calculation of the formation entropy  $\Delta S_f$  of the silicon vacancy.

The formation entropy is obtained by taking the difference of the entropy of the defective and the perfect supercell while accounting for the conservation of number of particles. In chapter 2.6 this formalism was explained and is now applied to the case of the silicon vacancy. One obtains for the formation entropy of a vacancy

$$\Delta S_f = S_{defect} - \left(\frac{N-1}{N}\right) S_{perfect} \tag{86}$$

In equation (86),  $S_{defect}$  is the entropy of the system containing the defect,  $S_{perfect}$  the entropy of the perfect system and N the number of atoms of the supercell. The factor  $\left(\frac{N-1}{N}\right)$  accounts for the conservation of particle numbers and the temperature dependence of the elemental chemical potential of Si. In comparison with chapter 2.6 the formation entropy can be written as

$$\Delta S_f^{vib} = -3k_B(N-1)\int_0^\infty \Delta g(\omega) \left[n\ln(n) - (1+n)\ln(1+n)\right] d\omega \tag{87}$$

where *n* is the Bose-Einstein distribution and  $\Delta g(\omega)$  the normalized difference of phonon density of states (DOS) between the defective and the perfect supercell. Thereby,  $\Delta S_f^{vib}$  depends on the number of atoms *N* in the supercell for which  $g(\omega)$ is calculated, and it is proportional to  $\Delta S_f \propto N \cdot \Delta g(\omega)$  In fact, the key quantity that needs to be calculated to obtain  $\Delta S_f$  is the difference of the normalized phonon DOS  $\Delta g(\omega)$ .

### 6.1 Formation entropy contributions

In Figure 26a the difference of phonon DOS  $\Delta g(\omega)$  is displayed for the neutral vacancy in the  $T_d$  symmetry. Different features can be recognized resulting in valleys and peaks which will be called valley-peaks and which represent bond strengthening (i.e. a shift of frequencies to higher energies). Two small valley-peaks can be observed at 4 and 9 THz and one larger valley-peak at 14 THz. In between from 0 to 4 THz and from 5 to 9 THz lie flat regions where  $\Delta g(\omega)$  is low. For all three valley-peaks, the area of the valley is slightly larger resulting in a negative contribution to  $\Delta g(\omega)$ .

According to the different observed features the difference of the phonon DOS is parted into several frequency domains. To get an estimate on how much each frequency region contributes to the overall formation entropy an integration by frequency domain is conducted and the result is showing in Figure 26b. Additionally, the total formation entropy  $\Delta S_f$  can be seen in Figure 26b as the red drawn through line.

Figure 26b shows that all frequency domains that include a valley-peak result in a negative contribution to  $\Delta S_f$ . The first valley-peak at 4 THz gives the largest negative contribution. The flat frequency domain from 0 to 4 THz gives the largest positive contribution and the frequency range between 11 and 13 THz the second positive contribution. In general, it appears that low frequency regions contribute significantly more to the formation entropy than high frequency optical modes.

This can be explained by taking a closer look at the integration factor of equation (87) in Figure 26c. This integration factor is highly dependent on the frequency  $\omega$  and even for high temperatures, still varies around a factor of 3-4 across the whole frequency range. This requires an accurate modeling of low frequency regions. Morever, especially in regions of low  $\Delta g(\omega)$  between 0 and 4 THz and between 5 and 9 THz the convergence of the phonon DOS with regards to **q**-point sampling is particularly difficult: it is observed that insufficient sampling easily leads to wiggles

and errors. The difficulties in modeling the phonon DOS in those regions can be explained by the low phonon density of states and the energy band lying close to  $\Gamma$ . This peculiar feature of the integration factor might have not been explicitly considered by previous studies [93] which obtained phonon DOS displaying strong fluctuation and variations.

By further examining equation (87) with n the Bose-Einstein distribution one can approximate n using  $k_B T \gg \hbar \omega$  resulting in  $n \approx \frac{k_B T}{\hbar \omega}$ . As the integrand in equation (87) is proportional to n, for large temperatures the contribution of different frequency domains increases. Furthermore, the integration factor, as seen in Figure 26c, is positive over the whole frequency range resulting in a negative contribution of the three valley-peaks.



Figure 26: Different frequency regions contributing to the formation entropy  $\Delta S_f$  of the neutral  $T_d$  vacancy

## 6.2 Finite size effects

The knowledge gained on the finite size effect for the defective and the perfect system (see section 5.4), shall now be described further when considering the finite size effects of the calculations for the formation entropy. In Figure 27 the difference of the phonon density of states  $\Delta q(\omega)$  is displayed for different defect concentrations,

where the defect concentration is given by the initial supercell size containing one defect.

Although the phonon DOS of 54 and 128 atoms fluctuate over the whole frequency range, one can see a trend towards smaller valley-peaks for the feature at 4 THz and the one around 10 THz. On the other hand, increasing defect concentration increases the area under the valley and the peak for the valley-peak located at 13 THz. Regions of low  $\Delta g(\omega)$  tend to be flattened out for smaller defect concentrations.



Figure 27: Finite size effect for the difference of density of states  $\Delta g(\omega)$  between the perfect cell and the cell containing the neutral  $T_d$  vacancy

The effect of different defect concentrations on the formation entropy can be seen in Figure 28. The left side (a) shows the obtained formation entropies for supercell of 54 to 1024 atoms. One observes that the formation entropy varies from -6 k<sub>B</sub> to 6 k<sub>B</sub> at high energies. When again conducting an integration by frequency domain analysis similar to the one earlier, one obtains the following trends: for 54 and 16atoms the low frequency region from 0 to 4 THz gives a large positive contribution resulting in a positive total formation entropy. Secondly, the negative contribution of the valley-peak at 4 THz increases with increasing supercell sizes, although visibly the area under the valley and the peak decreases. This could be due to the fact that the formation entropy is proportional to the number of atoms in the supercell N times the difference of the phonon DOS  $\Delta g(\omega)$ , or  $\Delta S_f \propto N \cdot \Delta g(\omega)$ . This means that any error made within the estimation of  $\Delta g(\omega)$  will be as well multiplied by the number of atoms N and lead to greater errors in  $\Delta S_f$  when using larger supercell sizes.

A trend of the obtained formation entropies for different supercell sizes at T = 800 K plotted against 1/N shows some linearity, with a difference of 2.7 k<sub>B</sub> between a supercell of 432 and 1024 atoms. Moreover, previous studies have shown that a linear extrapolation of  $1/N \rightarrow 0$  of constant volume calculations of formation entropies

for systems is possible [98]. This would mean that a supercell size of 432 atoms is sufficient for obtaining a good estimate of the formation entropy.



Figure 28: Linear interpolation to obtain  $\Delta S_f$  for the dilute limit

## 6.3 Accuracy of results

The accuracy of the calculated formation entropy shall now be quantified with regards to several parameters. It is noted that the level of accuracy required for calculations on the defective cell is significantly different from the requirements from the perfect cell. Important parameters setting the accuracy of the phonon calculations are the real space projection operators (LREAL), FFT-Grid precision (PREC,ROPT) and the **q**-point sampling of the phonon DOS (DOSSMEAR,**q**). Moreover, the parameter is kept ISMEAR=0, which is recommended by the VASP guide to use for semiconductors. When checking the electron density of states no partial occupancies of the electron bands for the **k**-point **k** = {000} are found.

### 6.3.1 k-point grid

While the choice of finer **k**-point grid used to compute total energies did not lead to a significant change for calculations of the phonon DOS of the perfect cell, it particularly impacts the defective cell. For a 432-atom cell containing one defect the precision of the calculation is increased by using a **k**-point grid of  $2 \times 2 \times 2$ , as seen in Figure 29a. Especially in the acoustic range, the phonon DOS of the defective cell reproduces quite well the perfect phonon DOS. Subsequently, the use of a finer **k**-point grid has a large impact on the formation entropy with a 9 k<sub>B</sub> difference for for the neutral vacancy with  $T_d$  symmetry and 5 k<sub>B</sub> difference for  $D_{2d}$ as observed at high temperatures as seen in Figure 29b.



Figure 29: Effect of k-point under sampling for the phonon density of states of the defective and the perfect cell for  $T_d$  symmetry and the formation entropy of the neutral vacancy with  $T_d$  and  $D_{2d}$  symmetry

### 6.3.2 Functionals LDA and GGA

Calculations of the formation entropy of the neutral vacancy are conducted using two different functionals. The difference of the Local Density Approximation (LDA) and the Generalized Gradient Approximation (GGA) functional are shown in Figure 30. The phonon density of states  $g(\omega)$  for LDA in Figure 30a displays a rather good reproduction of the perfect density of states in the acoustic region, except for the low frequency range from 0 to 2 THz. For this frequency domain small wiggles are observed. As stressed in section 6.1 this cosmetically small contribution can lead to the difference obtained for the formation entropy in Figure 30b. A partial analysis of the formation entropy for the  $T_d$  vacancy reveals that its positive contribution is mostly obtained from small differences in the frequency region of 0 to 4 THz explaining the 4 k<sub>B</sub> rise in formation entropy. Contrary, a partial analysis of the formation entropy for the  $D_{2d}$  vacancy shows a small contribution in the frequency region of 0 to 4 THz explaining the 2 k<sub>B</sub> fall in formation entropy.

Using a harder potential within the Generalized Gradient Approximation leads to marginal changes of less than 0.5  $k_B$  in the formation entropy.



Figure 30: Formation entropy of the neutral  $T_d$  and  $D_{2d}$  vacancy using different functionals

#### 6.3.3 Smearing of density of states

In section 3.2 it was explained how the phonon density of states for the frequencies  $\omega$  can be determined using

$$g(\omega) = \sum_{i,\mathbf{q}} \delta(\omega - \omega_{i,\mathbf{q}}) \tag{88}$$

where the sum goes over all  $\mathbf{q}$ -points of the Brillouin Zone and all states *i*. A Gaussian function is used to model the delta function in equation (88). The width of this Gaussian function the so-called smearing is defined by the parameter DOSSMEAR. The smearing is linked to the  $\mathbf{q}$ -point sampling for the construction of the dynamical matrix as it can help establish the phonon DOS of calculations of sparse  $\mathbf{q}$ -point sampling where only the eigenvalues at  $\mathbf{q}$ -points close to high symmetry points are calculated. A large smearing can also help to speed up the calculation while leading to an improper description of the phonon spectrum.

Applying a very broad smearing to the width of the Gaussian can lead to a poor reproduction of the phonon DOS, as shown in Figure 31a and discussed before in 4.3. For a DOSSMEAR of 1 THz the phonon DOS is expanded over a wider frequency spectrum and falls down to zero at 23 THz. Moreover, the peaks at 4 THz and at 13 THz get reduced by a third of their height. In Figure 31b the resulting formation entropies for different smearing widths are displayed. It is observed that an increase of DOSSMEAR and can lead to high formation entropies of around 14 k<sub>B</sub> for a smearing of 1 THz and even higher values around 70 k<sub>B</sub> at high temperatures for DOSSMEAR > 2 THz. This fact might not have been considered in studies obtaining 10 kB for the formation entropy of at thigh temperatures [91]. An integration by part reveals that for a smearing width of 1 THz the contributions of each frequency domain increase by a factor of 10 compared to a smearing width of 0.1 THz.

In addition, Figure 31b shows a convergence of the formation entropy to a finite value for DOSSMEAR < 0.02 THz. Therefore this value is used for all phonon

calculations. Moreover, the smearing also has a physical meaning, the phonon lifetime originating from phonon-phonon interactions. Thereby, the phonon lifetime is decreasing with an increase of the smearing of the peak, which is related to the energy spread of the phonons being indirectly proportional to their lifetime. The value of smearing chosen within this study is 0.02 THz and corresponds to a phonon lifetime of 5 ns which agrees with the experimental value found for longitudinal acoustic modes [99]. For the defective cell the smearing is difficult to interpret as the degeneracy of some states is removed by the perturbation through the defect.



Figure 31: Convergences with respect to Gaussian smearing parameter of the **q**-point sampling DOSSMEAR for the formation entropy of the neutral  $T_d$  vacancy

### 6.3.4 Convergence criteria for the remaining forces

Several previous studies [80,84] and guidelines for phonon calculations [73,100] have stressed the importance of conducting phonon calculations only on well relaxed structures, i.e. whose remaining forces are close to zero. Any remaining forces acting on the atoms after a structural relaxation would alter proceeding phonon calculations. The parameter EDIFFG which is controlling the convergence criteria for the remaining forces was introduced in section 4.1 and forces are converged until they are F < EDIFFG. The parameter EDIFFG also has an effect on the positions of the atoms and for more stringent convergence criteria for the remaining forces the PHON code finds more and more symmetries for the given atomic positions. Particular in the context of a flat energy landscape of silicon the precise description of the atomic positions is important.

In Figure 32 the obtained phonon density of states  $g(\omega)$  and the respective formation entropies  $\Delta S_f$  are displayed for different values of EDIFFG. Studying the neutral  $T_d$  vacancy one finds a trend towards lower formation entropies with higher accuracy for the forces F resulting in a 0.6 k<sub>B</sub> difference at high temperatures. For  $F < 5 \cdot 10^{-5}$  eV/Å the formation entropy converged to a value of -2.4 k<sub>B</sub> at high temperatures. Furthermore, performing an offset of the obtained force fields of the PHON calculation by subtracting the forces that remained after the structural relaxation does not alter the formation entropy more than 0.01  $\mathbf{k}_B$  at high temperatures.

Previous lectures and articles have described the effect of errors associated with evaluating the forces [100, 101] on the calculated phonon frequencies. Errors of abintio calculations cause second order errors in the energy, but result in first order errors for the forces. Using the expressions (67)-(71) of section 3.2 for an error of  $\delta F = 5 \cdot 10^{-5} \text{ eV/Å}$  one can deduce an error of  $\sim 70\%$  for low frequencies around 1 THz.



Figure 32: Effect of different convergence criteria for the forces F in eV/Å, that remain when relaxing the atomic positions, on  $g(\omega)$  and the formation entropy of the neutral  $T_d$  vacancy

#### 6.3.5 Central differences of the forces

Until now a forward difference of the forces F was used to numerically estimate the interatomic force constant matrix  $\Phi_{A\alpha,B\beta}$  introduced in chapter 3.2 by setting the parameter LCENTRAL=False

$$\Phi_{A\alpha,B\beta} = \frac{\partial F_{B\beta}}{\partial u_{A\alpha}} \tag{89}$$

Hereby, the difference is taken between the forces acting on the atoms when the atoms are not displaced, which are supposed to be zero, and the forces acting on the atoms after applying a displacement  $u_{l't\beta}$ . By setting the parameter LCENTRAL=True one calculates the phonon DOS using central differences: two displacements are applied in opposite direction and the difference of the resulting force fields is taken.

The obtained phonon DOS can be seen in Figure 33 as the blue dotted line. It is compared with the phonon density of states obtained from the defective cell using LCENTRAL=False and the perfect cell. The phonon DOS displays small wiggles in the low frequency region between 0 and 2 THz for central differences. Additionally, at around 13 THz the spectrum exhibits a small peak. An analysis of the integration by frequency domain showed that the observed difference in Figure 33b for the formation entropy can be traced back to the low frequency region between 0 and 4 THz. The contribution in that domain is slightly negative for central differences. Contrary to using forward differences where it gives a high positive contribution of 12 k<sub>B</sub> at high temperatures. The small peak for longitudinal optic modes at 13 THz had an impact of 1 k<sub>B</sub> at high temperatures. In total, the formation entropy for central differences is found to be 2.5 k<sub>B</sub> lower at high temperatures than for forward differences.



Figure 33: Using forward or central differences by setting the parameter LCEN-TRAL and its effect on  $g(\omega)$  and  $\Delta S_f$  for the neutral vacancy with  $T_d$  symmetry

### 6.4 Different symmetries and charge states

In Figure 34a the difference of the phonon DOS  $\Delta g(\omega)$  is displayed for the neutral vacancy in  $T_d$  and  $D_{2d}$  symmetry, for the +2 charged vacancy in  $T_d$  symmetry and for the -2 charged defect in  $D_{3d}$  symmetry. Considering the neutral defect, in Figure 34a the difference between the  $\Delta g(\omega)$  of the  $T_d$  and  $D_{2d}$  symmetry is difficult to visualize. However, Figure 34b shows that a change in local symmetry does induce a differences for  $\Delta S_f$  resulting in a formation entropy of -2.41 k<sub>B</sub> for  $T_d$  and -3.18 k<sub>B</sub> for  $D_{2d}$  symmetry at high temperatures. For the neutral vacancy in  $D_{2d}$  symmetry this would add 0.2 eV to the formation enthalpy of 3.67 eV obtained in section 5 at high temperatures. Considering formula (32) from section 2.6 one can obtain the concentration of defects of  $3.3 \cdot 10^5$  cm-3 which is in rough agreement with experimental studies who found a vacancy concentration of  $10^5$  cm-3 in silicon wafers [89].

Looking at the charged defects one can observe small wiggles for the  $\Delta g(\omega)$  of the +2 positively charged defect around 2 THz. This could be the cause of the increase of the formation entropy in Figure 34b for lower temperatures. An integration by part analysis shows that the contribution of the low frequency region to  $\Delta S_f$  is the highest for the +2 charged defect. At high temperatures the formation entropy of the +2 charge defect resulted in a -1.88 k<sub>B</sub> formation entropy and the -2 charged

defect in  $-2.04 \text{ k}_B$ .



Figure 34: Difference of the phonon density of states of the defective and the perfect cell and formation entropy for the neutral  $T_d$  and  $D_{2d}$  vacancy

## 7 Conclusions

Point defects can heavily influence the physical properties of a material and their formation depends strongly on temperature. Due to the interest for several device applications, including solar cells, particular focus has been put on computational models that accurately calculate the formation energies of point defects with regards to temperature. A common approach is to use first principle methods to compute formation enthalpies [22]. However, no agreement has been found in the literature on the best methodology to compute formation entropies. Large discrepancies can be found for the value of the formation entropy of the silicon vacancy.

This variation cannot be traced back to the use of certain formalisms, but more often to finite size effects of the used simulation box, a restriction of computational time [90–93] or to errors in describing the acoustic modes [101].

Within this study, calculations are conducted using first principle density functional theory and the frozen phonon method. For the energetic ground state structure, several theoretical [77, 78, 80, 84] and experimental studies [85, 86] come to the same conclusion of finding three stable charge states of the silicon vacancy. The +2 charge state of the defect exhibits a  $T_d$  structure and the -2 charge state a  $D_{3d}$  structure. For the neutral vacancy a Jahn-Teller distortion is observed, a symmetry breaking from  $T_d$  to the lower  $D_{2d}$  symmetry resulting in a lower ground state energy. The obtained formation enthalpy for the neutral  $D_{2d}$  symmetry of 3.67 eV lies close within the values obtained in recent studies [80, 84]. From this a vacancy concentration of  $3.7 \cdot 10^6$  per cm<sup>3</sup> is calculated which is in rough agreement with experimental studies who found a vacancy concentration of  $10^5$  per cm<sup>3</sup> in silicon wafers [89] which is a very low concentration of defects. The Jahn-Teller distortion is found to be strongly affected by finite size effects and is only displayed for system sizes larger than 216 atoms, which is probably due to the influence of the flat nature of the silicon energy landscape [74].

The lattice distortion is generally recognized to be more dependent on the symmetry of the defect structure than on the charge state of the defect and  $T_d$  is found to have the lowest distortion. Additionally, it is deduced that the distinct defect symmetries have a different impact on the formation entropy.

The calculations of the formation entropy of the neutral vacancy result in a value of -2 k<sub>B</sub> for  $T_d$  and -3 k<sub>B</sub> for  $D_{2d}$  symmetry at high temperatures. For the neutral  $D_{2d}$  vacancy this adds 0.2 eV to the total formation energy lowering the vacancy concentration to  $3.3 \cdot 10^5$  per cm<sup>-3</sup>. The formation entropy calculations for the neutral  $T_d$  vacancy display a linear decline with decreasing defect concentrations and a linear extrapolation can be performed to obtain the formations entropy for the dilute limit.

For several technical parameters of the calculation it is found crucial to take particular care of their stringent convergence, especially for the k-point and qpoint grid to obtain the phonon density of states as well as for the real space projectors. High accuracy for the convergence criteria of the forces also leads to an increase of the precision of the calculation. In addition, the formation entropy needs to be converged with respect to the width of the Gaussian function which is used to calculate the phonon density of states. The effect of different parameters is summarized in Figure 35a with the formation entropy varying between -5  $k_B$ and 2  $k_B$  at high temperatures. For each parameter an analysis of the different contributions of different frequency domains all point to peculiar features in the low frequency region which result in a large positive contribution to the formation entropy. In Figure 35b the contribution of the low frequency region from 0 to 4 THz is removed resulting in a more systematic trend for the formation entropy within  $3 k_B$  difference at high temperatures. This demonstrates that one of the problems within the calculation of the phonon DOS is the modeling of the low energy acoustic region. This region is difficult to model due to a low phonon density of states, where the phonon bands are degenerate and close to the high symmetry  $\Gamma$ -point. Further propositions are to use a larger supercell to obtain a finer **q**-point sampling of the Brillouin Zone to describe this low phonon density region better. However, the question arises if one could computationally afford a larger supercell size and still remain within the same high precision of the calculation. Generally, one should take particular care when treating the low frequency region of the phonon DOS.

Further propositions are to test the effect of using different functionals of GGA and LDA and softnesses of the effective ionic potential acting on the valence electrons. Finally, one has to consider that when going to more complex systems than silicon, it will be difficult to remain within a high level of precision for the mentioned parameters.



Figure 35: Total formation entropy (a), and formation entropy  $\Delta S_f$  without the contribution of low frequency regions (b), for the neutral  $T_d$  vacancy

Furthermore, the calculation of the forces by ab-intio methods results in first order errors and gives an especially large error of  $\sim 70\%$  for low frequencies around 1 THz.

Another point worth mentioning, is that by using the frozen phonon method the phonon density of states is calculated within the harmonic approximation and the interaction potential between the atoms is described by a spherically symmetric harmonic well. The displacements applied to the atoms to calculate the force fields cannot be too large to remain within the harmonic approximation. Additionally, a problem specific to silicon is that due to its flat energy landscape large displacements may lead to an extent into local minima of the potential. For smaller displacements the question arises if they will lead to small energy differences and therefore will be more prone to error and numerical noises. The inclusion of anharmonic terms and the investigation of possible displacements for which the forces can be reliably calculated are therefore propositions for future research.

Moreover, within this study entropies were calculated at constant volume  $S_V$ . In experiments however, thermodynamic quantities are much easier accessible at constant pressure. Therefore the inclusion of volume change within the calculation and the determination of the entropy at constant pressure  $S_p$  from the obtained entropy at constant volume  $S_V$  might be of interest. One could include a volume dependence using [102]

$$S_p - S_V = \beta B V_{rel} \tag{90}$$

whereas  $\beta$  is the expansion coefficient and *B* the bulk modulus which are both well known for silicon.  $V_{rel}$  is the relaxation volume which is given by the difference between the formation volume of the defect and the volume of the perfect cell.

Furthermore, there are different ways how the low density acoustic region of the phonon density of states could be treated. One could remove the contribution in this area or estimate it by an average constant value. Another idea would be to approximate the acoustic modes by a more simplified model in 1D to get an estimate on what effect the presence of a point defect has on the speed of sound in a material.

In the end, a further increase of the precision of the calculation and a better

description of the low frequency region of the phonon DOS will result in the possibility to benchmark a methodology for the computation of the formation entropy of point defects. This will give a deeper insight on the temperature dependence of defect formation energies and the processes going on in a material when a point defect is formed.

# Appendix



Figure 36: Phonon density of states  $g(\omega)$  for the neutral  $T_d$  vacancy using a 1024 atom supercell



Figure 37: Phonon density of states  $g(\omega)$  for the neutral  $D_{2d}$  vacancy



Figure 38: Phonon density of states  $g(\omega)$  for the perfect cell for different displacement lengths 'DISP'


Figure 39: Difference of phonon density of states  $\Delta g(\omega)$  for the neutral  $T_d$  vacancy using different EDIFFG



Figure 40: Difference of phonon density of states  $\Delta g(\omega)$  using LDA and GGA functionals



Figure 41: Total formation entropies for the neutral  $T_d$  vacancy using different displacement lengths 'DISP'



Figure 42: Partial formation entropies  $D_{2d}$ 



Figure 43: Partial formation entropies  $T_d$  for LDA



Figure 44: Partial formation entropies for the neutral  $T_d$  vacancy for the 54-atom supercell



Figure 45: Partial formation entropies for the neutral  $T_d$  vacancy for EDIFFG=5E-6



Figure 46: Partial formation entropies for the neutral  $T_d$  vacancy for the displacement length d=0.02 Å



Figure 47: Partial formation entropies for the neutral  $T_d$  vacancy for different frequency regions (a)-(f) and supercell sizes

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